BIOGAS UPGRADE USING NATURAL AND MODIFIED ADSORBENTS

BY

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DECLARATION

DECLARATION BY THE CANDIDATE

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This thesis is dedicated to my dear family members who have been supportive throughout my studies.

ABSTRACT

Biogas is an alternative energy source that is generated from anaerobic digestion. However, the biogas contaminants affect its performance by reducing the energy content. The general objective of the study was to upgrade biogas using natural adsorbents including; clay, zeolite, and wood ash through dry adsorption and carbonation method. The specific objectives were; to characterize the chemical composition of the adsorbents, to determine the effect of adsorption process parameters (adsorbent/water ratio, the slurry temperature, adsorbent mass to biogas volume ratio, and biogas flow rate) and to evaluate the adsorption equilibrium isotherms, kinetics models, and breakthrough curves of carbon dioxide (CO_2) removal from biogas. The chemical composition of the adsorbents was characterized using X-ray fluorescence (XRF). The biogas composition was analyzed using gas chromatography and a digital hand gas analyzer. The natural adsorbent mass to water ratios used were; 1:1, 1:2, 1:3, 1:4 and 1:5 while the slurry temperature was varied from 18^oC to 80^oC on carbonation process. The experiments were carried out at biogas flow rates; 45, 100, 150, and 250ml/min. The adsorbent mass to biogas volume ratios tested ranged from 0.5 to 7g/l. The Computer Adsorption Valuation Software was used to study equilibrium isotherms, kinetics models, and breakthrough curves for CO_2 removal. The analysis of the chemical composition of natural adsorbents showed that the calcium oxide (CaO) content in wood ash, clay, and zeolite was 46%, 2.21% and 1.47% respectively. The silica/alumina (SiO_2/Al_2O_3) ratio of activated clay and zeolite was 8.5% and 15.4% respectively. The wood ash to water ratio of 1:4 gave the highest methane increment of 70.4%. The best biogas flowrate for wood ash slurry was 100ml/min which improved methane by 70.4% while the slurry temperature of 75^oC produced the highest methane enhancement of 88%. Furthermore, the highest uptake capacity of wood ash slurry was 2.30mmol/g at optimum condition. In addition, the high pH value of 10.9 for slurry was found to favor the purification of biogas. In dry adsorption process, the activated clay produced the highest adsorption capacity of 5.72mmol/g. Moreover, an increase in adsorbent mass to biogas volume ratio from 0.5 to 7g/l decreased CO_2 uptake capacity from 5.72 to 2.89mmol/g but the removal efficiency of CO_2 increased from 13.66 to 93.79%. For activated clay, the data of CO_2 removal well fitted in Freundlich isotherms (R^2=95.9), pseudo-first order kinetics model (R^2=99.2) and Yan breakthrough curve model (R^2=99.5). Conclusively, wood ash/water slurry carbonation method and dry activated clay in fixed-bed adsorption are good alternative media for biogas upgrading. Their performance depends on CaO contents and SiO_2/Al_2O_3 ratio respectively. This study recommends activated clay and wood ash slurry as potential media for purifying biogas.

Keywords: - Natural adsorbents, Carbon dioxide removal, carbon dioxide purification,

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LIST OF ABBREVIATIONS

Al_2O_3:	Aluminum oxide
BET:	Brunauer, Emmett, and Telle
BA:	Bottom ash
CO_2:	Carbon dioxide
CaO:	Calcium oxide
$CaCO_3$:	Calcium carbonate
CMS:	Carbon molecular sieves
CA:	Cellular acetate
CNG:	Compressed natural gas
DEA:	Diethanolamine
DETA:	Diethylenetriamine
DFT:	Density functional theory
Fe_2O_3:	Iron (III) oxide
FID:	Flame ionization detector
GC:	Gas chromatography
H_2S:	Hydrogen sulfide
H_2SO_4:	Sulfuric acid
H_2SO_3:	Sulfurous acid
HK:	Horvath- Kawazoe
K_2O:	Potassium dioxide
KCl:	Potassium chloride
M:	Molar

MgO:	Magnesium oxide
MnO:	Manganese (II) oxide
MEA:	Monoethanolamine
Na_2O:	Sodium oxide
NaOH:	Sodium hydroxide
NF:	Not found
NH_4OH:	Ammonium hydroxide
PSA:	Pressure swing adsorption
PI:	polyimide
PSF:	Polysulfide
PEO:	Pseudo first order
PSO:	Pseudo second order
P_2O_5:	Phosphorus (v) oxide
PEI:	Polyethyleneimine
RMSE:	Root mean square error
SSA:	Specific surface area
SiO_2:	Silicon dioxide
SO_3:	Sulfur trioxide
SQE:	Sum of the square error
TCD:	Thermal conductivity detector
TiO_2:	Titanium dioxide
TEPA:	Tetraethylenepentamine
VMD:	Vacuum membrane distillation
W/V:	weight per volume

XDR: X- ray diffraction

XRF: X- ray fluorescence

XRD: X-ray diffraction

XPS: X- ray photoelectron spectroscopy

LIST OF SYMBOLS AND NOMENCLATURE

α	Initial adsorption rate mg/g.min
β	Desorption constant mg/g
b:	Langmuir constant
C_t:	Effluent concentration at any time mg/mL
C_o:	Influent concentration mg/mL
C_1	Adsorbate concentration after purification mg/mL
τ	Time required for retaining 50% of the initial adsorbate in min
K_1	Pseudo first order rate constant min^{-1}
K_2	Pseudo second order rate constant g/mg.min
K_{id}	Intraparticle diffusion rate $mg/g.min^{0.5}$
K_L:	Langmuir constant L/mg
K_F:	Freundlich adsorption constant L/g
K_{AB}	Adams Bohart model constant L/mg.min
K_{YN}	Yoon Nelson model constant min^{-1}
K_{Th}	Thomas rate model constant mL/min.mg
K_Y	Kinetic rate constant for yan model L/mg.min
m	Mass of adsorbent g
N_a	Bed sorption capacity mg/L
n:	Adsorption capacity
q_t	Adsorption capacity at particular time
q_e	Adsorption capacity mg/g
q_{max}:	Maximum adsorption capacity mg/g
q_{Th}	Adsorption capacity of column

Q	Feed flow rate ml/min
q_Y	Maximum adsorption capacity (mg/g) of adsorbent by Yan model
STD:	Standard deviation
t	Time min
Y	Removal percent
Z	Bed depth m

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CHAPTER 1: INTRODUCTION

1.1 Background

Currently, the leading energy supply worldwide comes from non-renewable sources like petroleum, oil and natural gas. Fossil fuel energy sources have limited supply, cannot be replenished, are expensive and environmentally damaging (Owusu & Asumadu-sarkodie, 2016). In addition, they release a high content of carbon dioxide into the atmosphere. According to Abdul et al., (2017), it is estimated that carbon dioxide account to 77% of greenhouse emissions. Carbon dioxide and other greenhouse gases cause global warming which has become a worldwide problem (Zhang, & Lu, 2015). One way to mitigate this problem and control the environmental, social and economic problems is to promote use of renewable energy like biomass, geothermal and nuclear sources (Owusu & Asumadu-sarkodie, 2016). Therefore, biogas is among the renewable energy sources that are currently used as replacement for fossil fuels.

Biogas is generated from organic matter by anaerobic digestion where microorganisms break down the raw materials to produce biogas as a metabolic side product (Kumar et al 2013). Biogas consists primarily of methane and carbon dioxide. Additionally, it contains trace components that include hydrogen sulfide, water vapor, siloxanes, ammonia, nitrogen and oxygen. The trace components and carbon dioxide gases in biogas reduce the application of biogas by reducing the energy content. The biogas methane content is in the range of 40-65% which has calorific value lower than 25MJ/m^3. At standard temperature and pressure (STP) conditions, the calorific value of methane is 36MJ/m^3 (Angelidaki et al., 2018). Therefore, the high content of carbon dioxide reduces the calorific value. Moreover, carbon dioxide has high contribution to global warming. Hydrogen sulfide and other trace components like water are the main causes of the corrosion. In addition, hydrogen sulfide is extremely toxic and affects human health and environment. The value of biogas can be enhanced by purifying and upgrading it using various methods. Purification entails the removal of contaminants like hydrogen sulfide, water vapor, oxygen and other trace components that prevents wide application especially in engines. The upgrade of biogas entails removal of carbon dioxide, which enhances the energy density and storability of biogas by increasing biomethane content. After upgrading, biogas can be used as a fuel for boiler/stoves, engines and gas turbines for producing electricity. Furthermore, it can be used as fuel for vehicles and fuel cells (Sun et al., 2015).

Various studies have reported the use of modern technologies in biogas purification and upgrading. These technologies include; pressure swing adsorption (Gomes & Yee, 2006), cryogenic separation (Yousef et al., 2016; Pellegrini et al., 2018), membrane separation (Makaruk et al., 2010), water scrubbing (Läntelä et al., 2012; Vilardi et al., 2020), physical scrubbing, chemical absorption (Abdeen et al., 2016), hydrate formation (Arca et al., 2011) and biological conversion process (Kougias et al., 2017). These commercial upgrading technologies are generally effective in capturing carbon dioxide and trace components in biogas. However, the main drawback of these technologies is the high investment capital and operation costs (Ullah et al., 2017). The process of biogas upgrade using modern technology has been reviewed (Ryckebosch et al., 2011). Biogas can also be purified using adsorbents such as clay (Chen et al., 2014) zeolite (Paolini et al., 2015; Wahono et al., 2020), coal fly ash (Ferella et al., 2017) and activated carbon (Adilla et al., 2013; Ogungbenro et al., 2020). They are low cost and simple operation methods. Therefore, natural adsorbent materials become an alternative choice for biogas upgrading. The main limitation of natural adsorbent materials is poor uptake of the contaminants (Yu et al., 2012). However, this can be improved by activation of the materials by physical and chemical methods to clean the surface of pores and increase their adsorption capability (Wiyantoko.B & Rahmah.N, 2017 ; Chouikhi et al., 2019). Therefore, this research investigated upgrading of biogas using natural and activated adsorbents that include zeolite, clay and wood ash.

Zeolites are found naturally on the earth's surface in certain regions. It is micro porous, aluminosilicate minerals. Zeolites are used for water purification (Arimi, 2017; Margeta et al., 2013), natural gas purification (Ackley et al., 2003), as drug carriers and catalysts(Donk et al., 2003), as nutrient carriers in agriculture and for pH and moisture adjustment (Eroglu et al., 2017; Ramesh & Reddy, 2011) and as adsorbents (Wang.S & Peng, 2010). Furthermore, zeolite has a high capacity for immobilization of microorganisms (Montalvo et al., 2012). Therefore, it is suitable for application in anaerobic digestion. There are different types of natural zeolites including chabazite, clinoptilolite, phillipsite, mordenite and others. There are also various types of artificial zeolites which are synthesized (Rashed & Palanisamy, 2018). Artificial zeolites include compounds such as 5A and 13X and are very effective adsorbents but are very expensive.

Clay is a finely grained natural rock and is hydrous aluminum phyllosilicates. It has layered crystal structure. Clay is mostly found in shales and it is the most common type of sedimentary rock. It can be used for various applications such as adsorption, air purification and as a catalyst. The major chemical components of clay are SiO_2, Al_2O_3, CaO, Fe_2O_3, K_2O, M_gO, Na_2O, SiO_2, SO_3 and TiO_2 (Marsh et al., 2019).

Wood Ash is generated from the combustion of wood in different settings such as industrial power production or home fire. In addition, ash could be prepared from municipal solid waste incineration where it is called bottom ash. Wood ash is used as a construction material, for land application or to increase the soil pH (Hansen et al., 2017; Siddique, 2012). It can also be used for removal of water and gas contaminants (Siddique, 2012). The chemical components of ash are; CaO, SiO_2, Al_2O_3, Fe_2O_3, K_2O, MgO, MnO, Na_2O, P_2O_5 and TiO_2 (Guo et al., 2015). This research investigated the upgrading of biogas using natural and modified zeolite, clay and wood ash through the dry adsorption and carbonation process with an aim of proposing an alternative, effective and affordable method for removing carbon dioxide from biogas.

1.2 Statement of the problem

Non-renewable energy sources are very expensive and unsustainable. Moreover, they have high contribution to global warming. Studies by Christophe Mcglade & Ekins, (2014) observed that to mitigate against climate change, the demand of gas, oil and coal reserves should be reduced by 50%, 33% and 80% respectively between 2010 and 2050. In addition, according to Gorre et al., (2019) the world price of natural gas is projected to increase from 4.9 to 9.6 $/MBtu from 2016 to 2040. Therefore, in the future, renewable energy source will be the best alternative energy source. Biogas is one of the promising alternative energy to reduce the consumption of non-renewable energy. It can be applied for different purposes including as engine fuel. However, in most developing countries including Kenya and Ethiopia, there is limited application of biogas where it is only used as household energy due to its contaminants. Biogas can be produced by converting waste to energy which reduces the environmental waste. Furthermore, it reduces greenhouse emissions from waste decay which generates high methane gas.

Biogas is composed of methane, carbon dioxide, hydrogen sulfide, nitrogen, siloxanes, oxygen and other minor components. The contaminants in biogas limit its application. The carbon dioxide in biogas reduces the heating value, compression ratio and flammability velocity. In addition, it causes global warming. Moreover, hydrogen sulfide is the cause of corrosion and wear which reduce the lifetime of metallic materials. Hence, the use of raw biogas energy in applications such as engine fuel without prior upgrading is not advisable. Biogas can be upgraded using modern technology such as membrane, pressure swing scrubbing and others (Sun et al., 2015). These methods have high adsorption capacity but they need high initial investment and their energy requirement is high. Furthermore, the methods are not accessible in most developing countries. Therefore, the use of natural adsorbent materials is an alternative choice for biogas upgrading. Low-cost materials are abundantly available but their capacity to upgrade biogas has not been well studied.

1.3 Research Objectives

1.3.1 The general research objective

The general objective was to investigate the biogas upgrade using natural clay, zeolite and wood ash.

1.3.2 Specific research objectives

The specific objectives of the study were to;

1. To perform physio- chemical characterization on natural and activated clay, zeolite and wood ash adsorption media
2. Determine the effect of the process parameters such as the ratio of adsorbent/water, carbonation temperature, biogas flow rate and adsorbent mass/biogas volume ratio on adsorption on the biogas upgrade
3. Evaluate the adsorption kinetics, adsorption equilibriums and breakthrough curves for carbon dioxide removal from biogas

1.4 Scope of the study

The scope of this study is upgrading of biogas using natural materials including; zeolite, clay and wood ash. Biogas was upgraded using natural and activated adsorbents by carbonation and adsorption process. In addition, the model of adsorption kinetics, adsorption equilibrium and breakthrough curve data of carbon dioxide were evaluated using Computer Adsorption Valuation Software (CAVS). The limitation of this study, there was lack of equipment so that unable to characterized the surface area and pore volume of adsorbents.

1.5 Justification and significance of the study

Biogas produced from organic waste is an environmentally friendly and sustainable energy source. In addition, it reduces environmental wastes. The global bioenergy demand will be increased by 20% in 2050 (Guo et al., 2015). This bioenergy is represented mostly by biogas, bioethanol, and bioelectricity (Guo et al., 2015). Few African countries including Rwanda, Ethiopia, Kenya, Uganda, Tanzania Benin, Burkina, Cameroon and Senegal installed a total of 3996 and 3501 biogas units in 2010 and 2011 respectively (Mwirigi et al., 2014). However, the biogas contaminants reduce the application of biogas. In 2015, Europe produced 18 billion $m^3$of methane, almost half the total global production (Scarlat et al., 2018). Based on the assumption that biogas contains 40% carbon dioxide, 12 billion m^3 of carbon dioxide was produced with biogas in Europe in that year. The carbon dioxide component can be eliminated by upgrading biogas to pure methane. In East Africa, it has been reported that the installation of biodigesters to replace fossil energy can save per country’s carbon dioxide emissions between 0.6 - 5.7 million tons annually (Wassie & Adaramola, 2019). The reduction of carbon dioxide emissions would be much greater if 40% of carbon dioxide in biogas is removed by upgrading before use. Furthermore, after upgrade, biogas can be converted to syngas a bio compressed natural gas which increases the range of biogas applications. In addition, purified biogas can be used in diesel and petrol engines (Jha et al., 2015). Therefore, it is important to purify biogas to enhance its applicability and environmental sustainability.

1.6 Outline of the research

This research contains five chapters. It covers the introduction, literature review, research methodology, results and discussion, and conclusion and recommendations. Chapter one gives the introduction for this research. Chapter two reviews the current and previous published papers and books related to this study. The chapter outlines the research gaps and evaluate the future studies plan. Chapter three presents the research methodology. Chapter four reports the results and discussion of the present research findings. Furthermore, chapter five finalizes this research by conclusion and recommendation.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

This chapter reviews previous studies on upgrading of biogas. The section begins by reviewing biogas production, composition and effects of biogas trace component on engines, environment and health. Afterwards, it reviews the purification and upgrading of biogas by commercial methods including: pressure swing adsorption, absorption, cryogenic, membrane, in situ methane enrichment, hydrate formation and biological method. Additionally, section reviews upgrading of biogas using low-cost natural materials including: clay, zeolite, fly ash and activated carbon. Furthermore, the chapter reviews the mechanism of carbon dioxide removal from biogas, factors affecting performance of biogas upgrade using locally available adsorbents and biogas analysis using gas chromatography. The adsorption kinetics models, adsorption isotherms and application of breakthrough curves in adsorption are reviewed. In addition, this chapter reviewed application of biogas and identified the research gaps in upgrade of biogas using low-cost natural adsorbents.

2.2 Biogas production

Biogas is one of the most favorable renewable energy sources. Anaerobic digestion is an effective method of treating food waste, agriculture remains, municipal residues, human excretes, landfills, commercial food waste, animal waste and organic waste materials (Kumar et al., 2013; Tomich & Vision, 2016). Figure 2.1 illustrates biogas production from different types of substrates.

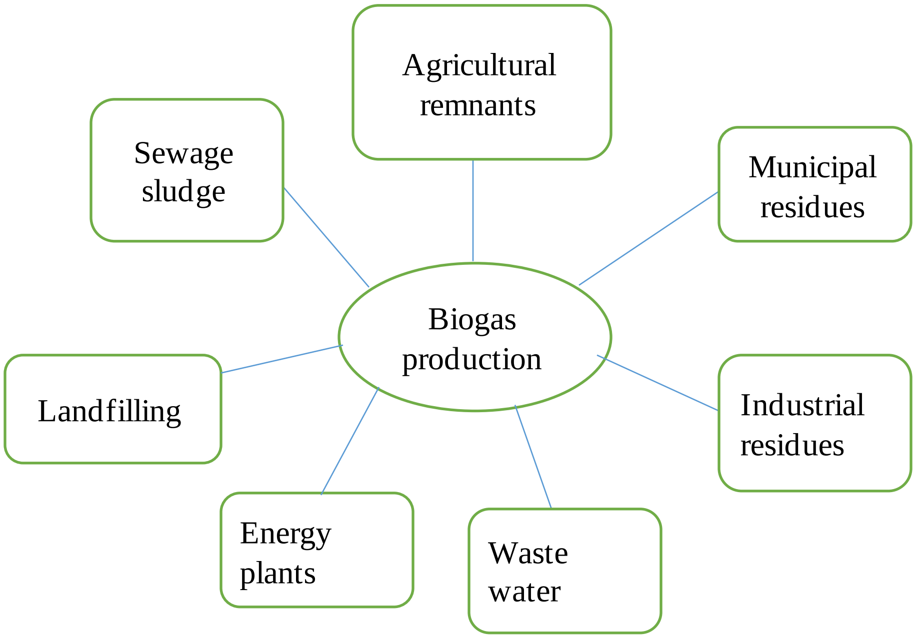


Figure 2.1:- Substrates for biogas production (Source: Kumar et al., (2013))

Biogas is produced by anaerobic digestion which consists of four main steps; - hydrolysis, acidogenesis, acetogenesis and methanogens. Hydrolysis is the breakdown of complex organics material (carbohydrate, protein and lipid) into simple monomers (monosaccharide, amino acid, long chain fatty acid) by hydrolytic enzyme. Acidogenesis bacteria convert simple monomers into volatile fatty acids. Acetogenesis bacteria convert the volatile fatty acid into acetic acid, carbon dioxide and hydrogen. The methanogenesis bacteria convert acetates into methane and carbon dioxide (Raja & Wazir, 2017). Figure 2.2 illustrates biogas production process.

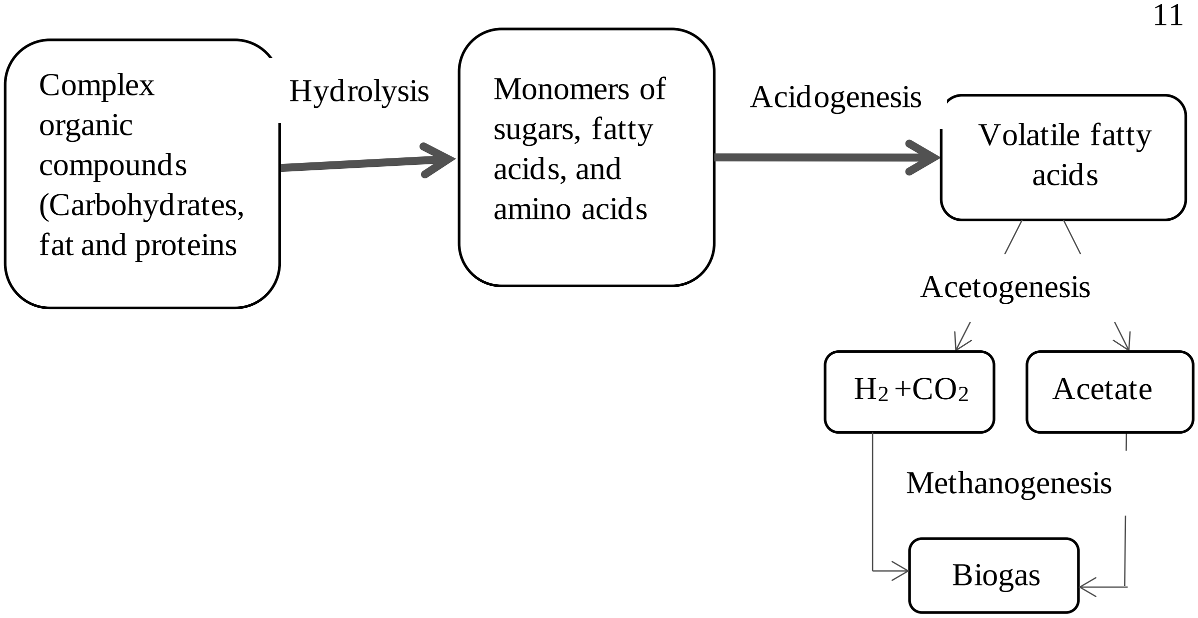


Figure 2.2:- Biogas production processes (sources -:Prasad et al., 2017; weiland, 2010)

2.3 Compositions of biogas

Biogas compositions are affected by the type of substrate and the production technology (Razbani et al., 2011 ; Rasi et al., 2007). Table 2.1 shows the biogas compositions produced from different types of substrates.

Table 2.1:- Biogas compositions from different biogas plants

Types of waste	CH_4 (%)	CO_2 (%)	H_2S ppm	O_2 (%)	N_2 (%)	Reference
Agricultural waste	45-75	25-55	7-20	0.01-2	0.01-5	(Razbani et al., 2011)
Agricultural waste	56-60	27-35	<0.001-0.009	NF	NF	(Onthong & Juntarachat, 2017)
Sewage waste	65-75	20-35	<5300	0.5	3.4	(Razbani et al., 2011)
Sewage waste	61-65	36-38	<0.1	<1	<2	(Rasi et al., 2007)
Landfill waste	45-55	25-30	<5300	1.5	10-25	(Razbani et al., 2011)
Landfill waste	47-57	37-41	36-115	<1	<1-17	(Rasi et al., 2007)
Farm waste	55-58	37-38	32-169	<1	<1-2	(Rasi et al., 2007)

Note: - NF- not found

According to Table 2.1 indicates that the average biogas composition was 45-75% methane and 20-55% carbon dioxide. The amount of methane is high in biogas produced from the sewage waste compared to landfill and farm waste. Landfill biogas has low content of methane because it contains nitrogen from air which affects the composition. In addition, the biogas production can vary by applying different production condition.

2.4 Effects of biogas trace components

Biogas trace components reduce the quality of biogas fuel and they affect the internal combustion engines, the environment and human health. Therefore, it is necessary to upgrade raw biogas before it is used as fuel for vehicles or other engines.

2.4.1 Effects of trace components on the engine

The contaminants in biogas affect the internal metallic components of combustion engine through corrosion. The presence of carbon dioxide reduces the laminar flame speed, flammability limits and burning rates. In addition, it reduces calorific value, lowers combustion efficiency and produces a narrow range of flame stability (Pizzuti et al., 2016; Pizzuti et al., 2014). Flammability limit is the range of concentration of the fuel in a fuel-air mixture at a specified temperature and pressure that allows ignition-initiated flame to propagate and sustain motion. It is mainly affected by the nature of the fuel, direction of the propagation, size and shape of the combustion chamber, temperature and pressure (Porpatham et al., 2008). Biogas has slightly lower flammability limit which makes it difficult to ignite at Reynolds number above 1200 (Razbani et al., 2011). The low flammability limit also lower the compression ratio by affecting the quality of fuel since it is not possible to raise the compression ratio without an engine knock (Razbani et al., 2011). The laminar flame is an important parameter of premixed combustible mixture which describes gases ability to make a planer flame steady. It depends on the fuel type, temperature, pressure and air-fuel ratio. This phenomenon affects the flame stability (Pizzuti et al., 2016). High quantity of carbon dioxide reduces the burning velocity and the content of energy in biogas (Nonaka & Pereira, 2016). The removal of carbon dioxide in biogas therefore increases the concentration and energy density of the fuel.

Hydrogen sulfide is produced from compounds of proteins during the period of anaerobic process. Its formation depends on the type of raw material and the digestion process. Hydrogen sulfide reacts with metals in the machines like lead to form metal salts. In the engines, it reacts with water to form sulphur dioxide. Further reaction with water forms sulfuric acid (H_2SO_4) which is highly corrosive and causes wear to engine components (Magomnang et al., 2014). Moreover, corrosion affects the heat exchangers during high exhaust gas backpressure and can also cause poisoning of the catalysts in reactors. Hydrogen sulfide may also react to form other kinds of acids such as sulfurous acid (H_2SO_3). The negative effects of hydrogen sulfide include, its hazardous nature, bad odor, causing of corrosion and health problems (Abatzoglou & Sherbrooke, 2009).

Biogas leaving the digester is normally saturated with water vapor. This water vapor condense in the engine parts and cause corrosion (Razbani et al., 2011). Ammonia in biogas is produced from organic molecules of protein nature during digestion process (Abatzoglou & Sherbrooke, 2009). This ammonia reacts with water to form ammonium hydroxide (NH_4OH), which can cause corrosion to certain metals such as aluminum and copper. The presence of ammonia may also increase nitrogen oxides in biogas which are environmental hazards (Razbani et al., 2011).

Siloxanes is yet another biogas contaminant that is commonly produced from anaerobic digestion of landfill. They form a thick deposit in engine parts like combustion chamber, exhaust manifolds, exhaust turbocharges and exhaust stacks. In addition to causing corrosion to these parts, they lower the heating value of biogas (Razbani et al., 2011). It may also reduce the flammability limit and cause a low compression ratio. One method of mitigating the negative effects of siloxanes is to modify the engine or provide for engine tolerance. There are several ways to provide for engine tolerance of biogas including the use of more corrosion resistance material, using cutting rings insert at the top of the cylinder and using stainless steel (Razbani et al., 2011). However, the use of corrosive resistant material is limited by high costs. Therefore, it is prudent to eliminate all biogas contaminants before usage in the engine.

2.4.2 Environmental effects of biogas contamination

Greenhouse emissions include gases such as methane, carbon dioxide, nitrous oxide and hydro fluorocarbons that contribute to global warming and climate change. Methane emission has more than 28 times global warming potential than carbon dioxide (Paolini et al., 2018). The emission occurs when organic matter is left to decay producing biogas which has methane as the main component. It may also occur when biogas produced in bio-digesters is not properly utilized or is allowed to leak. There are other greenhouse gases produced with methane during anaerobic digestion of organic matter such as carbon dioxide and hydrogen sulfide (Nevzorova & Kutcherov, 2019). Hence, it is important that methane is not released to the atmosphere by avoiding leakage in digester systems and utilizing all the biogas produced. One way to minimize the possibility of excess biogas from either formal digesters or rotting of organic deposits is by diversifying its applications. For example in East Africa, most energy from digesters is used for kitchen cooking (Wassie & Adaramola, 2019). It is possible to apply biogas in various ways such as running biodiesel engines. However, such applications would require upgrading of biogas to remove the contaminants that would harm machine parts like engines.

Carbon dioxide is the highest contributor to global warming due to population expansion and economic growth (Feng et al., 2020). The emission of carbon dioxide and other traces components have negative effects on the environment such as greenhouse effects on the stratosphere as demonstrated in Figure 2.3. The direct solar radiation has short wavelength and can easily penetrate the layers above the earth including the one formed by greenhouse gases. However, when solar radiation reaches the earth surface, some solar radiation is reflected back into the space while some of the infrared radiation is absorbed by the layer of greenhouse. The radiations that are reflected have long wavelengths which have poor penetrability. They are unable to penetrate the layer of greenhouse gases above the atmosphere therefore accumulating above the earth. The greenhouse emissions therefore prevent the earth cooling and cause global warming (Rasi et al., 2007). As a result, ocean waters absorb heat and rises its temperature. The trapped heat over time melts the ice cap and this causes flooding. Moreover, carbon dioxide reacts with moisture in the air to form acid rain which can cause corrosion. Nitrous oxide has higher global warming potential than carbon dioxide.

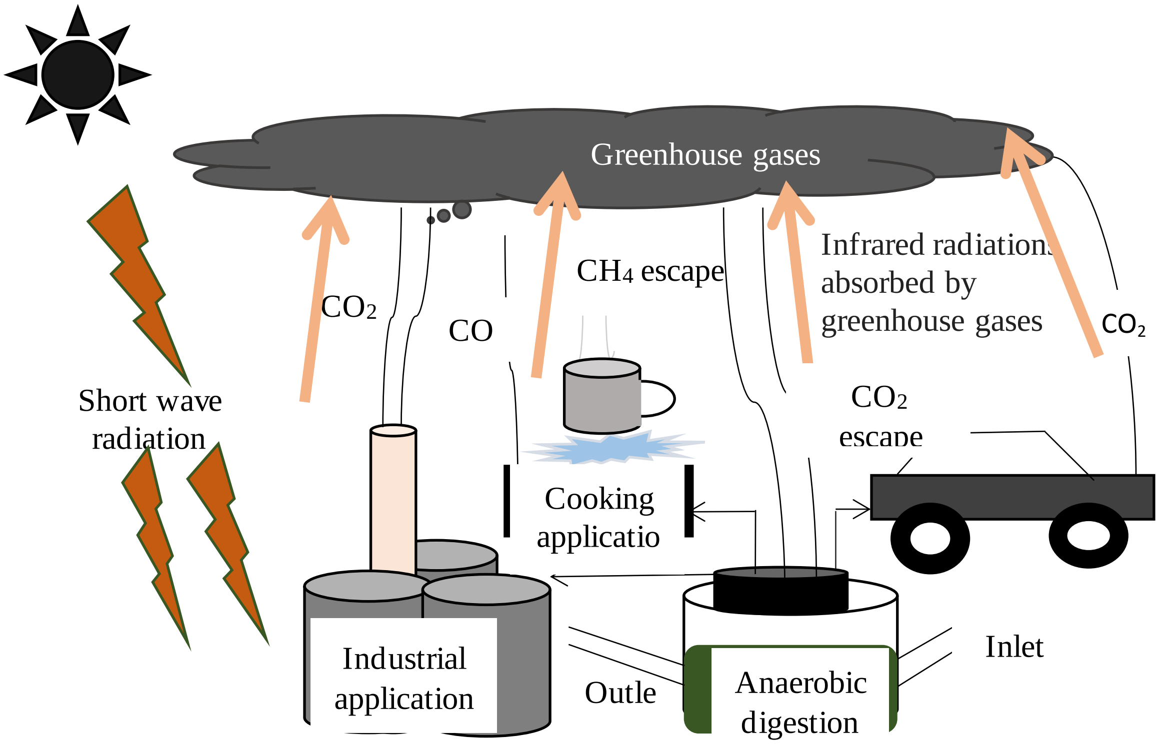


Figure 2.3:- An illustration of how greenhouse gases cause global warming (Source: Mulu et al., (2021))

There are various commitments by international players to reduce carbon dioxide emissions including Kyoto Protocol (Cha et al., 2008). The agreement committed the countries releasing most carbon dioxide to reduce emissions by 5%. In addition, changing from fossil fuels to renewable energy, cleaning of carbon dioxide from biogas before its usage can help reduce the emissions.

2.4.3 Health effects of biogas emissions

The health effect of methane emission in biogas process is negligible while carbon dioxide and hydrogen sulfide emission affect human health. Carbon dioxide emission affect the breathing system, cause sleeplessness and can lead to headaches and difficulty in clear thinking (Zhang et al., 2017). Hydrogen sulfide may cause poor memory, tiredness, dizziness, balance problems, headaches, respiratory illnesses, cardiovascular diseases, loss of consciousness and other health problems (Bates et al., 2002).

2.5 Purification and upgrade of biogas by commercial method

2.5.1 Biogas purification

The purification of biogas entails the removal of contaminants including hydrogen sulfide, water, oxygen, nitrogen, siloxanes and ammonia.

The water vapor in biogas can be removed by cooling, compression or absorption using solutions like glycol, through adsorption using adsorbents like SiO_2, activated charcoal or molecular sieves (Surata et al., 2014).

Hydrogen sulfide can be removed during digestion and after digestion by processes such as precipitation, chemical absorption, and adsorption on activated carbon and biological treatment. Riyadi et al, (2018) reduced hydrogen sulfide by use of steel wool as removal media by use of three different adsorption column heights (50, 75 and 100cm). Maximum elimination of hydrogen sulfide is desired to maximize methane content. The maximum removal efficiency of hydrogen sulfide in biogas was found to be 95% using steel wool in 100cm adsorption column (Riyadi et al, 2018).

Oxygen and nitrogen gases can be removed by adsorption with activated carbon, molecular sieves or membranes. These gases can also be removed using desulphurization process (Baspinar et al., 2011). Siloxanes can be removed by adsorption on activated carbon, activated aluminum or silica gel or by absorption and cooling. Moreover, other particulates are separated by mechanical filters (Petersson et al., 2009).

2.5.2 Modern technologies for biogas upgrade

Upgrading of biogas entails the removal of carbon dioxide which enhances the energy density by increasing biomethane concentration. The modern technologies for biogas upgrading include process such as pressure swing adsorption (PSA), absorption, membranes, hydrate formation and biological. New developments in upgrading technology include cryogenic upgrading and in situ methane enrichment (Ryckebosch et al., 2011).

2.5.2.1 Pressure swing adsorption

Pressure swing adsorption is a technology used to separate gas species from a mixture of gases under pressure according to the species molecular characteristics and affinity for an adsorbent. The upgrading of biogas using the PSA technology has been studied and documented (Augelletti et al., 2016). The technology has advantages including high efficiency, fast operations and high thorough put, and compactness of the equipment. It separates the carbon dioxide from biogas through adsorption on a surface under elevated pressure (Augelletti et al., 2016). Pressure swing adsorption plants are used mostly in Sweden and Austria. The process is expensive in terms of operation cost and investment capital and results in high methane loss (Niesner et al., 2014).

2.5.2.2 Absorption

Absorption uses liquid solvent in which carbon dioxide is soluble. The process selectively removes the high content of carbon dioxide which causes increase in methane concentration. There are different types of absorption process for carbon dioxide removal based on solvent media. These process include; water scrubbing, organic physical scrubbing and chemical scrubbing (Ryckebosch et al., 2011).

Water scrubbing

In the water scrubbing process, carbon dioxide is dissolved in the water which increase the methane concentration in the gas phase (Nie et al., 2013). Water scrubbing is the most commonly used upgrading technology in Europe. The process is limited in that it can result in clogging due to bacterial growth and foaming is possible (Niesner et al., 2014). The removal of carbon dioxide by water scrubbing is dependent on pressure. Nock et al., (2014) reported 95% methane content after biogas upgrade with the process at 4 bars.

Organic physical scrubbing

Organic physical scrubbing technology is similar to water scrubbing but applies organic solvent. An example of organic physical scrubbing method is the use of an organic solvent polyethylene glycol to purify biogas (Rajivgandhi & Singaravelu, 2014). Carbon dioxide is more soluble in polyethylene glycol than in water. The process of organic physical scrubbing is an expensive operation and requires huge investment because it requires high energy to regenerate the solvent. Organic physical scrubbing is one of the most commonly used technology in Europe (Niesner et al., 2014).

Chemical scrubbing

Chemical scrubbing technology uses chemicals such as calcium hydroxide, sodium hydroxide and mono-ethanolamine to treat raw biogas. Carbon dioxide is not only absorbed in the liquid but also reacts with the chemicals in the solvent. The use of chemical scrubbing to remove carbon dioxide and hydrogen sulfide has been found to improve the quality of biogas.

Chemical scrubbing technology is the most common upgrading technology in Europe (Chandra et al.,2012). However, the process requires that the chemical reactants are selective on biogas contaminants so that methane loss from the reactions is minimized (Tippayawong & Thanompongchart, 2010). Furthermore, the process is limited by the high cost of chemicals and capital investments (Chandra et al., 2012).

2.5.2.3 Membrane technology

The membrane technology is one of the biogas upgrade technology. The membrane is highly selective, stable and permeable (Sun et al., 2015). Membrane technology is used to separate carbon dioxide and hydrogen sulfide from methane and hydrogen using two different membrane process: membrane contactors and gas permeation membrane (Scholz et al., 2013; Harasimowicz et al., 2007). The gas permeation membrane uses conventional gas separation process to upgrade biogas at natural gas grid pressure and is done without any additives. However, the process is not suitable for single- stage operations (Scholz et al., 2013; Marzouk et al., 2010). The removal of carbon dioxide from biogas using membrane contactors can be improved by adding alkali solution or by using vacuum regeneration and vacuum membrane distillation (VMD) (He et al., 2018).

Types of membrane materials

The membrane uses two types of materials for gas separation: - polymeric and non-polymeric materials. Polymeric membrane materials include polysulfide (PSF), carbon molecular sieves, cellulose acetate (CA), polyimide (PI) among others (Basu et al., 2010). Non polymeric membrane materials are carbon molecular sieves (CMS), zeolite and non-zeolite molecular sieves among others. Non polymeric membrane materials have effective gas separation than polymeric membrane.

However, it requires higher chemical and thermal stability. Polymeric materials are more economical, cheaper, easily scalable, and easily fabricated into commercially viable hollow fiber (Basu et al., 2010). The process of membrane technology produces low methane yield in a single step and consumes high electricity per unit of gas production (Basu et al., 2010).

2.5.2.4 Hydrate formation

Hydrate formation can be used to remove carbon dioxide from gas. The process is stable under high pressure and low temperature. Hydrate formation separate carbon dioxide by pressurization of biogas using an adiabatic compressor to form a hydrate. Cooling the biogas is then done using heat exchange to remove the heat from the hydrate formation using brine stream (Tajima et al., 2004). Denderen et al., (2009) reported reduction of carbon dioxide from 25% to 16% using hydrate formation method. The process is however limited by high consumption of energy (Denderen et al., 2009).

2.5.2.5 Biological method for biogas upgrading

Biogas can be upgraded biologically using specialized microorganisms. Hydrogen and carbon dioxide in biogas can be converted to methane in anaerobic digesters by using hydrogenotrophic methanogens (Luo et al., 2012). Hydrogenotrophic methanogens are archaea which can convert carbon dioxide into methane in the presence of hydrogen. The reaction for conversion of hydrogen and carbon dioxide into methane is shown in equation 2.1.

$$4H_2 + CO_2 \xrightarrow{\qquad\qquad} CH_4 + 2H_2O \qquad (2.1)$$

Sun et al., (2015) reported an increase in concentration of methane in biogas from 60% to 96% using *methanobacterium thermoautotrophicum*.

Moreover, the process resulted in reduction of hydrogen sulfide to non-detectable levels (Sun et al., 2015). This implies that the process can be used to eliminate both hydrogen sulfide and carbon dioxide contaminants.

2.5.2.6 Cryogenic upgrading technology

The technology makes use of the distinct boiling/sublimation points of the different gases particularly for the separation of carbon dioxide and methane. This upgrading technology uses three types of cryogenic systems for capture of carbon dioxide; flash liquefaction system, distillation system and liquefaction combined with desublimation (Tan et al 2017) . Cryogenic upgrading technology is mostly used in Canada and Netherlands (Tan et al., 2017). The process is limited in that it is an expensive investment. Moreover, the maintenance and operation costs are high. The process also requires high energy which makes it impractical for application (Chandra et al., 2012).

2.5.2.7 In situ methane enrichment

In situ methane enrichment is one of the new upgrading biogas technologies. The sludge from the digester goes to desorption column and then back to the digester. The carbon dioxide is desorbed by pumping air through the sludge desorption column (Petersson et al., 2009). The loss of methane is minimized by an increased air flow rate through the desorption column and desorption column volume (Edstro, 2011).

The summary of biogas upgrading by commercially available technologies is show in Table 2.2. The application of the technologies indicates that biogas can be upgraded up to 99% purity making it suitable for use as fuel for engines. Comparison of the technologies indicates that pressure swing adsorption produced highest energy reduction due to methane loss during the upgrade process.

Table 2.2:- Comparisons of different biogas upgrading methods on methane

Upgrading technology	Methane concentration of upgraded biogas (%)	Methane loss (%)	Reference
PSA	96-98	4	(Adnan et al., 2019)
Water scrubbing	>97	<2	(Awe et al., 2018)
Organic physical scrubbing	93-98	1	(Bauer et al., 2013)
Chemical scrubbing	99	0.1	(Niesner et al., 2014)
Membrane separation	98	0.5	(Tomich & Vision, 2016)
Hydrate formation	95	-	(Tajima et al., 2004)
Biological method	90	-	(Luo et al., 2012)
Cryogenic separation	96-97	0.5-3	(Matthew D. et al., 2017.)
In situ methane enrichment	95	2	(Petersson et al., 2009.)

2.6 Upgrading of biogas using low-cost natural materials

Most commercial process of biogas upgrading require high capital investment and have high running costs. This limits there applications especially on small scale biogas plants. The use of natural materials presents a cheap alternative for biogas upgrade. This entails use of locally available materials such as clay, zeolite, fly ash and wood ash. The suitability of these materials unlike the commercial methods is mainly dependent on their capacity to remove biogas contaminants than their capital and running costs. Some of the locally available materials that are commonly applied in biogas upgrade are explained below.

2.6.1 Low-cost adsorbent material

Natural materials for adsorption of carbon dioxide are easily available and they provide cheap process compared to commercial methods. These natural materials include; clay, zeolite, fly ash and wood ash. Some of these materials contain inorganic and organic impurities that cover the pores, so that it has decreased adsorption ability. The physical and chemical activation cleans the pores surface and therefore increases the ability of adsorption (Wiyantoko & Rahmah, 2017 ; Chouikhi et al., 2019).

2.6.1.1 Clay

The main limitation to application of natural clay as adsorbent for biogas removal is low adsorption capacity (Chouikhi et al., 2019). Previous studies have reported the adsorption capacity of natural clay in the range of 0.53-1.48 (Chen et al., 2013, Elkhalifah et al., 2015, Chen et al., 2014, Cecilia et al., 2018). Hence, natural clay has low adsorption capacity. However, this can be solved by modification to produce superior products for biogas upgrading. The natural clay mineral can be activated with acid, organic compound, amino group and base. The activation of natural clay with different medium for carbon dioxide removal from biogas has been reviewed (Chouikhi et al., 2019). The activation of clay increased the adsorption of carbon dioxide, micro porosity and the texture properties. Acid treatment of clay can increase the pore volume and pores size with short treatment times. However, the process leads to loss of the cations which decreases the adsorption capacity of carbon dioxide (Komadel & Madejová, 2013). Acid treatment of clay showed that the specific surface area of clay increased by 44% while the adsorption capacity of carbon dioxide decreased by 37% (Franco et al., 2014). The treatment of clay using basic reagents produces adsorbents with excellent properties to capture carbon dioxide. For example synthetic zeolite can be prepared from clay minerals by using strong basic medium under hydrothermal condition which have high adsorption capacity in the range of 6.9-4.8mmol/g (Chen et al., 2014 ; Garshasbi et al., 2017).

2.6.1.2 Zeolites

Natural zeolite contains inorganic and organic impurities that cover the pores of zeolite, so that its adsorption ability is reduced. Natural zeolites can be activated by physical and chemical activation. This activation can help to clean the pore surface and increase the adsorption capacity. Physical activation is done using high temperature around 300-400°C. Chemical activation can be done using either acids or bases which remove the impurities especially oxides including silica and free aluminum thereby cleaning the pores surface (Wiyantoko & Rahmah, 2017).

The use of NaOH has been shown to improve the structure of zeolite. The chemicals clean the pore surface and increase the porosity of the adsorbent. The process removes the impurities especially oxides using sodium hydroxide as illustrated in equation 2.2 and 2.3 respectively.

$$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O \quad (2.2)$$

$$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O \quad (2.3)$$

Furthermore, chemical activation with sodium hydroxide replaces the hydrogen ion in zeolite structure with sodium ion thereby increasing its adsorption capacity. The reaction for this replacement is given in equation 2.4.

$$NaOH + \equiv Si\text{-}OH \longrightarrow \equiv Si\text{-}ONa + H_2O \quad (2.4)$$

A previous study used various concentrations of KCl to activate natural zeolite (Bacsik et al., 2016). It was observed that the adsorption capacity of carbon dioxide was in the range of 0.76-2.07mmol/g. In addition, published results have reported a carbon dioxide uptake in range of 0.2 to 4 mmol CO_2/g-adsorbent (Alonso-Vicario et al., 2010, Paolini et al., 2015, Deng et al., 2012, Bae et al., 2013).

2.6.1.3 Fly ash

Fly ash is another solid sorbent mineral for carbon dioxide capture whose source is coal fired power plant. Carbon dioxide can be captured by fly ash through carbonation and adsorption (Yan et al., 2015; Arenillas et al., 2005). The fly ash captures carbon dioxide when adsorption occurs on the surface of fly ash by stronger interaction between carbon dioxide and species in fly ash surface such as hydroxyl. Carbonation is another way to capture carbon dioxide by which a reaction occurs between carbon dioxide and metal oxide. After capturing of the carbon dioxide, the fly ash can be used as an admixture in cement mixtures. The adsorption of carbon dioxide occurs by physical interaction between carbon dioxide and the fly ash surface area. For carbonation, the free CaO reacts with CO_2 to form $CaCO_3$ (Siriruang et al., 2016).

According to Siriruang et al., (2016), the comparison of carbonation method and adsorption method, showed that a higher percent of carbon dioxide capture (870.1 (µmol/g fly ash) was obtained through carbonation method. Therefore, carbonization method is good for removal of carbon dioxide which is attributed to the amount of free CaO content. Alhamed et al., (2014) reported 26mg/g adsorption capacity of carbon dioxide using activated fly ash at partial pressure and temperature of 0.9atm and 25°C respectively (Alhamed et al., 2014).

2.6.1.4 Wood Ash

Wood Ash is generated from the combustion of wood such as burning wood when used as industrial power or home fire. In addition, ash could be prepared from municipal solid waste incineration where it is called bottom ash. The chemical compositions of ash are CaO, SiO_2, Al_2O_3, Fe_2O_3, K_2O, MgO, MnO, Na_2O, P_2O_5 and TiO_2 (Guo et al., 2015). Wood ash and municipal solid waste ash is used to remove carbon dioxide by accelerated carbonation method (Lombardi et al., 2016). Wood ash has a high content of calcium oxide compared to municipal solid waste incineration ash. The high content of calcium from ash combustion of wood fuels makes it very suitable for high carbon dioxide uptake from biogas. Wood ash adsorption capacity can be improved by modification with chemicals such as monoethanolamine (MEA), diethanolamine (DEA), tetraethylenepentamine (TEPA), polyethyleneimine (PEI) and diethylenetriamine (DETA) (P. Wang et al., 2017). In addition, Lombardi et al., (2016.) reported that, the carbon dioxide removal can be improved using rotating reactor. The rotating drum reactor had higher removal capacity compared to fixed bed reactor (Lombardi et al., 2016.).

From the literature, high removal of carbon dioxide (4.5 mmol/g-ash) using wood ash was achieved (Andersson & Nordberg, 2017). Another study with ash observed that the pH was reduced by 2-3 units due to the carbonation reactions (Andersson & Nordberg, 2017; Juárez et al., 2017). The uptake of carbon dioxide through the carbonation process causes a decrease in the pH of the media. This is because the oxides are converted to bicarbonates.

2.6.1.5 Activated carbon

Activated carbon can be derived from any rich carbon organic materials such as agricultural waste, plant biomass, industrial waste and household wastes (Rodriguez-reinoso et al., 2008). It can also be prepared from fossil carbon (Hsu & Teng, 2000). However, fossil sources are the main cause of global warming. Therefore, preparation of activated carbon from plant, agriculture waste or industrial waste is more sustainable and preferable method of preparing carbon adsorbents. Biochar is another cheap and widely available material from biomass that can be used for biogas cleaning. It can also be produced from carbon - rich materials like agricultural wastes (Adilla et al., 2013).

Activated carbon derived from biomass materials is activated by physical and chemical treatments. The adsorption capacity depends on the surface area and pore volume especially on the micropore (Paul. T 2006; Zabaniotou et al., 2008). Therefore, chemical activation is more effective than physical activation since chemical activation increases the surface area, micropore and pore volume.

2.6.2 Characterization of adsorbent

The physical and chemical properties of adsorbents before and after sorption process can be characterized using X- ray diffraction, X- ray fluorescence (XRF), scanning electron microscopy, Fourier transform infrared spectroscopy and N_2 adsorption/desorption Brunaure, Emmett and Teller (BET) surface area analyzer (Fatemi & Rad, 2013). X-ray diffraction is used to characterize physical properties of adsorbents such as channel dimension and free volume. X-Ray fluorescence is used to determine the chemical composition of adsorbent samples. Specific surface area (SSA) characterization plays an important role in adsorption process e.g. ion-exchange abilities, complexation and chelation (Balintova & Demcak, 2016). Siriwardane et al., (2003) analyzed the physical properties of natural zeolite micropores using the Horvath- Kawazoe (HK) method and obtained the surface area data from Density Functional Theory (DFT) and Langmuir methods (Siriwardane et al., 2003). The study used X- ray photoelectron spectroscopy (XPS) for analysis of chemical properties of natural zeolite (Siriwardane et al., 2003). Several studies have reported physical and chemical properties of adsorbent such as natural and modified clay, zeolite ash by using X-ray diffraction (XDR) and BET (Bertagnolli et al., 2011; Frantz et al., 2016).

The physical and chemical adsorbents depend on the nature of material and the activation chemical acid or base. Garshasbi et al., (2017) reported that synthesis zeolite 13X prepared from clay had 591m^2/g specific surface area and 0.250cm^3/g micropore volume analyzed using FT-IR spectrum. On the other hand, Chen et al., (2014) synthesized zeolite 13X from bentonite clay with 688m^2/g surface area and 0.30cm^3/g micropore volume. The natural zeolite and fly ash surface area has also been reported in the literature by many authors. A study on activated zeolite reported 120m^2/g surface area (Sholihah et al., 2018). Zhang.Z et al., (2010) also reported that, the surface area of activated zeolite was 164.3m^2/g. The surface area of fly ash reported by Alhamed et al., (2014) was 161.17 m^2/g.

2.7 Mechanism of CO_2 removal from biogas during upgrade process

Carbon dioxide can be removed by low-cost natural materials through; carbonation and physical adsorptions processes that are explained below.

2.7.1 Carbon dioxide removal by carbonation process

In wet carbonation process, free calcium oxide reacts with water to form calcium hydroxide. The hydroxide then reacts with carbon dioxide to form calcium carbonate and water (Jo et al., 2012). The high content of CaO increases the adsorption capacity of the adsorbents. Therefore, the adsorption capacity in the carbonation process depends on the contents of CaO in the adsorbents. In addition, the carbonation process is influenced by the adsorbent/water ratio, carbonation temperature and the gas flow rate (Ji et al., 2017). The presence of water in carbonation process improves the adsorption capacity of biogas. Water is required to hydrate the metallic oxide and form hydroxide. However, high water content reduces the concentration of ions. Therefore, the interaction between the ions and adsorbates is reduced which decreases the effectiveness of the contaminant removal.

2.7.2 Carbon dioxide removal by dry adsorbent process

Adsorption is a surface phenomenon. The adsorption process is the sticking of molecules, ions or atoms from a liquid, gas or dissolved solid to a surface of the substrate which can be liquid or solid (Kaithwas et al., 2012). The adsorption process depends on the surface energy. Surface atoms of the adsorbent are partially exposed so that they attract the adsorbate molecules. Adsorption process works best at low temperatures. In adsorption process, the enthalpy change is always negative when a gas is adsorbed on a solid surface. It has restricted movement and this leads to a decrease in the entropy. The entropy change (ΔS) of the gas is negative. The process causes a decrease in the surface energy of the adsorbent. Therefore, adsorption is an exothermic process (Sen & Gomez, 2011). Figure 2.4 illustrates the removal of biogas contaminants by adsorption process.

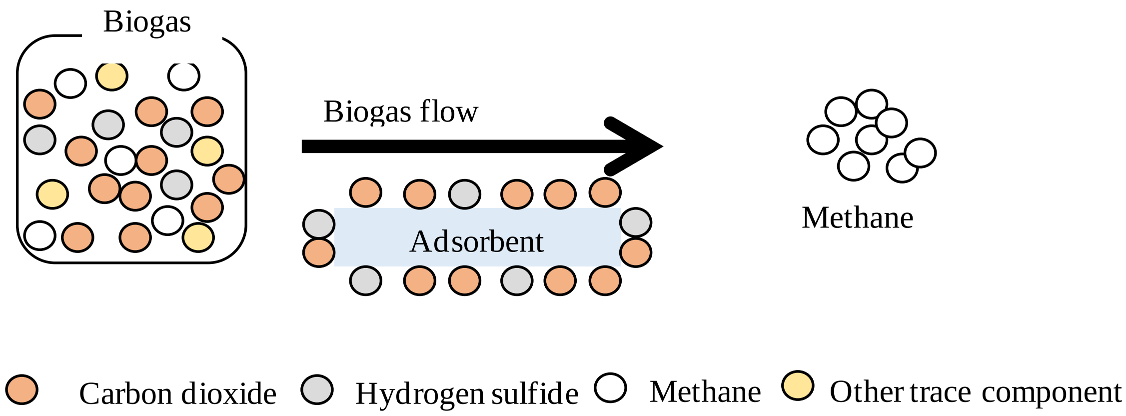


Figure 2.4:- The process of adsorption in biogas upgrade (Source: Mulu et al., (2021))

2.8 Factors that affect the performance of biogas upgrade using natural adsorbents

The removal of CO_2 using locally available adsorbents like natural zeolite, clay and ash is affected by process factors including: biogas flow rate, CO_2 inlet concentration, adsorption temperature, biogas pressure and SiO_2/Al_2O_3 molar ratio of adsorbent.

2.8.1 Effect of biogas flow rate on upgrade process

The gas flow rate affects the adsorption capacity. Yaumi et al., (2018) investigated the effect of gas flow rate and observed that the increase of flow rate from 30 to 60ml/min caused a decrease in the adsorption capacity from 4.41 to 3.4mmol/g. This is because the contact time between the adsorbent surface area and gases is reduced. In addition, it reduces the external mass transfer (Yaumi et al., 2018). These is also supported by another study where a decrease in total gas feed flow rate increased the adsorption capacity on the adsorption process. The total gas flow rate of 90ml/min produced the adsorption capacity of 27mg/g which reduced to 25.38mg/g and 25.73mg/g at 120ml/min and 150ml/min respectively (Tan et al., 2014). In contrary, it was found that very low and high gas flow rate reduced the adsorption capacity for the carbonation process. According to Ji et al., (2017), low gas flow rate (60ml/min) produced low adsorption capacity due to low mass transfer rate between gas and the slurry. Similarly, the high flow rate of gas reduced the contact time between adsorbate and the adsorbent (Ji et al., 2017).

2.8.2 Effect of carbon dioxide inlet concentration on biogas upgrade process

The effect of carbon dioxide inlet concentration was studied at 24% and 47% while the flow rate and breakthrough time were held constant at 50 ml/min and 180 seconds respectively. It was observed that at a high carbon dioxide concentration of 47%, the adsorption capacity was 1.388mmol/g. In contrary, at 24% concentration of carbon dioxide, the adsorption capacity decreased to 0.713mmol/g (Munusamy et al., 2012).

2.8.3 Effect of adsorption temperature on biogas upgrade process

Temperature is important in capture of carbon dioxide by adsorption. Mixed results have been posted on the effects of temperature on adsorption with different adsorbents. A study with fly ash reported 2.9 mmol/g fly ash at 30°C but the same reduced by 45% and 90% at 60°C and 100°C respectively (Siriruang et al., 2016). This was also observed in a study with clay where the adsorption of carbon dioxide from biogas decreased with an increase in temperature from 25°C to 35°C (Garshasbi et al., 2017). The high temperature affects the physical surface of adsorption. Adsorption of carbon dioxide is an exothermic process and therefore an increase in temperature decreases adsorption. However, there are other process like the removal of heavy metal using clay where increase in temperature increases adsorption (Uddin, 2017). In this regard, probably carbonation was more prominent than adsorption. Such reactions are endothermic which favors high temperature operations. A carbonation process of carbon dioxide removal reported an increase in removal capacity by increasing the temperature (Yan et al., 2015). Similar findings were reported in a study with activated fly ash with amine PEI where high temperature improved carbon dioxide removal (Arenillas et al., 2005).

2.8.4 Effect of biogas pressure on upgrade process

The carbon dioxide adsorption capacity increases with an increase in adsorption pressure. The study on adsorption of carbon dioxide using fly ash found that carbon dioxide removal increased by more than four folds on increasing the pressure from 1.2 atm to 1.5 atm (Siriruang et al., 2016). In another study with nitrogen-enriched activated carbon, the adsorption capacity at 0.1 bar and 298K was 0.23 mmol/g adsorbent. However, on increasing the pressure to 1 bar at 298K, the value increased to 1.89 mmol/g adsorbent (Bezerra et al., 2011). The concentration of gaseous adsorbate in this case carbon dioxide is proportional to the pressure. Therefore, an increase in pressure increases adsorbate particles that collide with the adsorbent surface.

In addition, the capacity of carbon dioxide adsorption was found to increase with an increase in the partial pressure of carbon dioxide at high ratio of SiO_2/Al_2O_3 (Bonenfant et al., 2008). This is because the concentration of adsorbate is proportional to the partial pressure in gaseous process.

2.8.5 Effect of SiO_2/Al_2O_3 ratio of adsorbent on biogas upgrade process

The low ratio of SiO_2/Al_2O_3 in adsorbent is desirable because it produces high adsorption capacity of carbon dioxide at low pressure (Bonenfant et al., 2008). The number of charge site on the surface of the adsorbents is high with low SiO_2/Al_2O_3 ratio. This increases the electric field of the adsorbents therefore increasing adsorption capacity. The electric field of the adsorbent increases by increasing the number of the charge sites present on the surface of the adsorbent. Harlick & Tezel, (2004) reported that low ratio of SiO_2/Al_2O_3 in zeolite H-ZSM structure has the strong electrostatic interaction with carbon dioxide. Similarly, Wilson & Tezel, (2019) observed that at low ratio SiO_2/Al_2O_3 of 30 on ZSM-5 zeolite had higher adsorption capacity compared to a ratio of 50.

2.9 Biogas quantity and quality analysis

The volume of biogas produced can be analyzed by water displacement, gas rotameter and gas flow meter. In laboratory scale, the biogas generation can be trapped in gas collection bags or balloons (Rathod et al., 2018). The methane, carbon dioxide and hydrogen sulfide content in biogas can be analyzed by Gas chromatography (GC), infrared sensor and thermo gravimetric analyzer. The GC is widely used for biogas analysis among other applications (Al-bukhaiti et al., 2017).

2.9.1 Gas chromatography

Gas chromatography is a type of chromatography used to separate the analytic substances in columns and analyzing them in detectors. The GC analysis method has high precision, accuracy, repeatability and reproducibility of retention times. Further, the method has good resolution, high peak capacity accuracy and speed. It is used to analyze the chemical components including biogas (Maggs, 2018), biodiesel (Ragonese et al., 2009), bioethanol (Hessami et al., 2019) and various organic contaminants (Santos & Galceran, 2002). The GC has a short analysis time and has high sensitivity (Maggs, 2018). The components of GC include carrier gas, column, injection port, detector, integrator chart recorder, heaters for maintaining a temperature of the injection port and oven (Eiceman, 2006). The carrier gas is chemically neutral and free of oxygen. It is usually an inert gas such as nitrogen, hydrogen, and helium. The choice of the carrier gas depends on the desired performance and the detector being used (Shankar et al., 2012). The separation of components depends on the mobile/stationary phase, characteristics (volatility and polarity) and mechanism (column). GC has different type of detectors, and the most common types of detector are: - flame ionization detector (FID) and thermal conductivity detector (TCD) (Zamorska-wojdyła et al., 2012). Thermal conductivity detector (TCD) uses helium or hydrogen as a carrier gas. The GC-FID is highly sensitive to hydrocarbons and most organic compounds such as CH_4 (Zamorska-wojdyła et al., 2012). The GC analyzes methane content based on the quantitative relationship of various volumes of standard gas injected into the GC system which are correlated to corresponding methane contents. The working condition of the GC is determined by the detector, injector and column temperature. It is also determined by the split ratio, purity and flow rate of gas.

A study of analysis of biogas reported good methane separation in GC by using 250^oC, 200^oC and 150^oC as temperatures for detector, inlet chamber (injector) and column respectively (Maggs, 2018). The nitrogen flow rate was 2.0ml/min, hydrogen flow rate was 45ml/min, oxygen flow rate was 450 ml/min and the split ratio of gas sample in inlet chamber was 20:1 (Maggs, 2018).

2.9.2 Adsorption Capacity

The ability of adsorbent to remove the adsorbate can be described by its adsorption capacity (q_e, mg g^{-1}) illustrated in equation 2.5. The carbon dioxide removal percentage (%) can be determined using equation 2.6 (Ates & Akgül, 2015).

$$q_e = \frac{(C_o - C_e)\,V}{m} \qquad (2.5)$$

$$\%\ \text{Efficiency of removal} = \frac{C_o - C_1}{C_0} \text{x}100\% \qquad (2.6)$$

Where, C_o is initial adsorbate concentration, C_1 is adsorbate concentration after purification, C_e is equilibrium adsorbate concentration, v is the volume of solution and m is the amount of adsorbent.

2.9.3 Adsorption kinetics

Adsorption kinetics is a line or curve which describes the retention time of gas- solid interface. The adsorption kinetics data can be fitted to pseudo first, pseudo second order model, Elovich model and intra particles diffusion models among other models. The kinetics model can also be done by linear and nonlinear methods. The linearizing method determines the goodness of fit to model using the least square regression (R^2). However, the estimation of parameter by the regression fit is not accurate enough.

Nonlinear method can be done by Microsoft excel or CAVS adsorption software and this gives more parameters for determining the suitability of the model. Therefore the method is more accurate in this regard than linear method (Karri et al., 2017). The equations for different linear and non-linear models are presented in Table 2.3.

Table 2.3:- Different types of kinetic models in linear and nonlinear forms

Types of kinetics model	Linear	Non linear	Equation
Pseudo first order model	$\log(q_e - q_t) = \log(q_t) - \left(\frac{k_1}{2.303}\right)t$	$q_t = q_1(1 - e^{-K_1 t})$	(2.7)
Pseudo second order model	$\frac{dq_t}{d_t} = k_2(q_e - q_t)2$	$q_t = \frac{k_2 q_2^2 t}{1 + k_2 q_2 t}$	(2.8)
Elovich model	$\frac{dq_t}{d_t} = \alpha exp^{-\beta q_t}$	$q_t = \frac{1}{\beta}(1 + \alpha\beta t)$	(2.9)
Intra-particles diffusion models	$q_t = K_{id}(t)^a$	$q_t = k_{id}t^{0.5} + C$	(2.10)

Whereas q_t the adsorption capacity at particular time, q_e the adsorption capacity at equilibrium, k_1 the pseudo first order rate constant (min^{-1}), t is time, K_2 pseudo second order rate constant (g/mg.min), α is the initial adsorption rate (mg/g.min), β is the desorption constant (mg/g), K_{id} is intraparticle diffusion rate mg/g.$min^{0.5}$ and C is constant.

Pseudo first order model

The pseudo first order model (PFO):- according to (Demirbas et al., 2004), PFO model was introduced by Lagergren in late 19th century. It describes the direct relationship between the surface of adsorption capacity and the adsorption rate (Demirbas et al., 2004). The equation is expressed linear and nonlinear form in equation 2.7.

Pseudo second order model

The pseudo second order (PSO) was according to Sari et al., (2019) first applied in 1984 by Blanchard (Sari et al., 2019). The PSO describes the linear relationship between the surface of adsorption capacity and the adsorption rate. The equation is given in linear and nonlinear form in equation 2.8.

Elovich

Elovich model was according to Sari et al., (2019) developed by Aharonic and Tompkins 1970 (Sari et al., 2019). It describes the chemisorption nature of adsorption and the interaction of gas molecules with heterogeneous surface. The equation is expressed in linear and nonlinear form shown in equation 2.9.

Intra particles diffusion models

Intra particles diffusion model is an old model that was developed by weber and Morris 1963 (Sari et al., 2019). It describes the diffusion controlled and diffusion mechanism. The equation is expressed in linear and nonlinear form shown in equation 2.10.

2.9.4 Adsorption isotherms

Adsorption isotherms describe the interaction of the adsorbate and the surface of the adsorbent. The adsorption equilibrium data of CO_2 can be described using isotherms; Langmuir, Freundlich, Toth, Temkin and Jovanovic-monolayer isotherm models (Eslek Koyuncu & Okur, 2021). The most commonly used adsorption isotherm is Langmuir and Freundlich models. The equations for the two models are presented in the Table 2.4.

The Langmuir model describes the monolayer type of adsorption. It describes adsorption on a homogenous surface (Benmessaoud, 2020; Hami et al., 2019). The equation is expressed in linear and nonlinear form shown in equation 2.11.

On other hand Freundlich Model is used to describe the multilayer heterogeneous adsorption model. It describes adsorption on the adsorbent with a heterogeneous surface (Benmessaoud, 2020; Hami et al., 2019). The equation is expressed in linear and nonlinear form shown in equation 2.12.

Table 2.4:- Linear and nonlinear of adsorption isotherm models

Types of kinetics model	Non - Linear	Linear	Equation
Langmuir isotherm	$q_e = \frac{q_{max}K_L\ C_e}{1 + K_L C_e}$	$\frac{1}{q_e} = \frac{1}{q_{max}\,K_L} + (\frac{1}{K_L b})\frac{1}{q_{max}\,C_e}$	(2.11)
Freundlich isotherm	$q_e = K_F\ C_e^{1/n}$	$\ln\ (q_e) = \ln(K_F) + \frac{1}{n}\ln\ (C_e)$	(2.12)

Where, q_{max} (mg g^{-1}) is the maximum adsorption capacity, K_L ($mg\ g^{-1}$) and b are the Langmuir constant, K_F (L g^{-1}) is the Freudlich adsorption constant, n is the adsorption intensity. The $1/n$ value is between 0 and 1.

2.9.5 Modeling of breakthrough curves

A breakthrough curve is important for modeling adsorptive separation process. It is used to evaluate the performance and breakthrough profile of a fixed bed column. The breakthrough curve of a fixed bed can be studied using different mathematical models such as Bohart-Adams, Thomas, Yan and Yoon-Nelson (Nam et al., 2020). The equations for the models are presented in the Table 2.5.

Bohart- Adams model describes the relationship between concentration and time. The model describes the initial portion of the adsorption in the column which is dominated by external mass transfer (Nam et al., 2020). The equation is expressed in linear and nonlinear form shown in equation 2.13.

Thomas model is one of the most common and widely used models. It describes the theoretical performance of the fixed bed breakthrough curves (Futalan et al., 2011). According to Chen et al., (2012) Thomas model was best fit for adsorption process that showed the external and internal diffusions were not the limiting step (Chen et al., 2012). The equation is expressed in linear and nonlinear form shown in equation 2.14.

Yan model is an empirical equation which is one of the best models to describe breakthrough curves. It overcomes the weakness in Thomas model in that it can make predictions of initial concentrations. Yan model is able to describe the initial portion of the breakthrough curve and predict the adsorption capacity (Shanmugam et al., 2016). The equation is expressed in linear and nonlinear form shown in equation 2.15.

Yoon – Nelson model is based on the assumption that the probability of adsorption of adsorbate and the probability of adsorbate breakthrough on the adsorbent is proportion to the decrease in adsorption (Calero et al., 2009). The equation is expressed in linear and nonlinear form presented in equation 2.16.

Table 2.5:- Linear and nonlinear of breakthrough curve models

Breakthrough models	Non - Linear	Linear	Equation
Bohart-Adams	$\frac{C_t}{C_o} = exp(K_{AB}C_o t - K_{AB}N_a\frac{Z}{Y})$	$\ln\left(\frac{C_t}{C_o}\right) = K_{AB}C_o t - K_{AB}N_a\frac{Z}{Y}$	(2.13)
Thomas	$\frac{C_t}{C_o} = \frac{1}{1 + exp[\left(\frac{K_{Th}q_{Th}m}{Q}\right)] - K_{Th}C_o t}$	$\ln\left(\frac{C_t}{C_o} - 1\right) = \left(\frac{K_{Th}q_{Th}m}{Q}\right) - K_{Th}C_o\text{t}$	(2.14)
Yan	$\frac{C_t}{C_o} = 1 - \frac{1}{1 + (\frac{Q^2 t}{K_y q_y m})\, K_y C_o/Q}$	$\ln[(\frac{C_e}{C_o - C_e})] = \left(\frac{K_y C_o}{Q}\right)\ln\left(\frac{Q^2}{K_Y q_y m}\right) + \left(\frac{K_y C_o}{Q}\right) lnt$	(2.15)
Yoon-Nelson	$\frac{C_t}{C_o - C_t} = exp(K_{YN}t - K_{YN}\tau)$	$ln(\frac{C_t}{C_o - C_t}) = K_{YN}t - K_{YN}\tau$	(2.16)

Where, C_t is the effluent concentration at any time (mg/mL), C_o is influent concentration (mg/mL), K_{AB} is Bohart Adams model constant (L/mg.min), N_a is bed sorption capacity (mg/L), Z is bed depth (m), Y is the removal percent, K_{YN} is Yoon Nelson model constant (min^{-1}), τ is the time required for retaining 50% of the initial adsorbate in min, K_{Th} is Thomas rate model constant (mL/min.mg), m is the adsorbent mass (g), q_{Th} is the adsorption capacity of column, Q is the feed flow rate (ml/min), K_y is the kinetic rate constant for Yan model L/mg.min) and q_y is the maximum adsorption capacity (mg/g) of adsorbent by Yan model.

2.10 Application of biogas

Biogas can be used to provide energy directly or indirectly. It can be applied directly to generate electricity, heat and thermal energy (Kadam & Panwar, 2017). Biogas can be converted into other gases like syngas using catalytic reforming (Kohn, 2012).

Furthermore, it can be compressed like natural gas and used as a transportation fuel (Jha et al., 2015). After upgrading of biogas, the methane rich biogas can be compressed into bio-compressed natural gas (Bio CNG) which can be used directly as engine fuel (Kadam & Panwar, 2017). The summary of various applications of biogas is given in Figure 2.5.

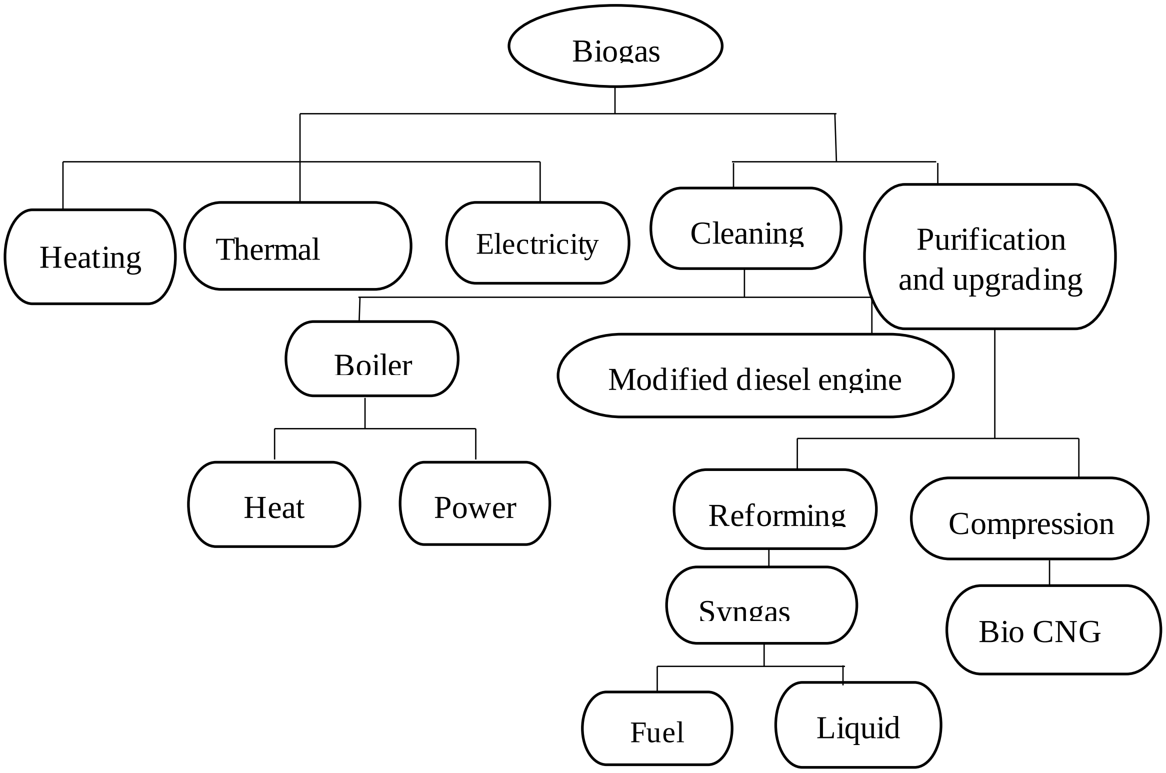


Figure 2.5:- Biogas applications (Sources: Mulu et al., (2021))

2.11 Literature gap identified

Different scholars have done some work on biogas upgrading using low-cost natural materials as reviewed (Chouikhi et al., 2019: Alonso-Vicario et al., 2010, Paolini et al., 2015: Mulu et al.,2021). Despite their great contributions, some research gaps were identified which include no documented comparative investigations between dry adsorption and sorption in slurry form for natural adsorbents. Furthermore, the effect of adsorbents to water ratio, slurry temperature, biogas flow rate and the activated adsorbents to biogas volume ratio on the adsorption capacity has not been fully investigated. Therefore, this research addressed the identified gaps and fills the knowledge voids by doing experimental investigation on biogas upgrading using natural materials clay, zeolite and wood ash.

CHAPTER 3: RESEARCH METHODOLOGY

3.1 Introduction

This chapter presents the collections of materials, methods and experimental procedures that were followed in conducting the research. In addition, it discusses the research station, materials collection and preparation, research equipment, activation of adsorbent, characterization of adsorbents and upgrade process of biogas.

3.2 Research area

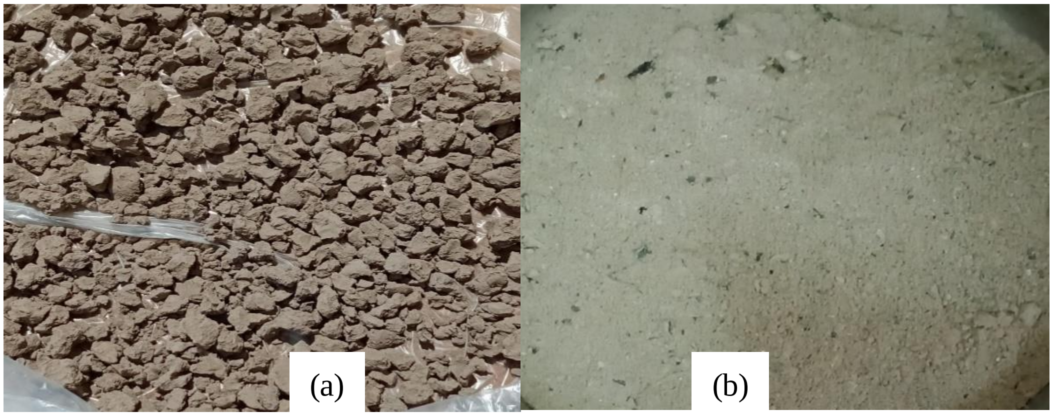
This study was carried out at Moi University biogas plant farm, Chemical and Processing Engineering Laboratory and Analytical Chemistry Laboratory in Eldoret, Kenya. Furthermore, the chemical composition of adsorbents was characterized at Ministry of Petroleum and Mining State Department of Mining, Nairobi Kenya.

3.3 Materials used in the study

The natural adsorbent materials that were used for biogas upgrading in this study includes clay, zeolite and wood ash. The adsorbents were collected from Ethiopia and Kenya due to their abundance availability. Natural clinoptilolites zeolite samples were collected from Hawassa zeolite area, located in the South Nations, Nationalities Regional State, Ethiopia. It is about 280km from South of Addis Ababa (capital city of Ethiopia). Plates 3.1 shows are natural zeolite.

Plate 3.1:- Natural zeolite

Natural clay samples were collected from the Awasi in Kisumu County, Kenya. Wood ash waste was collected from Moi University farm kitchen, Eldoret Kenya. This ash had been generated during cooking. Plates 3.2 show natural clay (a) and wood ash (b).



(a)

(b)

Plate 3.2:- Natural clay (a) and wood ash (b)

Sodium hydroxide was purchased from commercial laboratory chemicals shop Eldoret, Kenya. It was used for activation of the adsorbents. Distilled water was collected from civil engineering department of Moi University Eldoret, Kenya. It was used for activation of adsorbents. Raw biogas was collected from Moi University biogas plant constructed by ASALI project and located at Moi University farm Eldoret, Kenya. It was a fixed dome biogas digester, 24m^3 volume which used cow dung as substrate. The fixed dome biogas digester operated at low pressure in the range of 0-9 kpa.

3.4 Equipment tools

The following equipment and instrument were used in this research. Table 3.1 shows the list and description of the equipment.

Table 3.1:- List and description of equipment

Equipment	Descriptions
Flow meter	BPC oxygen flow meter from India was used, to measure the flow rate of a gas
Gas sample bag	Multi-layer bag and PTFE valve, MBT4l-1liters and 5 liters gas bags from China were used to collect biogas. They were used for containing/holding the biogas samples
Gas chromatography	The GC used for analysis of methane content in biogas was Shimanzu from Japan.
Laboratory glassware	Glass beakers of 500ml and 1000ml, graduated cylinder, 250 and 500ml of Erlenmeyer flask, crucible, spatula, dish tongs and foil from India were used.
Magnetic heating stirrer	Model 78-1 from China was used to shake a mixture solution. The stir had a magnetic bar that was immersed into the solution and was rotated by the magnetic field
Mesh	The sieves prufsieb, ISO 3310-1 from China were used. They were of sizes 400 micrometer. They were used to separates the sample in various particles sizes
Mortar and pestle	The two were from China and were used for grinding or crushing the adsorbents and convert them into fine powder. The mortar and pestle used consist of a bowl and a rounded grinding club for crushing
Oven	Model-DFO-36 oven from China was used for the heating, drying or baking of a substance. The voltage of oven was 220V and its frequency was 50cycle per second (Hz)
Pressure gauge	LN-TKAB model from China was used to measure the range of the gas pressures
Portable gas detector	ATO-SKY2000 series portable gas detector from China was used to analyzed biogas compositions including; methane, carbon dioxide, hydrogen sulfide and oxygen
XRF	Bruker model S1 titan from China was used to characterize the chemical components of adsorbent
Weight balance	Mettler Toledo weight balance from India was used to measure the mass or weight of the substrate

3.5 Construction of upgrading reactors

3.5.1 Dry powder adsorption process

The upgrading bed reactor was done using plastic container which had a top container, lid and a bottom container. On the middle part of the container (lid), holes were made and covered by a mesh placed 5cm on the packed bed reactor. The packed bed reactor had two holes; inlet on the bottom part and outlet on the top part of container. The two holes were of diameter 2.75cm. The dimension of the packed bed reactor consisted of 8.5cm and 9.5cm diameter at the top and bottom respectively. The total volume of top and bottom sides was 310ml and 360ml respectively. The bottom hole and the flow meter were interconnected with a hose pipe while the top hole was connected to gas bag which collected biogas sample after upgrading. Figure 3.1 illustrates the biogas upgrading set up used for adsorption process.

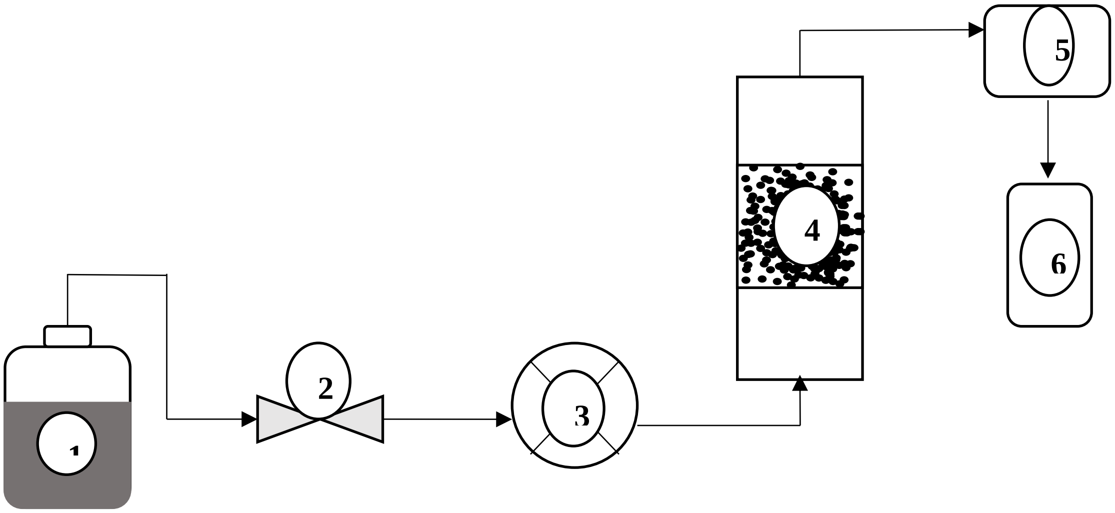


Figure 3.1:- Biogas upgrading set up for dry adsorption process

(1) biogas digester, (2) pressure gauge, (3) flow meter, (4) column bed height, (5) gas bag, (6) gas analyzer

3.5.2 Adsorbents in slurry form

Three different volumes of conical flask of 250, 500 and 1000ml were used as upgrading reactors. The mixture of adsorbent and water was filled into the reactor. After that, the reactor was put on magnetic stirrer for homogeneous mixing of adsorbent and water. Figure 3.2 illustrates the biogas upgrading set up on carbonation process used in the study.

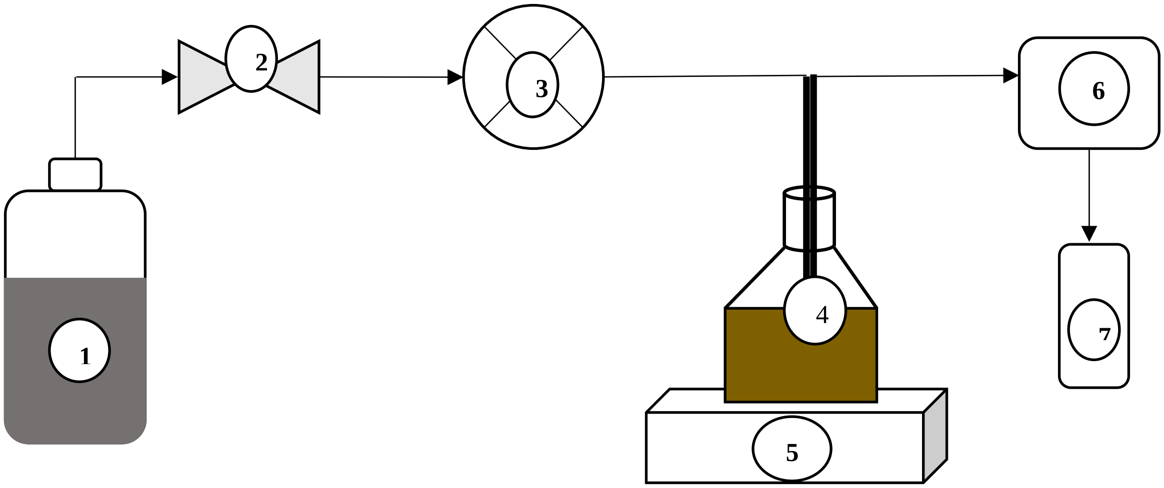


Figure 3.2:- Biogas upgrading set up for carbonation process

(1) biogas digester, (2) pressure gauge, (3) flow meter, (4) upgrading reactor, (5) magnetic stirrer, (6) gas bag, and (7) gas analyzer

3.6 Activation of adsorbents

3.6.1 Activation of zeolite

The zeolite was collected and reduced to smaller particle sizes using mortar and pestle. Zeolite was milled to powder and then separation to different particles sizes was done using a sieving mechanical shaker. The particle size less than 400 µm was separated and used for adsorption studies. The small particles size was chosen to increase the surface area of adsorbents. Subsequently, 200g of zeolite was soaked in the deionized water for 24 hours and air dried for 24 hours. A 10% NaOH solution was prepared by adding 20g of NaOH to 200ml distilled water.

Zeolite was washed, dried then mixed with 10% of NaOH solution. After mixing and stirring for 2 hours at a constant temperature of 70° C, the mixture of zeolite powder and NaOH solution was left to stay for 24 hours (Angkat & Seminar, 2017). The pH of zeolite and sodium hydroxide mixed solution was measured and noted. The activated zeolite was washed with distilled water until the final pH value of the filtrate reduced to 7. Finally, the activated zeolite powder was dried in an electric oven for an hour at 110°C. The preparation of activated zeolite by physical and chemical activation processes from natural zeolite is illustrated in Plate 3.3.

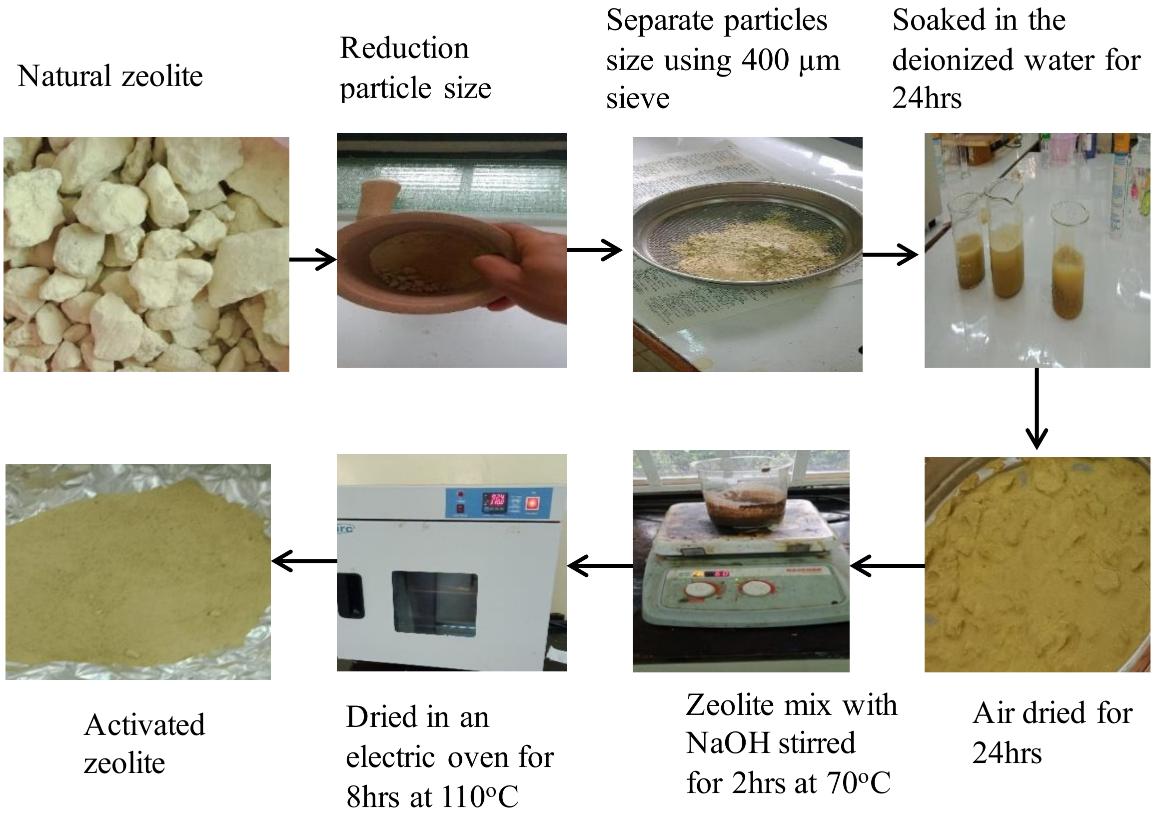


Plate 3.3:- Preparation of activated zeolite by physical and chemical activation of natural zeolite

3.6.2 Activation of clay

A total of 200g of the sieved clay was dispersed in 120ml of distilled water to form slurry. The slurry was pre-heated to 60°C for 5 minutes. Afterwards, 10% of NaOH solution was added to the preheated slurry and the mixture heated to 90°C for a specific experiment run under continuous stirring for 2 hrs. at 600rpm. The mixture was washed until the final pH value reduced to 7 (Kusrini, 2016). The slurry formed was dried conventionally in oven at 80°C for 4hrs until reached constant weight. The dried clay was ground to fine powder less than 400µm. The preparation of activated clay by physical and chemical activation processes from natural clay is illustrated in Plate 3.4.

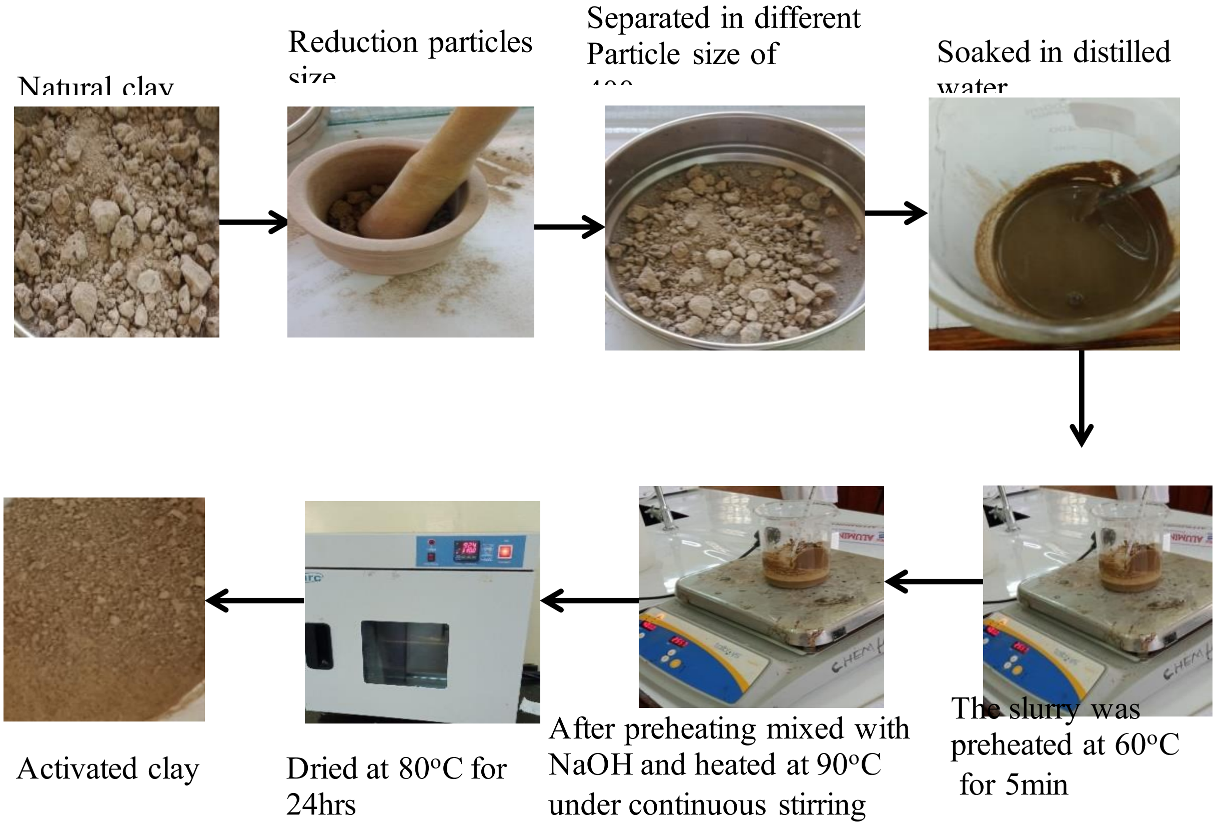


Plate 3.4:- Steps followed in physical and chemical activation of natural clay

3.6.3 Activation of wood ash

The wood ash powder was sieved into less than 400µm particles. Two hundred grams of wood ash was mixed with 10% of NaOH solution and kept under magnetic stirrer for an hour. After that, the mixture was dried at 110°C for 24hours and the adsorbents packed in the column. The preparation of activated wood ash by physical and chemical activation processes and the filling of the adsorbent in the column are illustrated in Figure 3.3.

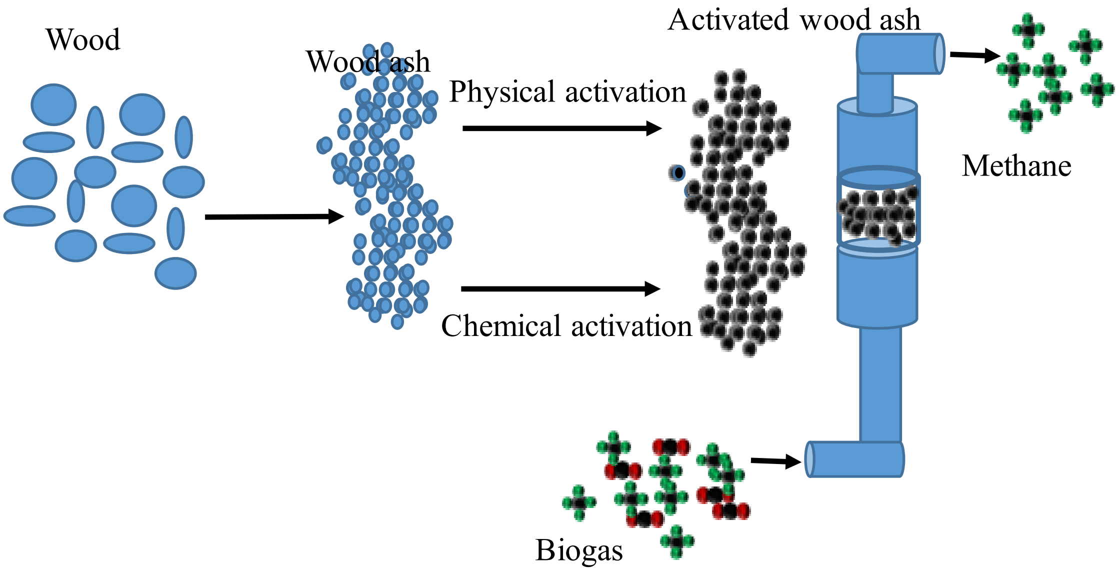


Figure 3.3:- Physical and chemical activations processes of wood ash for column adsorption (Source: Mulu et al., (2021))

3.6.4 Characterization of chemical properties of adsorbent samples

Natural and activated zeolites, clay and wood ash were characterized to determine their chemical compositions. Samples of zeolite, clay and wood ash were characterized by X–ray fluorescence (XRF) in ministry of petroleum and mining, state department of mining, Nairobi Kenya. Plate 3.5 illustrates the Bruker S1 Titan LE Handheld spectrometer portable X ray used for sample characterization.

Plate 3.5:- Characterization of the chemical components of adsorbent using X-ray fluorescence

3.7 Upgrade of biogas

The materials were used as sorbents to purify biogas via carbonation reaction and dry adsorption method. Each experiment was conducted in triplicate under the same condition to minimize the error by taking the average values of final methane content or carbon dioxide removed.

3.7.1 Upgrade of biogas using carbonation process

3.7.1.1 Preparation of slurry sorbent

Different ratios of adsorbent to water were prepared by adding different amount of water to 100g adsorbent. For example, 100g of air-dried wood ash was weighed and mixed with 100ml of water to make 1:1 ratio. The summary of adsorbents and water mixture for different ratios is given in Table 3.2.

Table 3.2:- The summary of the adsorbent to water mixture for different ratios

Ratio	Adsorbent in mass (g)	Water in volume (ml)
1:1	100	100
1:2	100	200
1:3	100	300
1:4	100	400
1:5	100	500

The mixture was put on the magnetic stirrer for 10min. After that, the initial pH and temperature values were taken. The mixture was put into the reactor and sealed then placed on the magnetic stirrer. It was then connected to a flow meter and biogas source for upgrade experiment. The setup for biogas upgrading experiment was as shown in Plate 3.6.

Plate 3.6:- The setup of biogas upgrading by carbonation process

The effect of adsorbent to water ratio on carbonation process

Biogas was upgraded with slurry as the sorbent. The tests were done using different ratio of adsorbent and water mixture. The slurry ratio of adsorbent and water in terms of weight and volume respectively (1:1, 1:2, 1:3, 1:4 and 1:5) were examined.

The adsorbent mass was constant at the same time the water was varied. The effects of these ratios on the purification of biogas were investigated. Biogas was passed through the upgrade reactor column at a constant flow rate of 100 ml/min. The adsorbents particle size was less than 400µm. The same procedure was applied for each type of adsorbents used.

The effect of biogas flow rate on the carbonation process

The effect of biogas flow rate on the carbonation process was studied at the maximum biogas purification capacity found of a ratio of 1:4 (adsorbent to water) and at room temperature. The biogas flow rates studied used were; 45, 100, 150, 200 and 250 /min. The flow rate was controlled by oxygen flow rate meter. Thereafter, the methane and carbon dioxide content of biogas were taken for each flow rate.

The effect of slurry temperature on the carbonation process

The effect of slurry temperature or carbonation temperature on the purification of biogas was studied at the maximum ratio and flow rate of biogas. Therefore, the effect of temperature was studied using the ratio of 1:4 and at biogas flow rate of 100 ml/min. The temperature of the reactor used for upgrade was controlled using a hot plate. The carbonation temperatures studied were between 18^{o}C and 80^{o}C. Thereafter, the methane and carbon dioxide content of biogas were taken for each flow rate.

3.7.2 Upgrade of biogas using dry adsorption process

The glass beads were packed at the top and bottom of the upgraded column. The middle section of the column was filled with various adsorbent mass. After that the column was sealed and connected to the flow meter and the biogas source digester as shown in plate 3.7.

Plate 3.7: - The set-up of biogas upgrade using dry adsorbent

The effect of biogas flow rate by dry adsorption process

The effect of biogas flow rate was studied using activated clay, activated zeolite and activated wood ash. The flow rate was varied from 45ml/min to 250ml/min. In addition, the effect of adsorbent mass to volume of biogas was investigated. Activated adsorbent was varied as follows; 5, 10, 15, 20, 25, 30 and 35g while the volume of biogas was kept constant 5litters.

3.7.3 Biogas analysis

The biogas samples were collected before and after upgrade using gas bags. Thereafter, the biogas components including CH_4, CO_2 and H_2S were analyzed using portable gas detector and gas chromatography.

Portable gas detector

The portable gas analyzer has a pump that transfers the gas through a sensor. The flow rate of biogas was regulated to less than 1L/min.

The sensors had been calibrated to analyze hydrogen sulfide (up to 2000ppm), methane (100% v/v), carbon dioxide (100% v/v) and oxygen (30% v/v). Plate 3.8 illustrates portable gas detector used in this study to analysis methane, carbon dioxide and hydrogen sulfide content of biogas before and after upgrading.

Plate 3.8: - Analyze the biogas components using portable gas detector

Gas chromatography

In this experiment, Flame ionization detector (GC-FID) was used to determine the chemical composition of biogas. The sample was injected into the injection port and was carried through the column by the carrier gas. The gas emerging from the column was combusted with hydrogen and air mixture. The reaction produces ions, which conduct an electric current that can be amplified and recorded on a chart recorder (Al-bukhaiti et al., 2017). Plate 3.9 illustrates GC used in this study to analysis methane content of biogas before and after upgrading.

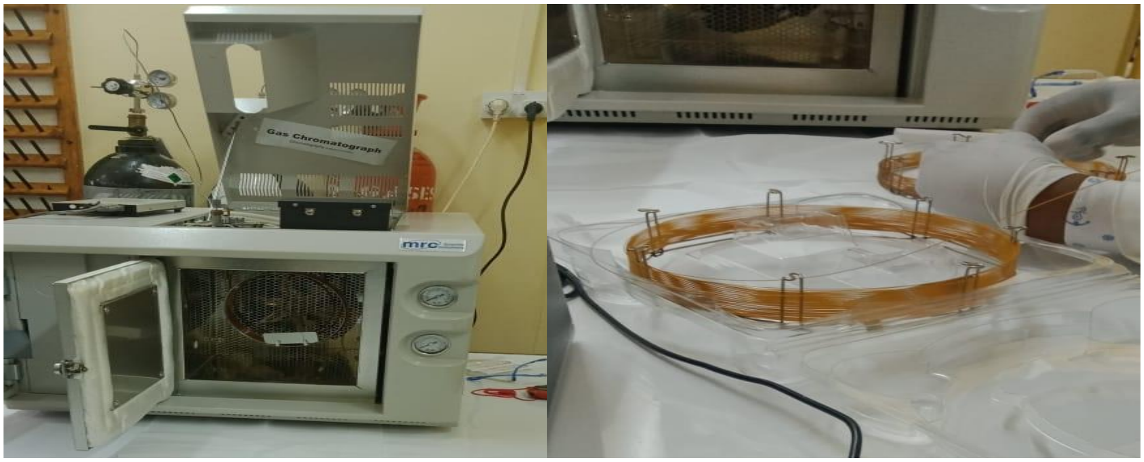


Plate 3.9: - Gas chromatography used for biogas analysis

The working condition of the GC is determined by the detector, injector and column temperature. It is also determined by split ratio, purity and flow rate of gas. Table 3.3 shows that the GC specifications and set up used in this study.

Table 3.3:- Gas chromatography analysis parameters

Gas chromatography components	Set up
Capillary column	Temp-150°C, Stationary phase HP-PLOT/Q Description 30m X 0.320mm X 20µm
Detector	250 °C, Flame ionization detector
Injector	200 °C
Nitrogen	2.0ml/min
Hydrogen	45ml/min
Oxygen	450ml/min
Spilt ratio	The inlet chamber spilt ratio 20:1

3.7.4 Adsorption capacity

The quality of biogas compositions of methane, carbon dioxide and hydrogen sulfide were determined before and after upgrading by using gas chromatography and digital biogas analyzer. The CO_2 adsorption capacity and percentage removal efficiency of the adsorbents were determined using the following equation 3.1 and 3.2 respectively (Ates & Akgül, 2015).

$$q_e = \frac{(C_o - C_1)V}{m} \qquad (3.1)$$

$$\% \text{ efficiency} = \frac{C_o - C_1}{C_0} * 100\% \qquad (3.2)$$

Where, C_o is CO_2 concentration (moles/liter) before purification, C_1 is CO_2 concentration after purification, and % efficiency is the effectiveness of biogas upgrade.

3.7.5 Experimental design

The experimental design involved investigating individual parameters independently for each study. The adsorbents behaviors were studied using adsorption kinetics, adsorption isotherm and breakthrough curves. The adsorption kinetics onto wood ash slurry were studied at different temperature (low, medium and high). Moreover, the breakthrough curve using activated clay was studied at different adsorbents mass at low, medium and high levels.

3.7.5.1 Adsorption kinetics

Adsorption kinetics models using dry activated clay and wood ash slurry were investigated. The kinetic data was fitted into four nonlinear kinetic models that included; pseudo-first order, pseudo-second order, elovich and intra-particle diffusion. The nonlinear kinetics model was done using CAVS adsorption software.

3.7.5.2 Adsorption isotherm

The experimental data on adsorption capacity of CO_2 from biogas using activated clay was evaluated for fitness into the adsorption equilibrium isotherms. In this study, the most common isotherm models of Langmuir and Freundlich nonlinear forms were studied. The nonlinear adsorption equilibrium was done using CAVS adsorption software.

3.7.5.3 Breakthrough curve

The experimental data on adsorption capacity of CO_2 from biogas using activated clay in a fixed bed column was used to analyze breakthrough curves.

The study investigated the effects of mass of activated clay on the breakthrough curves. The mass of adsorbents that were studied include: - 5g, 20g and 35g. The models that were used to evaluate the experimental data included; Bohart- Adams, Yan model and Yoon-Nesoln.

Data analysis

The adsorption kinetics, adsorption isotherm and breakthrough curve carbon dioxide data were analyzed using regression analysis (R^2) and error parameters including the root mean square errors (RMSE), sum of the square error (SQE) and person's chi-square measure (X^2) (Dissanayake et al., 2016). The goodness for fit of the models was determined using non linearization regression (R^2) and RMSE described the total magnitudes of the errors. The error function like SQE was used as an optimization criterion to determine the fit between the model and the experimental data used. The analysis of X^2 which expresses the closeness of the predicted model result to the experimental data was also found. The higher value of R^2 ($R^2 \geq 95$) and the lower value of the RMSE, SQE and X^2 was used to determine the best fitted model.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Introduction

This chapter presents the results of the findings that were achieved in the study and the discussion of the same.

4.2 Characterization of adsorbent

4.2.1 Chemical composition of adsorbents

The chemical compositions of adsorbents zeolite, clay and wood ash were analyzed using XRF. The removal of CO_2 from biogas by dry adsorption process depends on the SiO_2/Al_2O_3 ratio at low pressure. On the other hand, the removal of CO_2 from biogas by the carbonation process depends mainly on the CaO content. A decrease in SiO_2/Al_2O_3 increases the polar molecules electric field which improves the electrostatic interactions with carbon dioxide at low pressure (Harlick & Tezel, 2004). Table 4.1 shows that the summary of chemical composition of natural and activated adsorbents. The molar ratio before activation for natural zeolite was 16.1. However, the value for activated zeolite with 10% of NaOH ratio decreased to 15.4. This result shows that the activated zeolite adsorption capacity of carbon dioxide could be better than natural zeolite. Similarly, the molar ratio of SiO_2/Al_2O_3 for modified clay was lower than that of natural or unmodified clay. The results for unmodified and modified clay were 11.2 and 8.5 molar ratio respectively. The modified clay had slightly lower silica to alumina ratio compared to unmodified clay which is required to achieve high adsorption capacity. Wilson & Tezel, (2019) studied the effect of SiO_2/Al_2O_3 ratio on ZSM-5 zeolite. It was observed that at 50 ratio and 10.5atm the adsorption capacity of carbon dioxide was higher compare to a ratio of 30. However, at lower pressure in the range of 0 to 9 atm, the adsorption capacity was higher at a ratio of 30 than 50 (Wilson & Tezel, 2019).

Therefore, in this study, the low ratio of SiO_2/Al_2O_3 could be desirable due to the fact that the fixed dome digester of biogas operates at low pressure (<9kpa). Garshasbi et al., (2017) also reported that clay with silica to alumina molar ratio of 2.5 and activated with 4M NaOH had the highest adsorption capacity compared to the one with ratios 3.5 and 4.5 (Garshasbi et al., 2017). The results support the argument that activated clay with low molar ratio silica/alumina has high adsorption capacity.

Table 4.1:- Chemical composition of natural and activated adsorbents

Adsorbents	SiO_2/Al_2O_3 ratio	CaO (%)	K_2O (%)
Natural clay	11.2	2.21	6.05
Activated clay	8.5	1.03	3.95
Natural zeolite	16.1	1.47	2.18
Activated zeolite	15.4	1.41	1.96
Wood ash	-	46.02	20.47
Activated wood ash	-	59.84	11.74

The findings from XRF show that the main components of wood ash are calcium oxide. The percentage compositions for natural and activated wood ash of CaO were 46% and 59.84% respectively. the increase in percent mass of CaO for wood ash was due to removal impurities. According to Andersson & Nordberg, (2017) the high content of CaO indicates a high potential of carbon dioxide removal from biogas through carbonation process. The results suggest that carbon dioxide adsorption using wood ash is dominated by carbonation process.

A comparison between the ratio of SiO_2/Al_2O_3 in activated clay and activated zeolite indicate that modified clay has lower ratio, which indicates that clay has high carbon dioxide adsorption capacity. According to the Tables 4.1 clay and zeolite adsorption capacity is dominated by physical adsorption process due to the low ratio of SiO_2/Al_2O_3. The chemical composition of natural and activated wood ash indicates that CaO which was more than 46% is the major component. This value was much higher compared to that of clay (2.21%) and zeolite (1.47%). Therefore, the purification of biogas using wood ash is dominated by the carbonation process.

4.3 Upgrade of biogas using carbonation

4.3.1 The effects of adsorbent/water ratio on the carbonation process

4.3.1.1 The effects of wood ash to water ratio on carbonation process

The presence of water in the metallic oxides has significant role of hydrating the oxides to form hydroxides which reacts with carbon dioxide to form carbonates. This is the carbonation method of carbon dioxide removal from biogas. In addition, some carbon dioxide is directly adsorbed by the particles of adsorbent. Therefore, the process is a sorption process. Figure 4.1 shows that the results of different ratios of wood ash to water mixture (wood ash slurry) on the sorption capacity of biogas. It was observed that the 1:4 ratio had highest biogas purification (70.4%) compared to 1:1, 1:2, 1:3 and 1:5 ratios which showed lower improvement in methane content. Therefore, the maximum biogas purification capacity was found to be 1:4 ratio. The increase in the amount of water up to optimal ratio increases ionization of metallic oxides like CaO and K_2O to form hydroxides that reacts with the carbon dioxide.

Similar observations were made by other researchers where semi-wet fly ash was found to be more effective in CO_2 capture than dry fly ash due to high content of metallic oxides (Kim & Kwon, 2019). Moreover, the continuous stirring of the slurry improved the hydrating of the oxides and the mass transfers of gas and slurry by ensuring adequate mixing which improves the CO_2 capture. Ukwattage et al., (2017) also reported that the continuous stirring of slurry enhanced the CaO extraction efficiency thereby improving the adsorption capacity of CO_2 (Ukwattage et al., 2017). However, further increase in water beyond the optimal ratio decreases the interacting concentration of the ions and adsorbent particles which consequently lowers the rate of biogas uptake. These results are supported by GC analysis of methane in biogas is as presented in the Appendix 1.

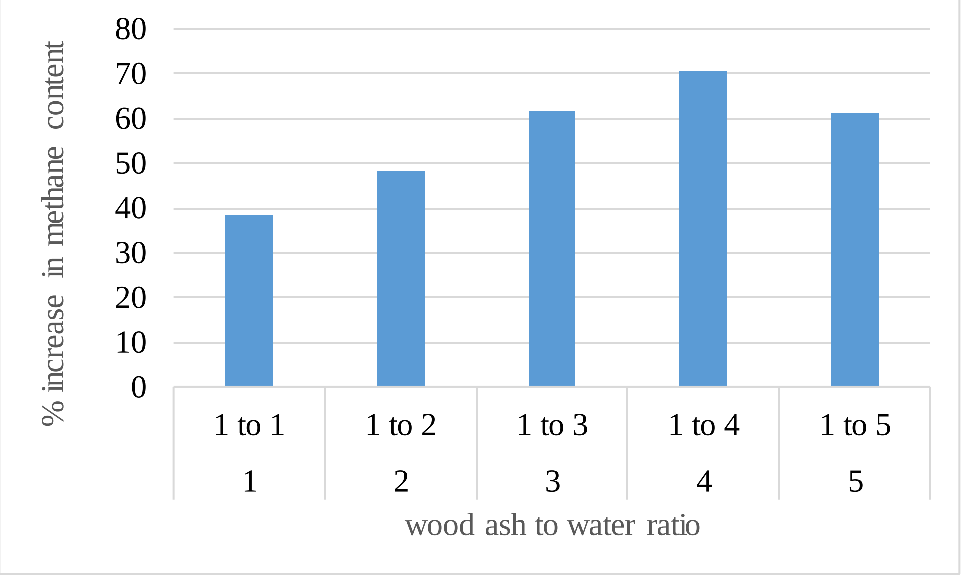


Figure 4.1:- Upgrade of biogas using different ratio of wood ash/water at 100ml/min

4.3.1.2 The effects of clay to water ratio

Figure 4.2 shows that the results of different ratios of clay and water mixture (clay slurry) on the capacity of biogas purification. Bases such as CaO and K_2O found in clay dissolve in water to form hydroxides like calcium hydroxide and potassium hydroxide that react with carbon dioxide to form carbonates. The highest biogas purification was gotten at 1:3 ratio. The increase in methane contents by carbonation system using natural clay was low (18.9% - 34.9%) compared to wood ash. This could be attributed to low content of alkaline oxides (2.21 % CaO or 6.05% K_2O). High absorption capacity of carbon dioxide by using CaO-based sorbent had been reported by other studies (Skoufa et al., 2016). Therefore, high content of CaO can enhance upgrade of biogas. The results of GC analysis of methane in biogas are as shown in Appendix 2.

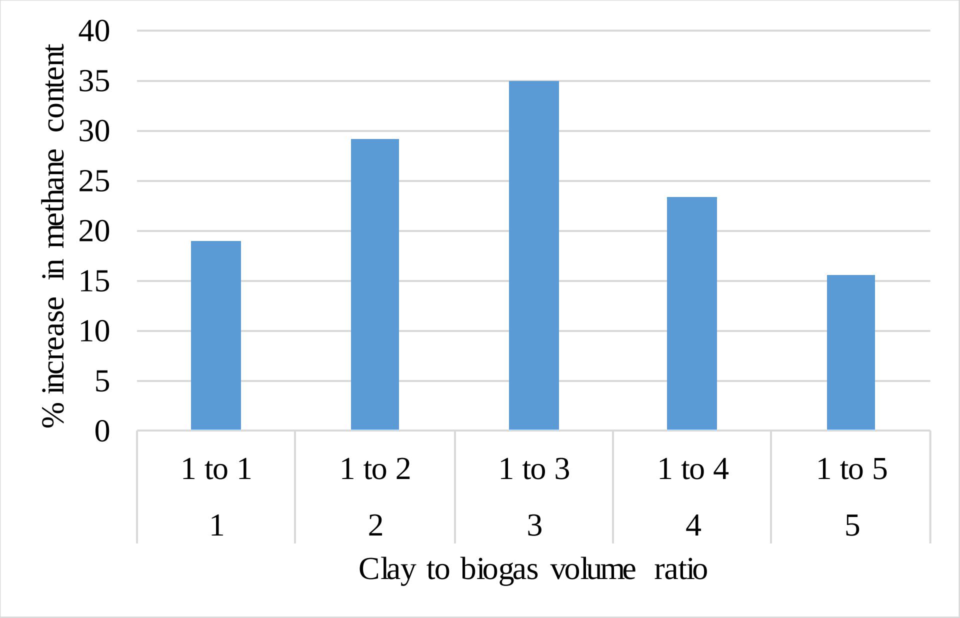


Figure 4.2:- Upgrade of biogas using different ratios of clay/water at 100ml/min

4.3.1.3 The effects of zeolite to water ratio

Figure 4.3 shows that the results of different ratio of zeolite and water mixture on biogas purification capacity. The highest biogas purification capacity was found with the 1:1 ratio. The results of GC analysis of methane in biogas are as shown in Appendix 3.

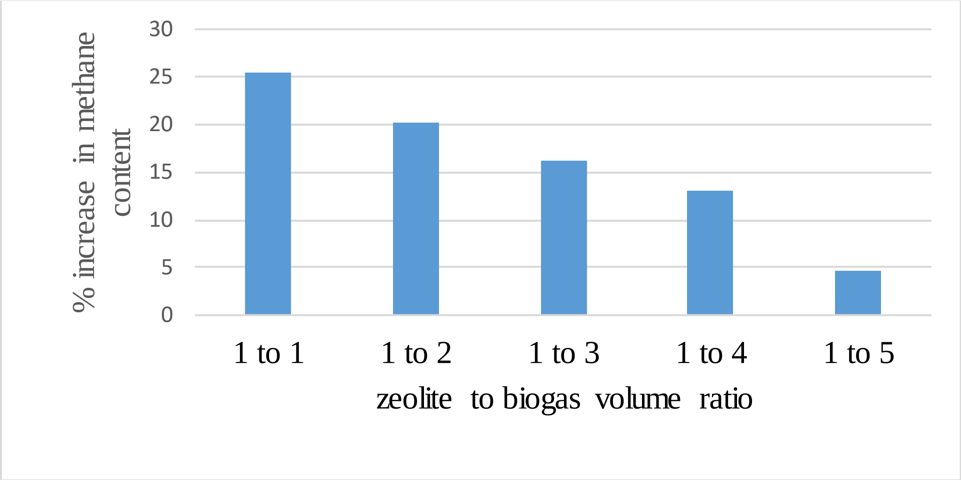


Figure 4.3:- Upgrade of biogas using different ratio of zeolite/water at 100ml/min

The mixture of wood ash/water had higher biogas purification capacity compared to clay and zeolite. The wood ash/water increased the methane content of biogas by 70.4% while clay/water and zeolite/water increased the methane content by 34.9 % and 25.31% respectively. This could be due to the high content of CaO (46%). Therefore, the biogas purification capacity is attributed to the percentage of alkaline oxides such as (CaO) present within each adsorbent. The removal capacity of carbon dioxide from biogas using zeolite and clay slurry is dominated by surface adsorption and therefore less than that of wood ash which is dominated by carbonation process. Moreover, the presence of water in the zeolite surface created the strong polar which adsorbed on the exchangeable cation. This reduces the strength and heterogeneity of the electric field which decreases the adsorption capacity (Bonenfant et al., 2008). The chemical reaction of carbon dioxide removal from biogas by carbonation method is presented in equation 4.1 and 4.2.

$$CaO + H_2O \xrightarrow{\qquad} Ca(OH)_2 \qquad (4.1)$$

$$Ca(OH)_2 + CO_2 \xrightarrow{\qquad} CaCO_3 + H_2O \qquad (4.2)$$

4.3.1.4 The effect of biogas upgrade on the slurry pH

The pH of raw wood ash was initially around 10.9. The biogas from a digester was made to flow through the wood ash slurry. The reaction between the carbon dioxide and calcium bases in the slurry produced $CaCO_3$ and H_2O and this reduced pH value to around 9.9 in 60 minutes. The dissolution of $CaCO_3$ slowly dropped the pH value to around 6.2 after around 6 hours. Similarly, the raw biogas was bubbled through the clay slurry where the concentration of hydroxide ions was consumed by reaction with carbon dioxide to form carbonates. Therefore, the clay slurry pH of 9.2 was reduced to 6. The natural zeolite pH value also reduced from 8.5 to 5.8. This reaction shows that the pH value of the slurry dropped due to the capture of carbon dioxide. Therefore, increasing the alkalinity of slurry increases the purification of biogas. The carbon dioxide removal by carbonation process was favored by high pH value. The findings from this study are in agreement with those from Huijgen, (2005) where high pH value of slag was found to produce high CO_2 adsorption capacity (Huijgen, 2005). The effect of biogas upgrade on the media pH for carbonation process is illustrated in Figure 4.4.

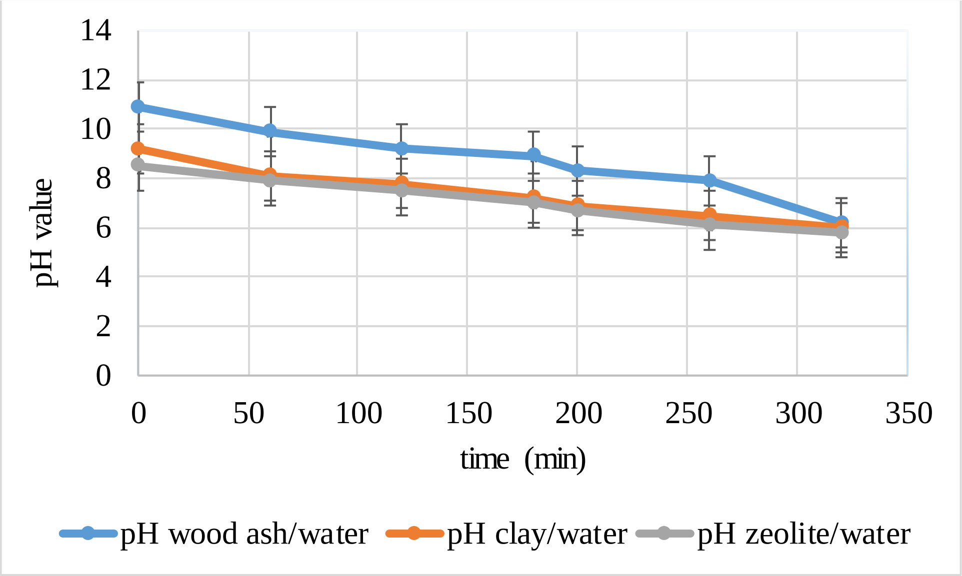


Figure 4.4:- The variation of media pH during the upgrade process

4.3.2 The effects of biogas flow rate on the biogas upgrade using carbonation process

The wood ash to water ratio of 1:4 gave the highest biogas purification capacity. As a result, it was used for further studies to investigate the effects of biogas flow rate on the upgrade process. Various biogas flow rates were studied on the carbonation process at room temperature. The effect of flow rate on the carbonation process is as summarized in Table 4.2. The results of GC analysis of methane in biogas are as shown in Appendix 4.

Table 4.2:- The effect of biogas flow rate on methane enhancement by the carbonation process

No	Flow rate (ml/min)	% Increase CH_4 content
1	45	63.58
2	100	70.46
3	150	45.86
4	200	33.63
5	250	15.72

The biogas purification was conducted in the range of 45-250ml/min. The results show that 100ml/min flow rate of biogas gave the highest purification of biogas due to adequate carbon dioxide mass transfer rate and contact of adsorbate and slurry. At a higher biogas flow rate such as 250ml/min, the biogas flow was so high that it could have resulted to lower contact time between the solvent and the adsorbate hence producing lower mass transfer rate. However, at lower biogas flow rate such as 45ml/min, the adsorption capacity was so low because the process produced low turbulent and that resulted in lower carbon dioxide mass transfer rate. These results are in agreement with those documented in literature (Ji et al., 2017).

4.3.3 The effects of slurry temperature on biogas upgrade using carbonation process

Figure 4.5 shows the effect of slurry temperature on the biogas upgrade by carbonation process. The temperature of the adsorbent mixture (wood ash to water) was varied from 18^{o}C - 80^{o}C. The results indicate that the lowest temperature of 18^{o}C produced lowest sorption capacity. This is because low temperature of slurry reduces the kinetic energy. On other hand, the upgrade of biogas was enhanced by the increase in the temperature of slurry. The results agrees with other studies on the carbonation reactions which observed that the increase in slurry temperature increased the mass transfer rate and consequently increased the reaction rate (Ji et al., 2017). Moreover, it improved the thermal motion of molecules which caused an increase in the average kinetic energy (Ji et al., 2017). However, the highest temperature of slurry also reduces the solubility of carbon dioxide in the slurry. This decreased the carbonate ions available for carbonation reaction. In addition, the upgrade by slurry method entails sorption reactions that contains both adsorption and absorption process. For the adsorption process, increases in temperature decreases the CO_2 adsorption capacity. On the contrary, in the absorption process, the reverse occurs.

This also could be the reason why at 80°C, biogas purification is low. The highest upgrade capacity was found at 75°C. Similar conclusions were made by Mustafa et al., (2020) who observed that the increase in the slurry temperature reduced the capacity of carbon dioxide capture (Mustafa et al., 2020). Therefore, these studies recommend 75°C of slurry wood ash temperature.

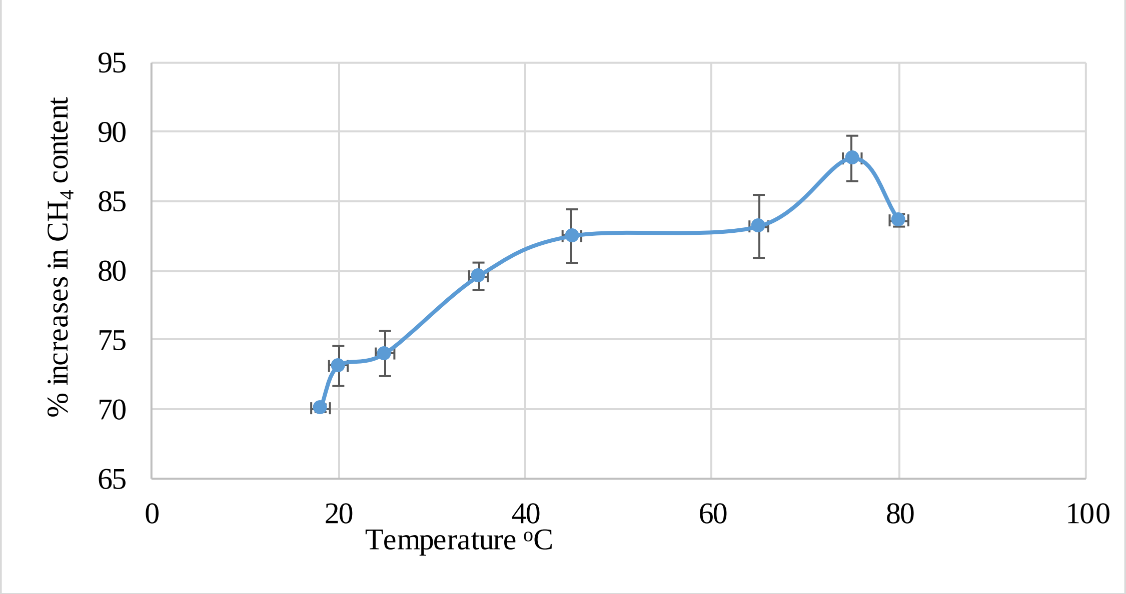


Figure 4.5:- The effect of slurry temperature on biogas upgrade by carbonation process

The highest removal capacity of natural wood ash/water was 88.3% at uptake rate of 2.30 mmol CO_2 /g-adsorbent. The results obtained from this study agree with the findings from (Wang. P et al., 2017) which showed adsorption capacity of carbon dioxide in the range of 2.02 mmol/g using wood ash that was produced from biomass modified with amine. On the contrary, Andersson & Nordberg, (2017) reported 4.5 mmol CO_2 /g-wood ash pellets which is higher than the results in this study (Andersson & Nordberg, 2017). This could be due to the method of storage of the wood ash and the use of high concentration of CO_2 in the sequestration process. It could also be due to the type of the wood ash. The wood ash pellets collected and stored indoor were not exposed to moisture.

According to Romero-güiza et al., (2015), weathered bottom ash that had been exposed to water vapor in air produced lower adsorption capacity compared to fresh bottom ash. This was due to some of free CaO being carbonized before application (Romero-güiza et al., 2015).

Increasing the slurry temperature of clay from 19.2°C to 75°C increased the methane content in biogas from 34.93% to 38.96%. The highest adsorption capacity was approximately 0.63 mmol CO_2/g-clay at 75°C. This did not have a significant enhancement in the purification of biogas. Wang et al., (2014) found that at 75°C, clay slurry had 2.5mmol/g uptake which is much higher than the results in this study (Wang et al., 2014). However, the slurry clay had been modified by treatment with 50 wt % of polyethleneimine (PEI) on 6M HCl. On the contrary, increase in the temperature of zeolite slurry produced negative effects on biogas purification. The treatment of biogas with zeolite slurry at temperature; 25, 35, 55 and 65°C produced; 20.2%, 17.3%, 12.57% and 4.57% methane increase respectively. In comparison to wood ash and clay, natural zeolite slurry has low enhancement of methane contents in biogas. This could be due to the sorption process by zeolite dominated by physical adsorption process rather than carbonation process. The carbonation process on zeolite forms carbonates that are very stable monodentate on the surface of zeolite. However, due to interaction with carbon dioxide the aluminum oxygen bond and the stable monodentate carbonate species rupture on the surface of zeolite (Bonenfant et al., 2008). Thereby, the adsorption capacity of carbon dioxide was very low because the pores were blocked by the surface ions. This also reduced the electric field strength and the heterogeneity of adsorbent.

4.3.4 The removal of hydrogen sulfide

The biogas from the digester contained some hydrogen sulfide of up to 203ppm. The small content of hydrogen sulfide is an enormously hazardous gas. However, after upgrade of biogas all H_2S gas was completely removed using carbonation process. Figure 4.6 show as the removal efficiency of hydrogen sulfide.

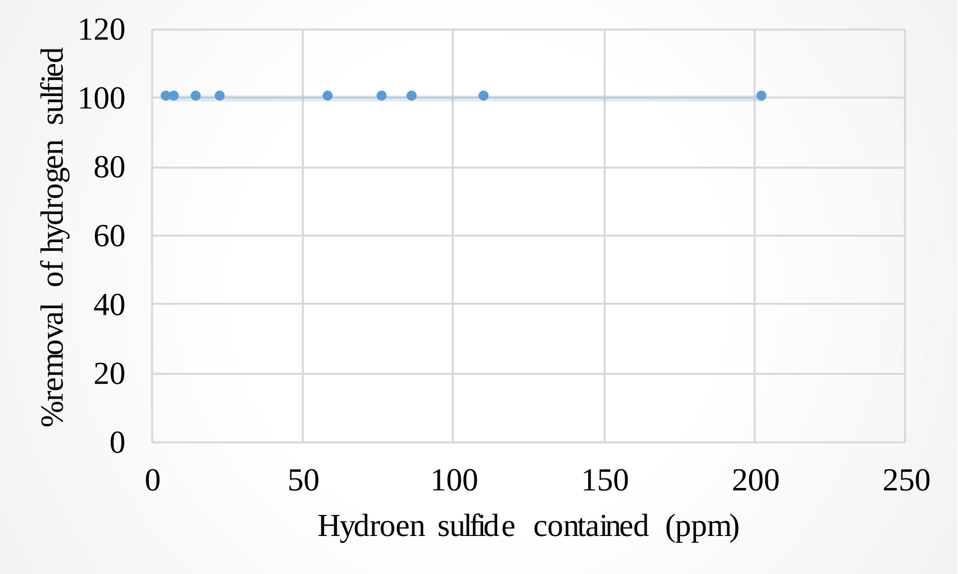


Figure 4.6:- Percent removal of H_2S through wet adsorption processes

4.3.5 Kinetics analysis of carbon dioxide sorption with wood ash slurry

The CO_2 removed by the wood ash slurry at 75°C, 50 °C and 25 °C was used to investigate the kinetics models of adsorption. The kinetic models studied included; pseudo first order, pseudo second order, elovich and intra particle diffusion. The summary of the kinetics parameters obtained for various models are presented in Table 4.3.

Table 4.3:- Kinetics parameters of adsorption of CO_2 from biogas using wood ash slurry

Kinetics models	Parameters	Kinetics parameters at temperature ^{o}C		
		75 ^{o}C	50 ^{o}C	25 ^{o}C
Pseudo first order	q_e (mg/g)	163.369	162.818	97.485
	K_1(1/min)	0.020	0.017	0.021
	R^2	0.995	0.995	0.995
	SQE	159.624	170.723	104.248
	RMSE	2.694	2.786	2.177
	X^2	2.126	2.395	2.220
Pseudo second order	q_e (mg/g)	236.537	245.736	140.136
	K_2(1/min)	6.42E-05	4.77E-05	0.00012
	R^2	0.991	0.991	0.985
	SQE	328.876	281.375	188.835
	RMES	3.866	3.576	2.929
	X^2	14.282	3.886	3.928
Elovich	α((mg/(g.min))	4.038	3.120	2.546
	β(mg/g)	0.013	0.011	0.021
	R^2	0.985	0.987	0.977
	SQE	531.436	403.637	284.509
	RMSE	4.915	4.283	3.596
	X^2	6.854	5.538	5.851
Intra particles diffusion	Kwm(mg/g.min^2 (0.5))	16.579	15.974	10.003
	B (mg/g)	19.192	24.612	11
	R^2	0.973	0.982	0.963
	SQE	920.886	564.774	466.889
	RMSE	6.469	5.067	4.607
	X^2	9.918	5.974	8.205

The kinetics data of carbon dioxide removal using wood ash slurry was investigated using; pseudo-first order, pseudo second order, elovich and intra particles diffusion models at 25^{o}C, 50^{o}C and 75^{o}C. The high R^2 and lower SQE, RMSE and X^2 predicted the goodness of the fit for the model. According to Table 4.3, removal of carbon dioxide at different carbonation temperature was best fitted to pseudo first order kinetics model. The model had the highest R^2 and lowest SQE, RMSE and X^2 compared to the other models.

The pseudo first order indicates that the adsorption rate is directly related to the concentration of carbon dioxide. Figure 4.7 and 4.8 show the kinetics model of carbon dioxide uptake from biogas using wood slurry.

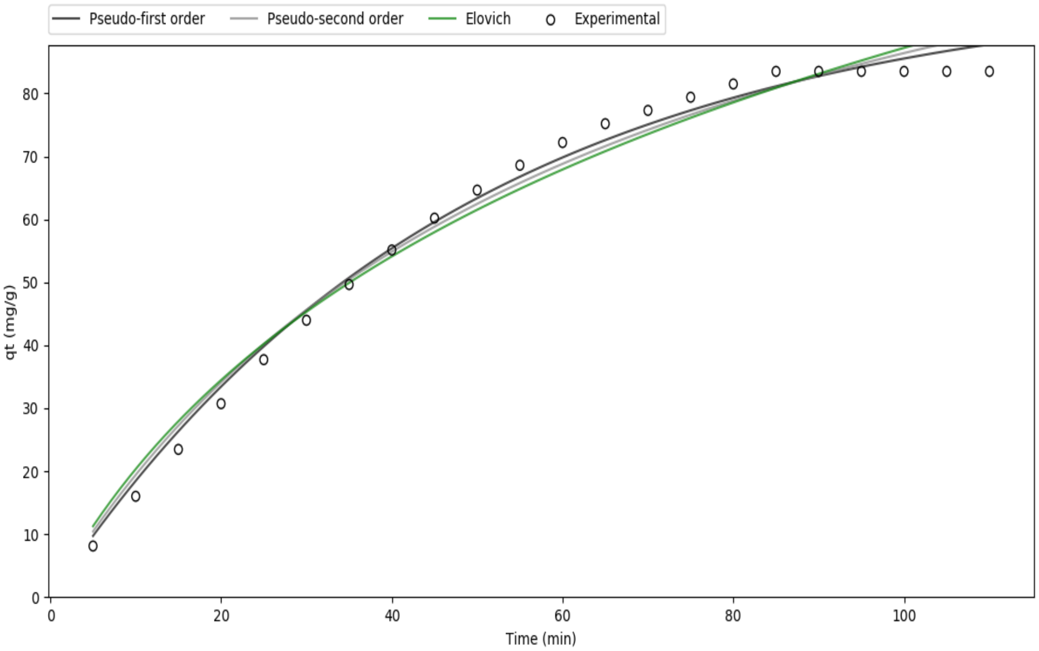
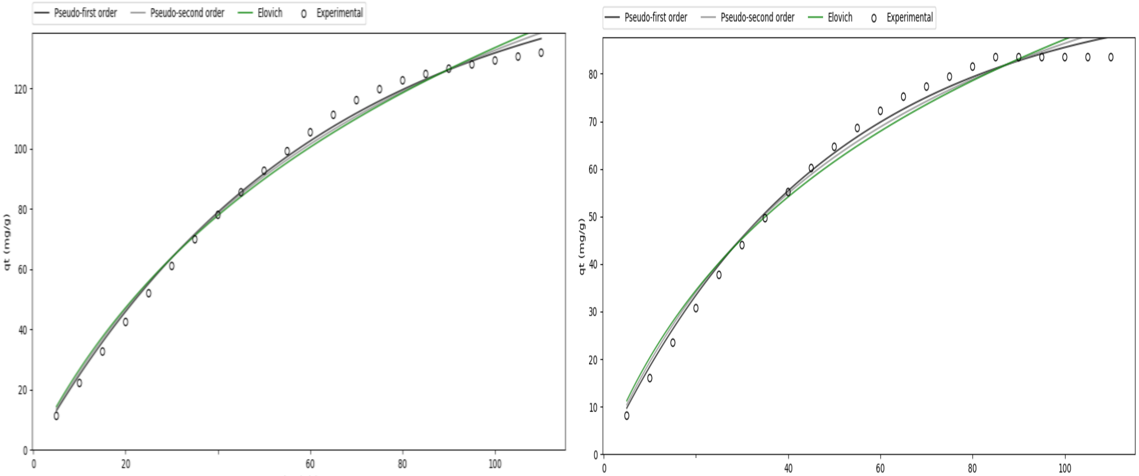


Figure 4.7:- Kinetics model of carbon dioxide uptake from biogas using wood ash slurry at 25°C



(a) (b)

Figure 4.8:- Kinetic models of carbon dioxide uptake from biogas using wood ash slurry at 50°C (a) and 75°C (b)

4.4 Upgrade of biogas using dry adsorbent

4.4.1 The effects of biogas flow rate on the dry adsorbents

The flow rate of biogas is important in the capture of carbon dioxide by adsorption. The capture of CO_2 using activated clay at low flow rate of 45ml/min with 2.5g adsorbent produced the highest uptake capacity of 5.72mmol/g. However, the value reduced by 36.4%, 47.6%, 59.4% and 70.5% at flow rate of 90ml/min, 150ml/min, 200ml/min and 250ml/min respectively. Montanari et al., (2011) observed that carbon dioxide adsorption capacity was dependent on flow rate and purge time. Similar findings were made by a study using synthesized zeolite adsorbent from fly ash which observed that the highest adsorption capacity of carbon dioxide was 1.07 mmol/g-adsorbent at a flow rate of 100cm^3/min (Lee et al., 2014). It was also observed that at a low flow rate the adsorption capacity was increased (Lee et al., 2014). Similar results were found in the experiment with activated zeolite and wood ash where the highest carbon dioxide adsorption capacity was 4.84 mmol/g-zeolite and 3.95 mmol/g-ash respectively at 45ml/min biogas flow rate. Table 4.4 shows the effects of biogas flow rate on upgrade process using activated clay.

Table 4.4:- The effect of biogas flow rate on the CO_2 uptake using 2.5g activated clay

No	Biogas flow rate (ml/min)	CO_2 uptake mmol/g-activated clay
1	45	5.72
2	90	3.64
3	150	3
4	200	2.32
5	250	1.69

The results from this study agree with the findings from Chen et al., (2014) which reported carbon dioxide adsorption capacity of 4.8mmol/g using activated clay. Other studies have reported that, higher uptake of carbon dioxide at 6.9mmol/g for activated clay (Garshasbi et al., 2017). However, the clay in the study had been activated with 4M NaOH that resulted in high concentration of bases. Other studies have also investigated adsorption of carbon dioxide using clay which had been activated with PEI, MEA, DEA, TEA, TEPA (Pires et al., 2018, Cecilia et al., 2018, Yuan et al., 2018, Elkhalifah et al., 2015). The findings showed that the uptake in the range of 0.79-3.7mmol/g (Pires et al., 2018, Cecilia et al., 2018, Yuan et al., 2018, Elkhalifah et al., 2015) which is in the range of this study. The capacity of carbon dioxide uptake by adsorbents treated with acids and amine compounds was found to be lower than that treated with sodium hydroxides (Franco et al., 2014, Pires et al., 2018). Table 4.5 shows that the effects of biogas flow rate on activated zeolite on carbon dioxide uptake.

Table 4.5:- The effect of biogas flow rate on the CO_2 uptake using 2.5g activated zeolite

No	Flow rate (ml/min)	CO_2 uptake mmol/g-activated zeolite
1	45	4.84
2	90	3.2
3	150	2.72
4	200	2.08
5	250	1.68

The highest uptake of zeolite was found to be 4.84mmol/g at 45ml/min. These results agree with those from studies by Kongnoo et al., (2017) which used zeolite 13X from palm oil mill fly ash and observed 4.75mmol/g uptake capacity.

The adsorption capacity of activated zeolite was lower than that of activated clay. This could be due to low molar ratio of SiO_2/Al_2O_3 in activated clay which is good for adsorption of carbon dioxide at low pressures.

Table 4.6 shows that the effect of biogas flow rate on carbon dioxide uptake by dry activated wood ash. The highest adsorption capacity of 3.95 was found at 45ml/min. The adsorption capacity of dry activated wood ash was lower than that of activated clay and activated zeolite. This could be due to the fact that the carbon dioxide uptake using dry adsorbent is dominated by adsorption while in wet process, carbonation process dominates.

Table 4.6:- The effect of biogas flow rate on CO_2 uptake using 2.5g activated wood ash

No	Biogas flow rate (ml/min)	CO_2 uptake mmol/g-activated wood ash
1	45	3.95
2	90	2.72
3	150	2.48
4	200	1.89
5	250	1.08

4.4.2 The removal of hydrogen sulfide

The biogas from the digester contained some hydrogen sulfide of up to 203ppm. However, after upgrade of biogas all H_2S gas was completely removed using dry adsorption method.

4.4.3 The effects of adsorbent mass to biogas volume ratio on biogas upgrade using dry adsorbent

The adsorption capacity and percentage removal of carbon dioxide data were obtained by varying the mass of dry adsorbent but maintaining the volume of biogas constant. The results were plotted in a graph. Figure 4.9 shows the adsorption capacity and removal efficiency of carbon dioxide of activated clay.

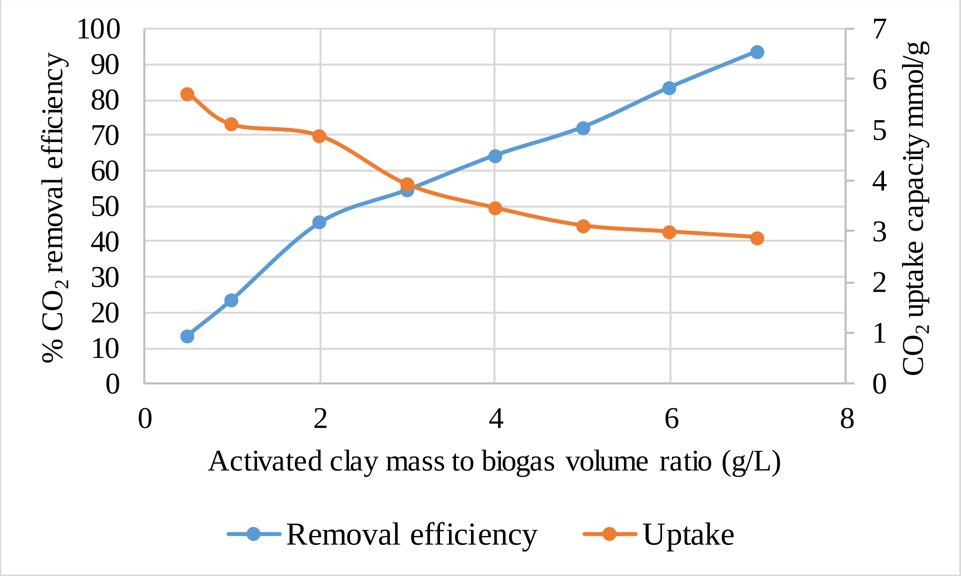


Figure 4.9:- The effect of activated clay mass to biogas volume ratio on biogas upgrade

The % CO_2 removal defines the total amount of adsorbate or contaminants removed from the biogas. Therefore, an increase in the mass of adsorbent produces higher removal efficiency. The adsorption capacity describes how much adsorbate is taken by the adsorbent. Therefore, the uptake capacity of CO_2 is high with little amount of adsorbent. The increase in the mass of adsorbent means, that the average rate of interaction between each free adsorbent site and the adsorbates particles is low due to overlapping adsorbents' free active sites.

Dawodu & Akpomie, (2014) also reported that the uptake capacity of adsorbent decreases by increasing the adsorbent mass due to overlapping adsorbent site. The results from this study are supported by pervious documented reports in literature (Dawodu & Akpomie, 2014).

4.4.4 Kinetics analysis of adsorption of carbon dioxide using dry activated clay

The adsorption of CO_2 into the dry activated clay kinetics was modeled using pseudo first order, pseudo second order, elovich and intra particle diffusion kinetic models. The kinetics parameters of adsorption of carbon dioxide using activated clay are summarized in Table 4.7.

Table 4.7:- Kinetic parameters of carbon dioxide adsorption using activated clay

Kinetics models	Parameters	Kinetics parameter
Pseudo first order	q_e (mmol/g)	6.96
	K_1(1/min)	0.031
	R^2	0.992
	SQE	576.178
	RMSE	5.822
	X^2	4.239
Pseudo second order	q_e (mmol/g)	9.73
	K_2(1/min)	5.77E-05
	R^2	0.986
	SQE	1328.306
	RMES	8.839
	X^2	9.105
Elovich	α((mg/(g.min))	12.356
	β(mg/g)	0.007
	R^2	0.976
	SQE	2261.519
	RMSE	11.534
	X^2	14.961
Intra particles diffusion	Kwm (mg/g.min^2 (0.5))	35.707
	B (mg/g)	23.615
	R^2	0.954
	SQE	4367.425
	RMSE	16.028
	X^2	25.773

It was observed that the kinetic data fitted best into pseudo-first-order model. Figure 4.10 presents the kinetic plots of carbon dioxide adsorption fitted in pseudo-first order, pseudo-second order, elovich and intra particle diffusion models.

Figure 4.10:- Kinetic plot of carbon dioxide uptake using activated clay for pseudo-first order, pseudo-second order, elovich and intra particle diffusion models

4.4.5 Adsorption isotherm

The equilibrium data of adsorption of CO_2 on activated clay was modeled using Langmuir and Freundlich isotherm models. Table 4.8 shows various parameters of the two adsorption isotherms for adsorption of CO_2 from biogas using activated clay.

Table 4.8:- Adsorption isotherms parameters of carbon dioxide adsorption using activated clay at 25^oC

Isotherms	Parameters	Kinetics parameter
Freundlich	K_F (mg/g)	0.645
	1/n	1.293
	R^2	0.959
	SQE	142.082
	RMSE	3.973
	X^2	2.625
Langmuir	q_1 (mg/g)	303.589
	K_1(1/mg)	0.0007
	R^2	0.949
	SQE	178.941
	RMES	4.459
	X^2	4.476

The results indicate that the adsorption of carbon dioxide on dry activated clay fitted best into Freundlich model which describe adsorption on the adsorbent with a heterogeneous surface. Figure 4.11 shows the isotherm plots of Langmuir and Freundlich for adsorption of carbon dioxide using dry activated clay.

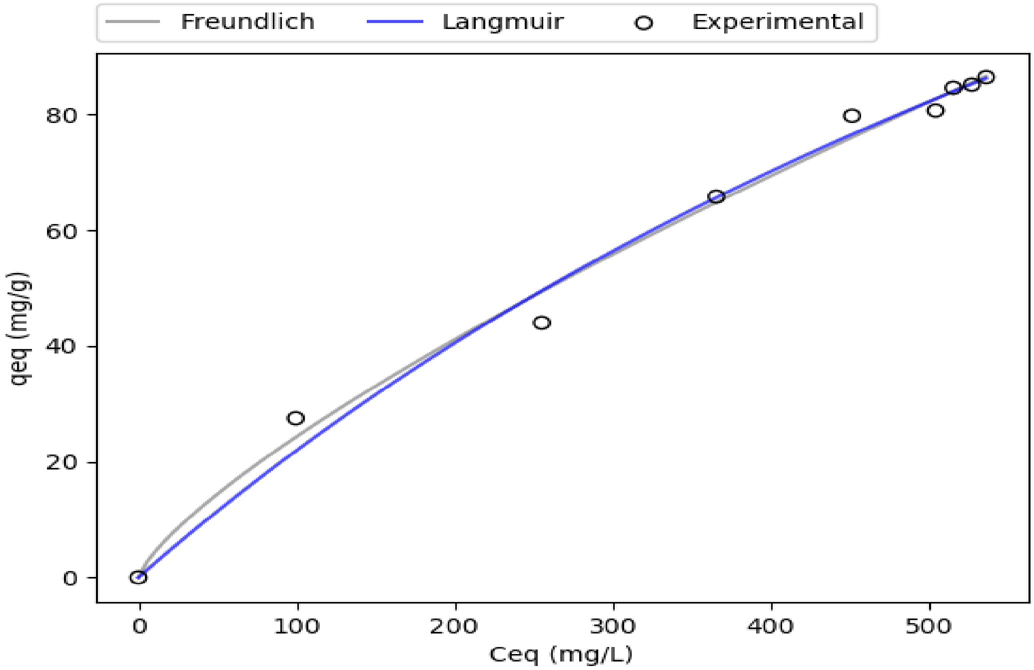


Figure 4.11:- Isotherm plot of carbon dioxide uptake from biogas using activated clay at 25°C

4.4.6 Breakthrough curves for fixed bed

The continuous biogas flow adsorption in fixed bed was studied using breakthrough curves. The fixed bed adsorption of CO_2 using activated clay dosages; 5, 20 and 35g were modeled using Bohart-Adams, Yan and Yoon-Nelson models. Table 4.9 shows that the parameters for breakthrough curves of adsorption of CO_2 from biogas using activated clay.

Table 4.9:- The summary of the parameters for breakthrough curves of carbon dioxide adsorption using activated clay

Fixed bed models	Parameters	Breakthrough curves parameters		
		35g	20g	5g
Bohart-Adams	K_{ab} (ml/mg.min)	0.132	0.127	-
	N_{ab}(mg/ml)	13.512	9.610	-
	R^2	0.989	0.980	-
	SQE	0.017	0.025	-
	RMSE	0.035	0.044	-
	X^2	0.095	0.139	-
Yan	q_{yan} (mg/g)	55.005	67.797	70.837
	Ayan	2.761	1.982	1.225
	R^2	0.995	0.985	0.989
	SQE	0.009	0.019	0.009
	RMES	0.026	0.038	0.028
	X^2	0	0	0
Yoon and Nelson	tal (min)	23.607	17.718	6.283
	Kyn (1/min)	0.117	0.112	0.221
	R^2	0.989	0.981	0.878
	SQE	0.017	0.025	0.103
	RMSE	0.035	0.044	0.097
	X^2	0.095	0.139	0.298

The breakthrough curves were plotted for column adsorption using different adsorbent mass; 5, 20 and 35g at constant flow rate. The Bohart-Adams, Yan and Yoon-Nelson models were used for modeling the data using nonlinear regression techniques. According to Table 4.9, the breakthrough curves using Yan model described best the experimental data. The Yan model had the highest R^2 and lowest SQE, RMSE and X^2 values which indicate that the data well fitted the model. It was observed that at low adsorbents mass, the saturation time arrived faster and the productive adsorption time decreased. This can be explained by the fact that an increase in the adsorbent mass increases the bed height and vice versa. The maximum uptake capacity of 5g adsorbent mass was 70.83 mg/g which was recorded after 50min of adsorption.

Conversely, the increase in the adsorbent mass to 35g reached saturation time after 65min. However, the carbon dioxide uptake capacity for 35g activated clay was 55.01mg/g. Therefore, the use of low adsorbent mass produces a column with short saturation time. Nevertheless, the uptake capacity was higher with low mass of adsorbent because higher concentration of un-adsorbed adsorbates exerts a pressure for more uptake. On contrary, the increase in the adsorbent mass causes increase in the free adsorption sites in comparison to available adsorbates. This reduces the uptake capacity of adsorbent due to overlapping adsorbents’ free active sites. This is illustrated in Figures 12 and 13 which are the breakthrough curves for adsorption of carbon dioxide using dry activated clay at 35g, 20g and 5g respectively. The curves show that the breakthrough time shortens at low adsorbent mass while the breakthrough time increases with increase in adsorbent mass.

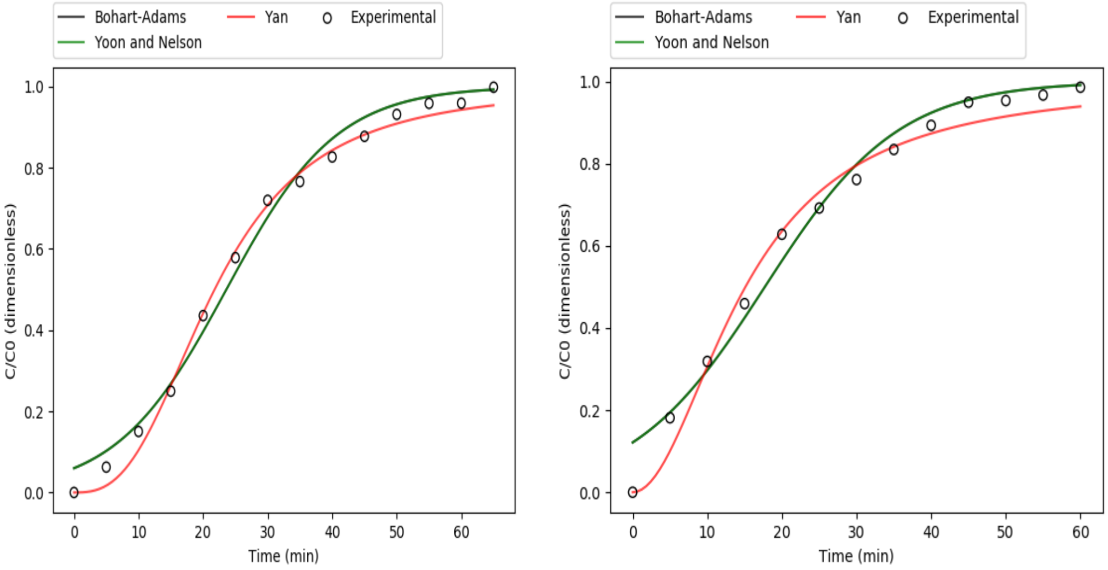


Figure 4.12:- Breakthrough curves of carbon dioxide uptake from biogas at adsorbent mass of 35g and 20g

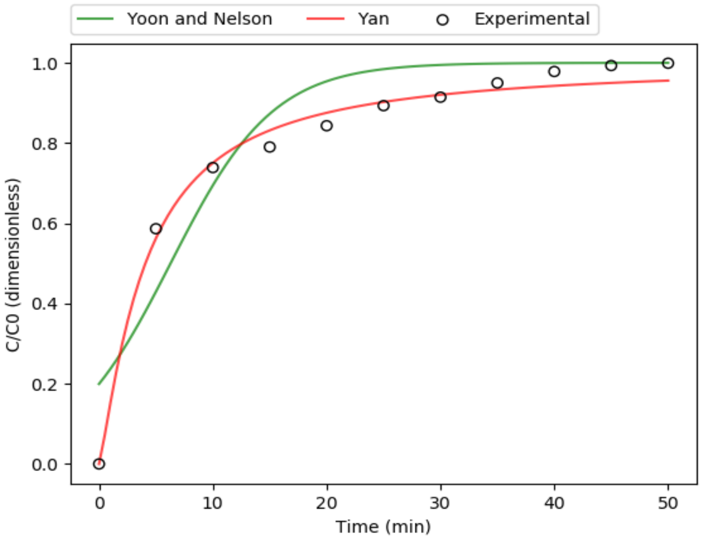


Figure 4.13:- Breakthrough curves of carbon dioxide uptake from biogas at adsorbent mass 5g

The diagrammatic plot indicates that the effluent from the fixed bed after 50 minutes was 95% of the influent concentration at 5g. While the effluent from the fixed bed after 65 minutes was 95% of the influent concentration at 35g. The breakthrough curve can be used to approximate the breakthrough point of the column. It is the time when the column is just fully saturated with the adsorbates. Adsorptive processes with long breakthrough points are more cost-effective because their bed requires less frequent replacements.

4.5 Comparison of the carbon dioxide uptake by dry adsorption and carbonation process

Table 4.10 shows the adsorption capacity of carbon dioxide by adsorption and carbonation process at 35g of adsorbents. The results indicate that for dry adsorption, activated clay had higher uptake of 2.79mmol/g than zeolite due to its lower ratio of SiO_2/Al_2O_3 of 8.5 compared to 15.4 molar ratio for zeolite. However, the highest (2.79mmol/g) was much lower than 5.72mmol/g which was achieved by using 2.5g of activated clay. The lowest uptake in dry adsorbent was in wood ash.

This could be explained by its very low contents of both silica and alumina which implies that the surface charges for adsorption were also low. However, wood ash had much higher CaO content (46%) compared to clay and zeolite. This could be the reason why the purification of biogas capacity by carbonation process was much higher compared to the other two. The natural wood ash/water has lower purification capacity compared to activated clay. However, it is cheap, easily available and has simpler working process.

Table 4.10:- Carbon dioxide uptake from biogas by dry adsorption and carbonation process

Adsorbents	Carbonation method (natural adsorbent) (mmol/g)	Dry adsorption	
		Activated adsorbents uptake (mmol/g)	Natural adsorbents uptake (mmol/g)
Wood Ash	2.30	1.93	0.65
Clay	0.47	2.79	0.98
Zeolite	0.19	2.32	0.77

CHAPTER 5: CONCLUSION AND RECOMMEDATIONS

5.1 Conclusions

The aim of this study was to investigate the upgrade of biogas using low-cost natural materials including; clay, zeolite and wood ash. Characterization results revealed that the highest content of CaO content was found in wood ash which was 46% while low molar ratio of SiO_2/Al_2O_3 was found in activated clay which was 8.5. From the adsorption results high content of CaO favors carbon dioxide uptake by carbonation method. In addition, high pH value of slurry is good for high purification of biogas. The highest adsorption capacity 2.3mmol/g was found with the ratio of 1:4 wood ash to water and at 75^{o}C and 100ml/min of slurry temperature and biogas flow rate respectively. Further, the highest adsorption capacity for unmodified natural adsorbents was with wood ash slurry which was 2.30mmol/g wood ash at the optimum conditions. This suggests that natural wood ash is the most potential material for biogas upgrade among unmodified natural adsorbents. The experimental data on removal of carbon dioxide by wood ash slurry through the carbonation process fitted well into the pseudo first order kinetics model.

In dry adsorption process, the natural dry adsorbents showed low carbon dioxide adsorption capacity. The adsorption capacity for natural wood ash, clay and zeolite were 0.65, 0.98 and 0.77 mmol/g respectively. The highest adsorption capacity was found on clay activated with NaOH. This suggests that adsorption can be improved by chemical activation with sodium hydroxide. The enhancement of adsorption capacity is due to reduction of SiO_2/Al_2O_3 which favors carbon dioxide uptake by dry adsorption process. Furthermore, the results indicate that, the low biogas flow rate favor high adsorption capacity compared to high biogas flow rate.

In dry adsorption using 2.5g activated clay, an uptake of 5.27 CO_2 mmol/g at biogas flow rate of 45ml/min was achieved. Therefore, it has great potential for application in biogas upgrade.

The percentage removal of carbon dioxide was found to increase with increases in the adsorbent mass. Therefore, high mass of adsorbent is required for high removal of carbon dioxide. Furthermore, the kinetics data and equilibrium data were well fitted to pseudo-first order and Freundlich model respectively. Additionally, breakthrough curve of fixed bed adsorption data was well fitted to Yan model on adsorption process.

5.2 Recommendations

From this research several recommendations were made based on the findings on application of natural and activated natural materials on biogas upgrade.

- Clay activated with NaOH produced very high carbon dioxide uptake. Therefore, modification of clay by treatment with NaOH is recommended for use in biogas upgrade.
- The activated clay should be applied in fixed bed dry adsorption method because it has higher methane enhancement than carbonation process.
- The natural wood ash/water had the highest purification capacity for carbonation method. Therefore, wood ash is recommended among the unmodified material for biogas upgrading.
- The carbon dioxide uptake by dry adsorption using modified zeolite had higher uptake compared to that of carbonation method and unmodified zeolite. Therefore, application of zeolite in biogas purification should be by dry adsorption after NaOH modification.

For further studies,

- The adsorbents surface area and pore volume should be characterized. This could help to shed more light on the adsorption mechanism of the natural materials.
- Furthermore, investigations on biogas with high H_2S contents should be carried out to fully understand its removal using natural adsorbents.
- In addition, the removal of other biogas contaminants like water and nitrogen using natural adsorbents should be done.

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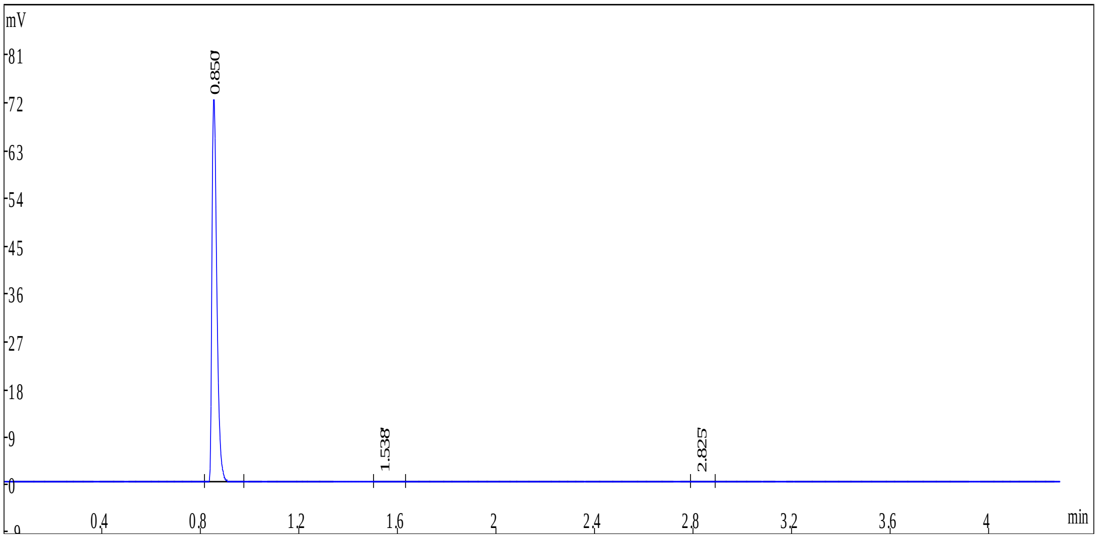
APPENDIXES

Appendix 1: Upgrade biogas using wood ash to water mix at different ratio

Methane content at 1:2 wood ash/water ratio Report

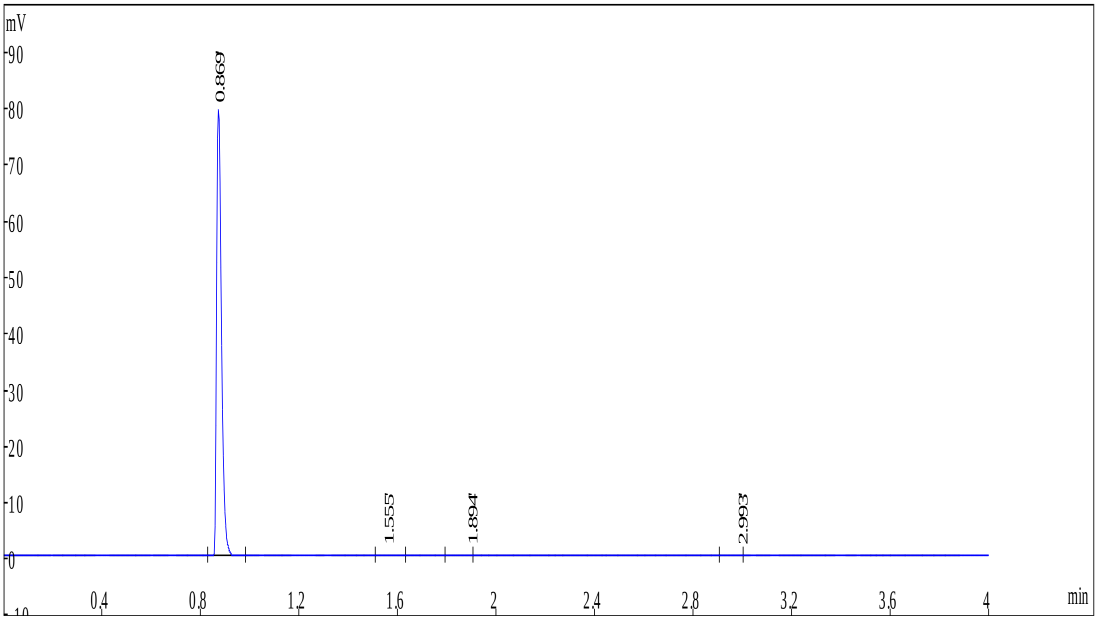
Printing time: Thu Jan 14 18:43:54 2021
Injection time: Tue Oct 13 14:32:03 2020
File opened: G:\sample 1(20201013 14;32;03).hw



```
--------------------------------------------
Rank   Time     Name   Area%      Area
--------------------------------------------
1      0.850          99.38      89126
2      1.538          0.5104     458
3      2.825          0.1127     101
--------------------------------------------
Total                100       89685
```

Methane content at 1:3 wood ash/water ratio Report

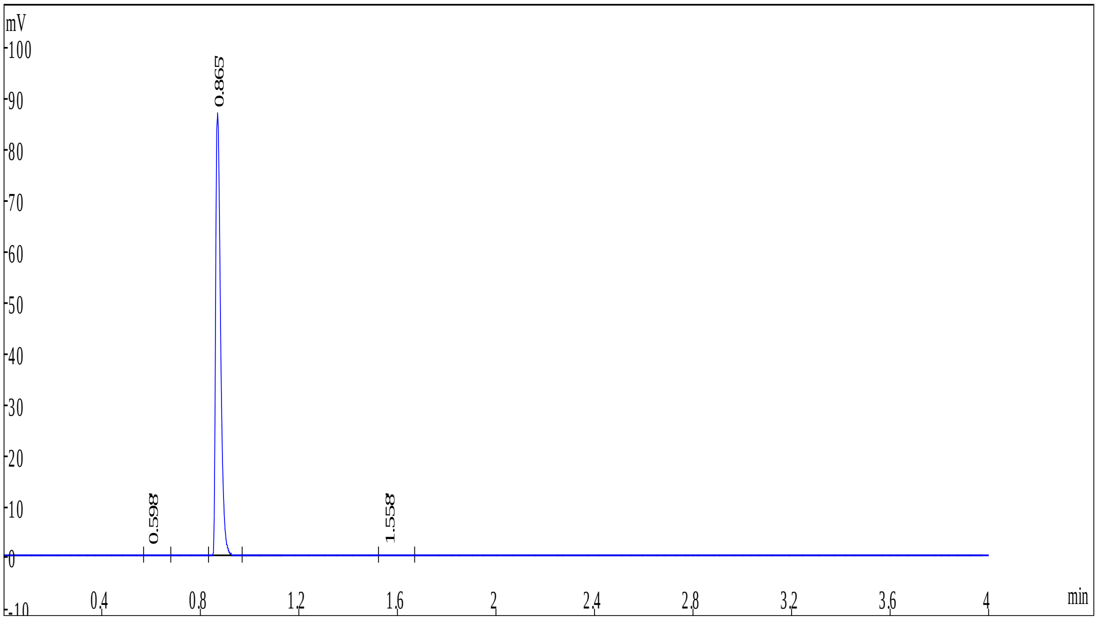
Printing time: Thu Jan 14 18:41:21 2021
Injection time: Tue Oct 13 14:45:18 2020
File opened: G:\sample 2(20201013 14;45;18).hw



```
-----------------------------------------------
Rank   Time      Name   Area%       Area
-----------------------------------------------
1      0.869           99.31      97232
2      1.555           0.4794      469
3      1.894           0.1076      105
4      2.993           0.1065      104
-----------------------------------------------
Total                  100       97910
```

Methane content at 1:4 wood ash/water ratio Report

Printing time: Thu Jan 14 18:47:14 2021
Injection time: Tue Oct 13 15:13:05 2020
File opened: G:\sample 3(20201013 15;13;05).hw



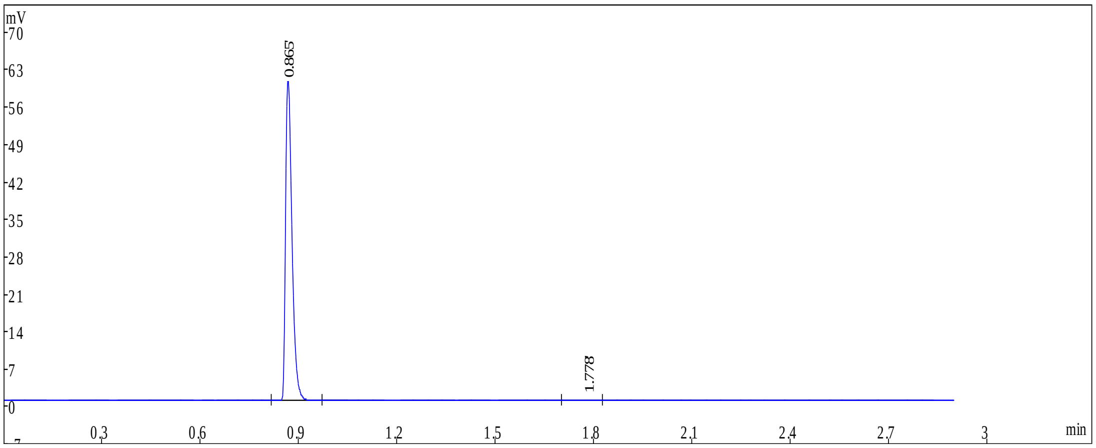
```
---------------------------------------------
Rank   Time      Name   Area%      Area
---------------------------------------------
1      0.598          0.79639    105
2      0.865          98.7       107914
3      1.558          0.4805     525
---------------------------------------------
Total                100        108544
```

Appendix 2: Upgrade biogas using clay to water mix at different ratio

Methane content at 1:2 clay/water ratio Report

Printing time: Mon Feb 22 23:47:20 2021
Injection time: Wed Oct 14 16:26:39 2020

File opened: G:\sample 4(20201014 16;26;39).hw

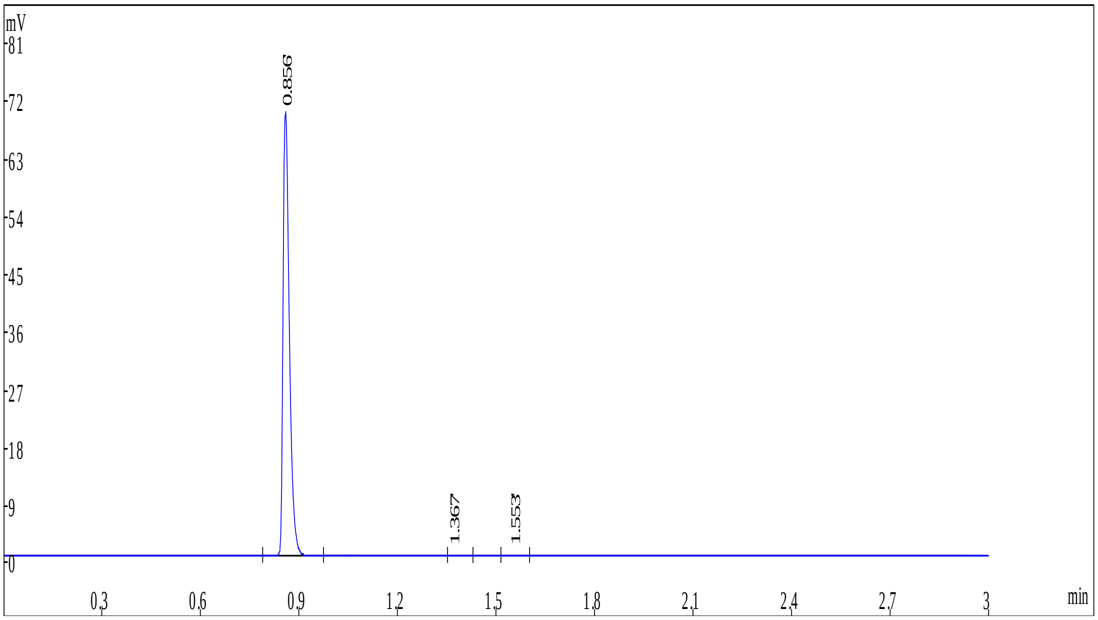


```
---------------------------------------------
Rank   Time      Name   Area%      Area
---------------------------------------------
1      0.865          99.86      75898
2      1.778          0.138      105
---------------------------------------------
Total                100       76003
```

Methane content at 1:3 clay/water ratio Report

Printing time: Mon Feb 22 23:45:08 2021
Injection time: Wed Oct 14 15:56:27 2020

File opened: G:\sample 5(20201014 15;56;27).hw



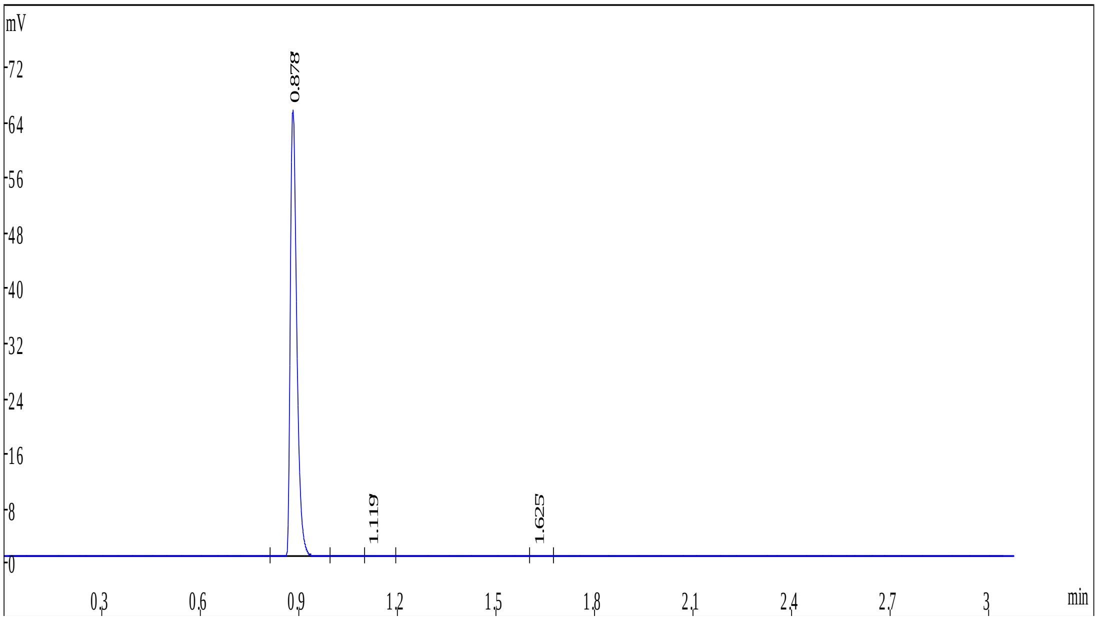
```
---------------------------------------------
Rank   Time      Name   Area%      Area
---------------------------------------------
```

```
1     0.856          99.66      86111
2     1.367          0.1185     103
3     1.553          0.2215     188
---------------------------------------------
Total                 100        86402
```

Methane content at 1:5 clay/water ratio Report

Printing time: Mon Feb 22 23:49:09 2021
Injection time: Wed Oct 14 15:48:00 2020

File opened: G:\sample 6(20201014 15;48;00).hw

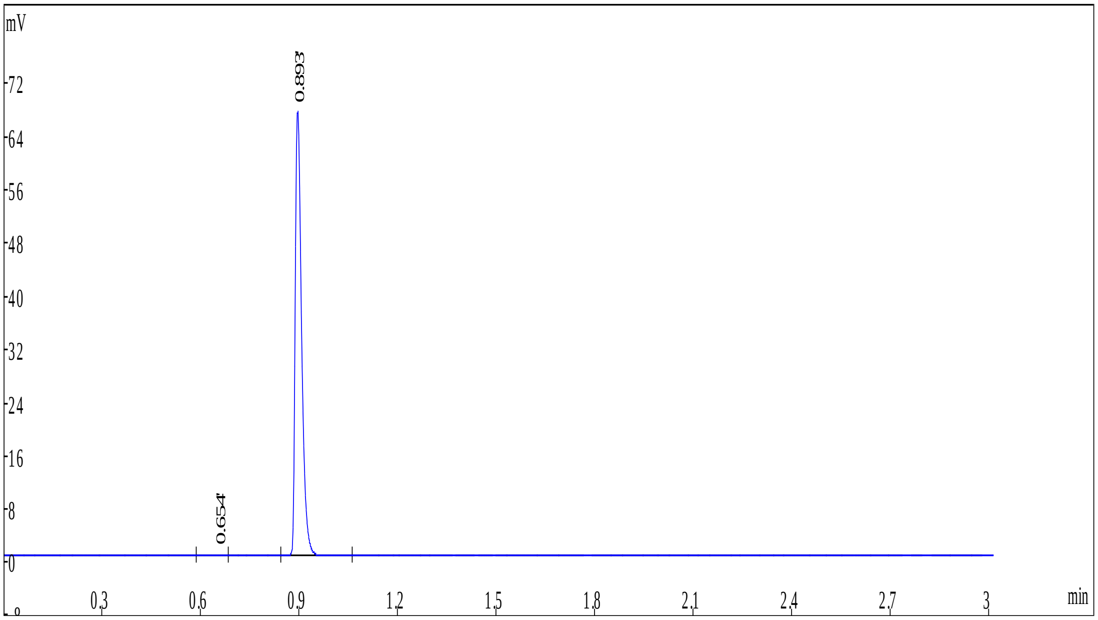


```
---------------------------------------------
Rank   Time     Name   Area%      Area
---------------------------------------------
2     0.878          99.7       82367
3     1.119          0.1397     116
5     1.625          0.135      112
---------------------------------------------
Total                 100        82595
```

Appendix 3: Upgrade biogas using zeolite to water mix at different ratio

Methane content at 1:1 zeolite/water ratio Report

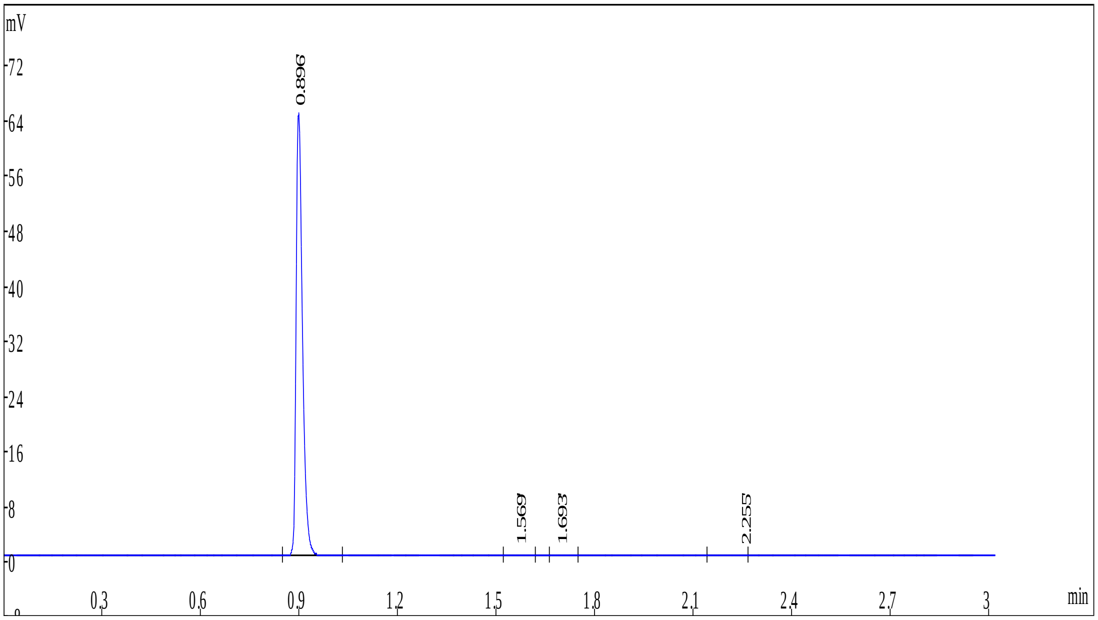
Printing time: Thu Jan 14 18:28:17 2021
Injection time: Thu Oct 15 14:17:45 2020
File opened: G:\sample 1(20201015 14;17;45).hw



```
---------------------------------------------
Rank   Time      Name   Area%      Area
---------------------------------------------
1      0.654           0.1311     110
2      0.893           99.87      84065
---------------------------------------------
Total                  100        84175
```

Methane content at 1:2 zeolite/water ratio Report

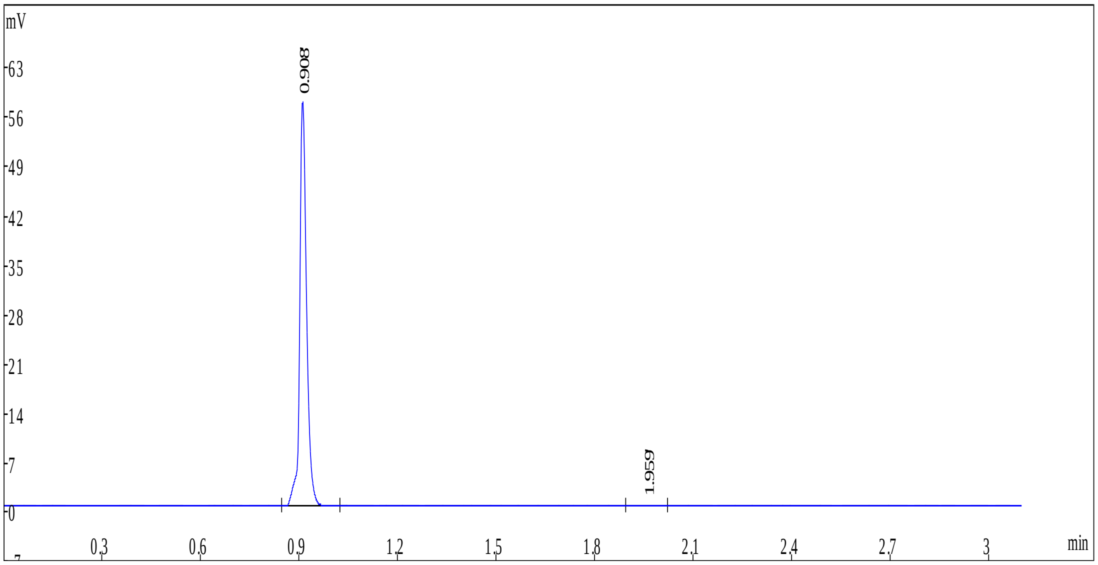
```
Printing time: Thu Jan 14 18:35:45 2021
Injection time: Thu Oct 15 14:30:55 2020
File open
ed: G:\sample 2(20201015 14;30;55).hw
```



Rank	Time	Name	Area%	Area
1	0.896		99.58	80294
2	1.569		0.1266	102
3	1.693		0.1301	105
4	2.255		0.1662	134
Total			100	80635

Methane content at 1:3 zeolite/water ratio Report

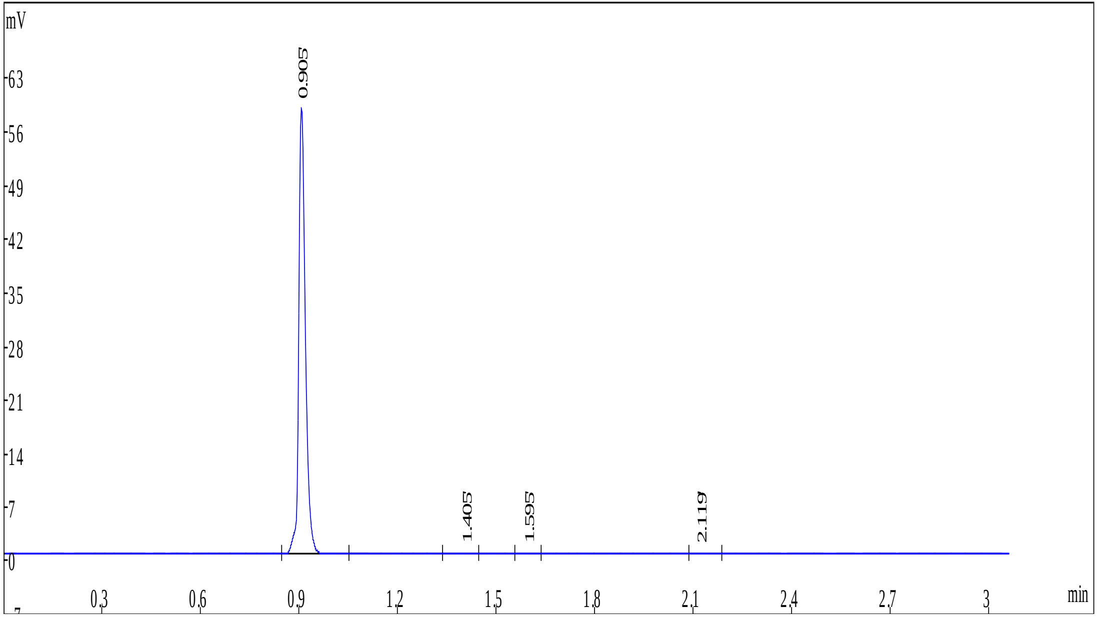
Printing time: Thu Jan 14 19:01:45 2021
Injection time: Thu Oct 15 14:44:37 2020
File opened: G:\sample 3(20201015 14;44;37).hw



```
---------------------------------------------
Rank   Time      Name   Area%      Area
---------------------------------------------
1      0.908          99.86      78146
2      1.959          0.141      110
---------------------------------------------
Total                  100       78256
```

Methane content at 1:4 zeolite/water ratio Report

Printing time: Thu Jan 14 19:04:35 2021
Injection time: Thu Oct 15 14:35:14 2020
File opened: G:\sample 4(20201015 14;35;14).hw

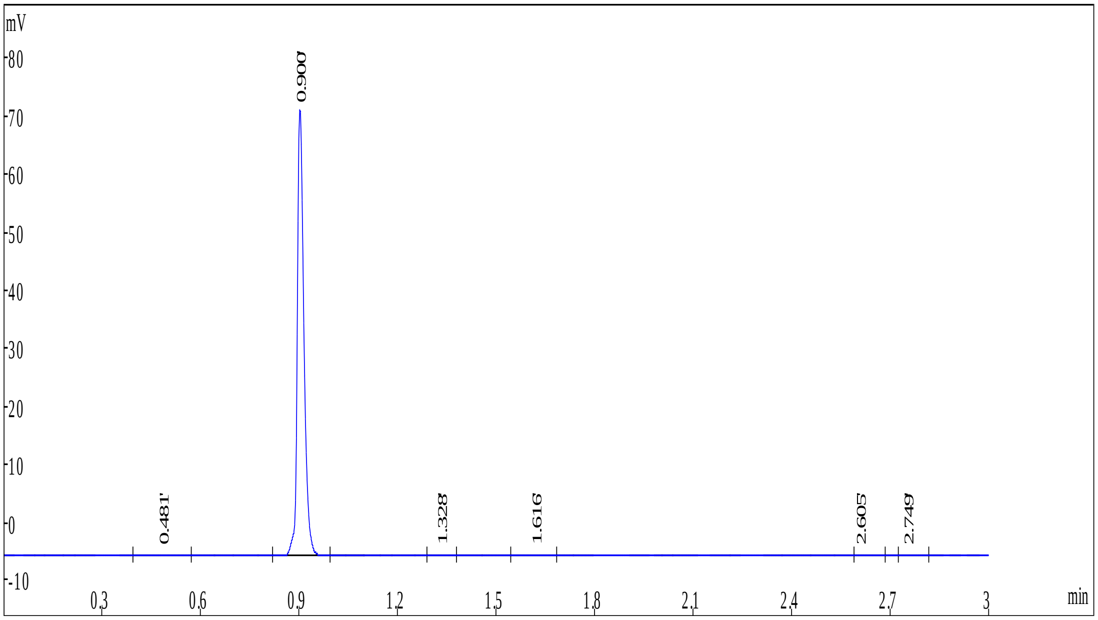


```
---------------------------------------------
Rank   Time      Name   Area%      Area
---------------------------------------------
1      0.905          99.55      76446
2      1.405          0.1783      137
3      1.595          0.1338      103
4      2.119          0.136      104
---------------------------------------------
Total                  100       76790
```

Appendix 4: Upgrade biogas at different biogas flow rate

Upgraded methane using wood ash/water @ 100ml/min Report

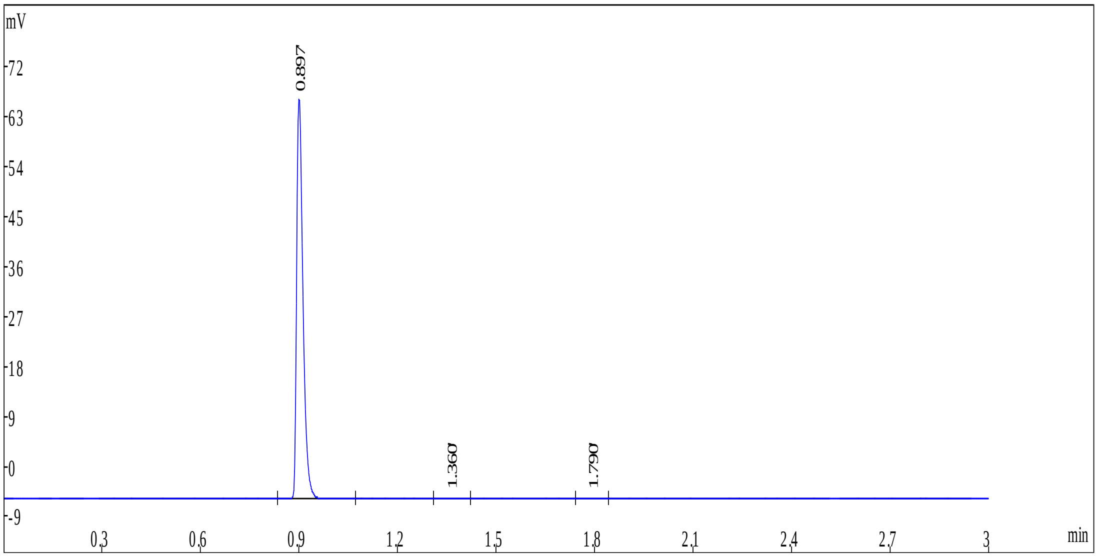
Printing time: Thu Jan 14 19:14:57 2021
Injection time: Mon Oct 19 15:44:40 2020
File opened: G:\ sample 8(20201019 14;49;28)(20201019 15;44;40).hw



```
--------------------------------------------
Rank   Time      Name   Area%       Area
--------------------------------------------
1      0.481            0.25975    159
2      0.900            99.37      104591
3      1.328            0.22365    122
4      1.616            0.1466     148
--------------------------------------------
Total                  100        105020
```

Upgraded methane using wood ash/water @150ml/min Report

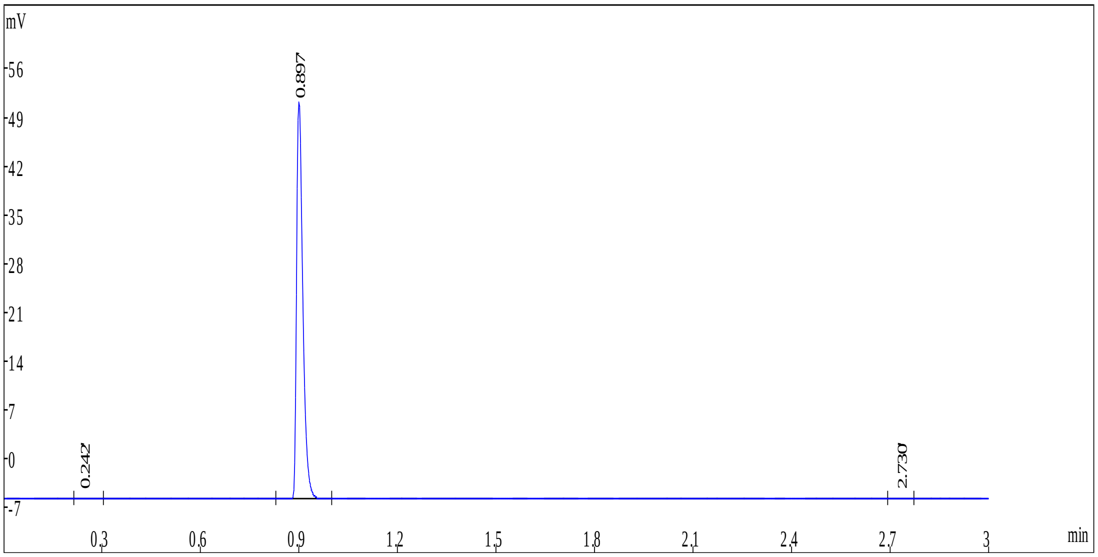
Printing time: Thu Jan 14 19:26:00 2021
Injection time: Mon Oct 19 15:39:54 2020
File opened: G:\sample 10(20201019 15;39;54).hw



```
---------------------------------------------
Rank   Time      Name   Area%       Area
---------------------------------------------
1      0.897          98.61       89498
2      1.360          0.1978       180
3      1.790          0.1922       127
---------------------------------------------
Total                  100        89805
```

Upgraded methane using wood ash/water @ 250ml/min Report

Printing time: Thu Jan 14 19:39:39 2021
Injection time: Mon Oct 19 15:54:07 2020
File opened: G:\sample 11(20201019 15;54;07).hw

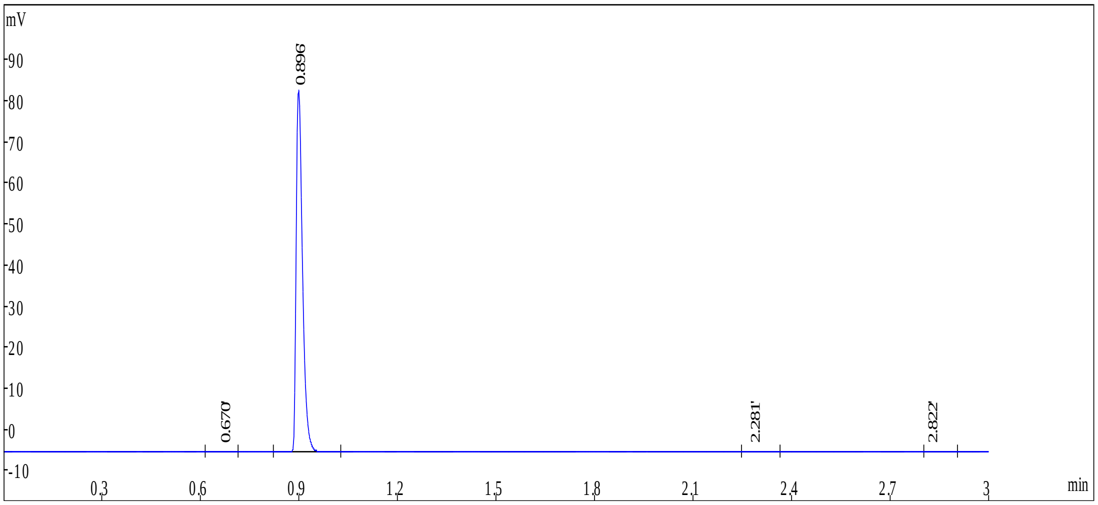


```
---------------------------------------------
Rank   Time      Name   Area%       Area
---------------------------------------------
1      0.242          0.147      103
2      0.897          99.69      71006
3      2.730          0.1591      112
---------------------------------------------
Total                 100        70221
```

Appendix 5: Upgrade biogas at different temperature

Upgraded methane using wood ash/water @65°C Report

Printing time: Thu Jan 14 20:57:07 2021
Injection time: Mon Oct 19 15:22:34 2020
File opened: G:\sample 14 (20201019 15;22;34).hw

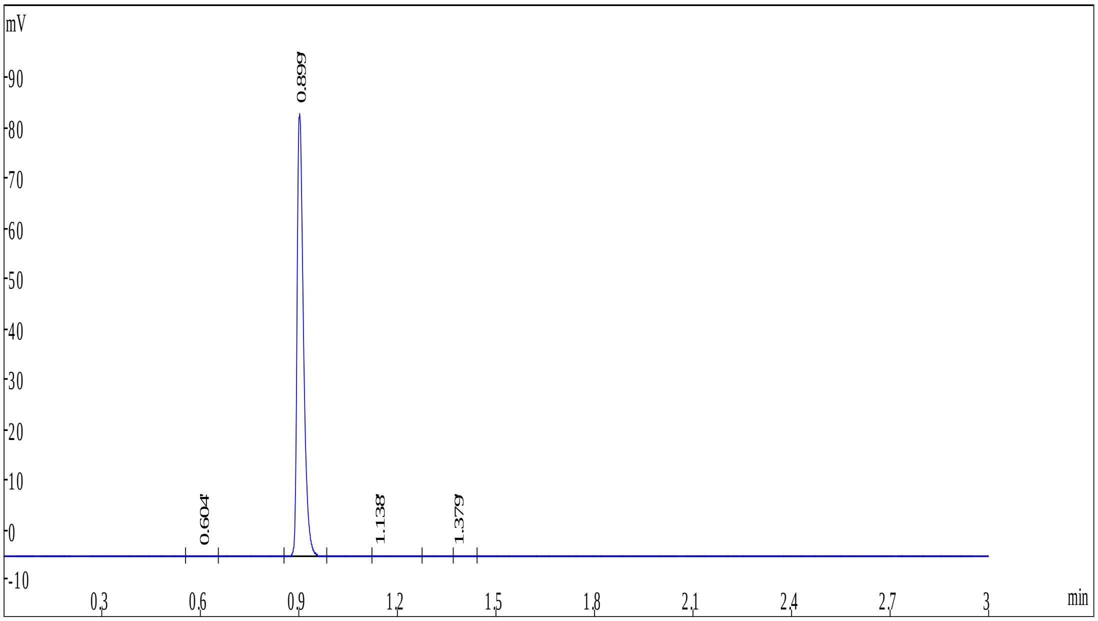


```
---------------------------------------------
Rank   Time      Name   Area%       Area
---------------------------------------------
1      0.670          0.09825    108
2      0.896          99.65      109784
3      2.281          0.1527      168
4      2.822          0.1036      114
---------------------------------------------
Total                 100        110174
```

upgrade methane using wood ash/water @ 75°C Report

Printing time: Thu Jan 14 20:14:09 2021
Injection time: Mon Oct 19 15:03:31 2020

File opened: G:\sample 15 (20201019 15;03;31).hw

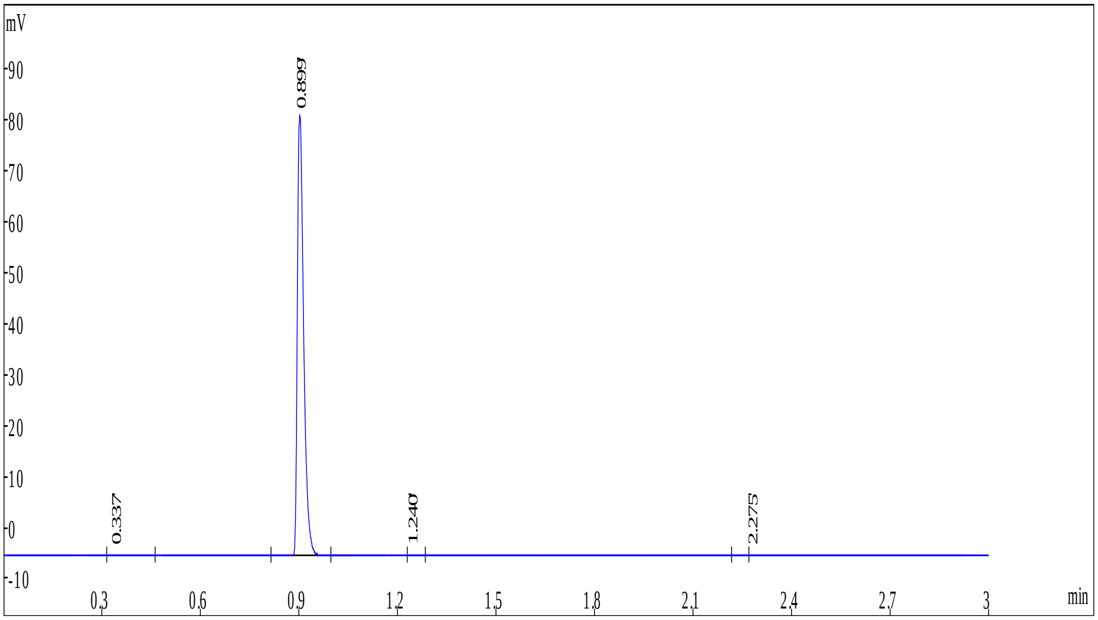


```
--------------------------------------------
Rank   Time      Name   Area%       Area
--------------------------------------------
1      0.604          0.1282     146
2      0.899          97.98      115545
3      1.138          0.2211     252
4      1.379          0.1544     176
--------------------------------------------
Total                 98.48      116119
```

upgraded methane using wood ash/water @80^{o}C Report

Printing time: Thu Jan 14 20:30:43 2021
Injection time: Mon Oct 19 15:08:20 2020

File opened: G:\sample 16(20201019 15;08;20).hw

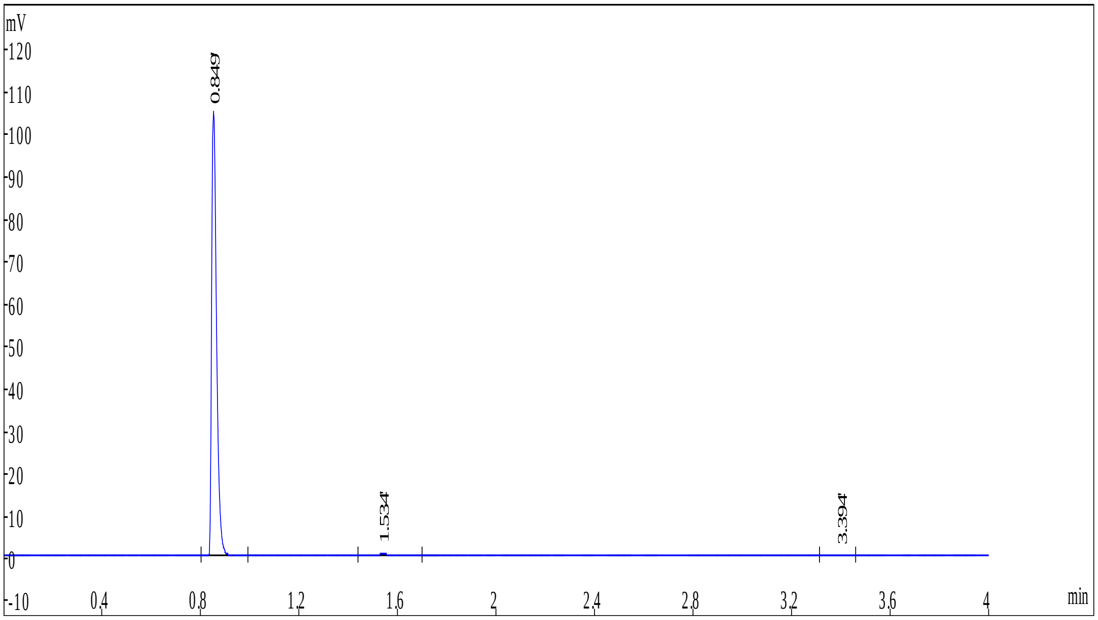


```
---------------------------------------------
Rank   Time      Name   Area%      Area
---------------------------------------------
1      0.337          0.1031     115
2      0.899          95.37      111619
3      1.240          0.3154     353
4     2.275          0.1161     130
---------------------------------------------
Total                95.91      112217
```

Appendix 6: Upgrade biogas using dry activated clay

Upgrade biogas using activated clay @45ml/min Report

Printing time: Thu Jan 14 21:00:31 2021
Injection time: Mon Oct 12 17:45:08 2020
File opened: G:\sample 15 (20201012 17;45;08).hw

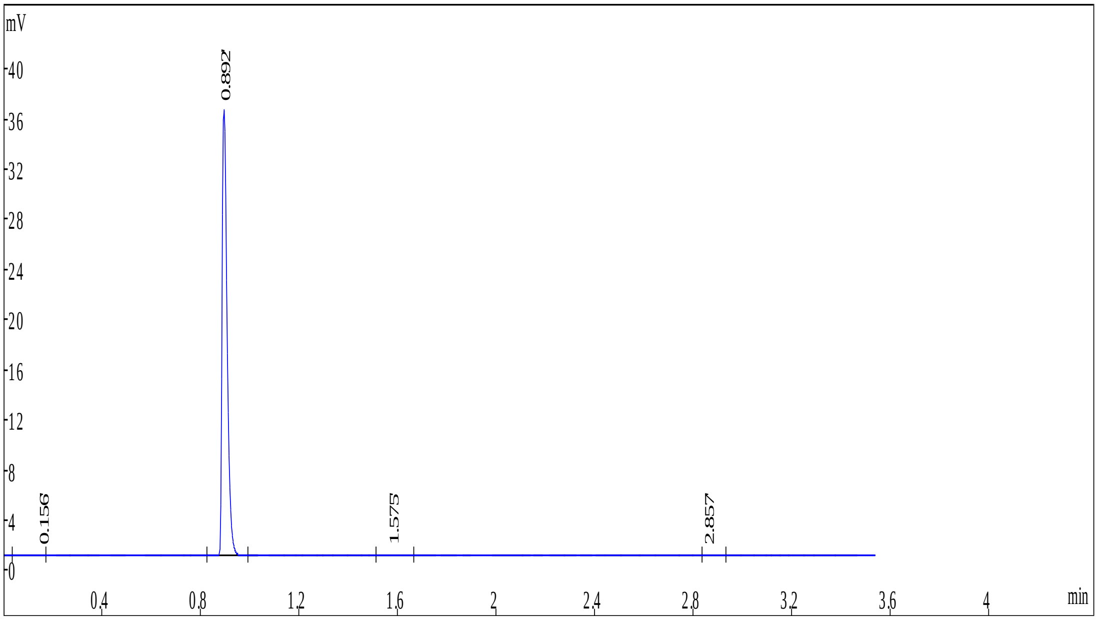


```
--------------------------------------------
Rank   Time      Name   Area%       Area
--------------------------------------------
1      0.849          98.56      130266
2      1.534          1.344      1776
3      3.394          0.1008     133
--------------------------------------------
Total                100        132175
```

Appendix 7: Raw biogas

Raw biogas 1 report

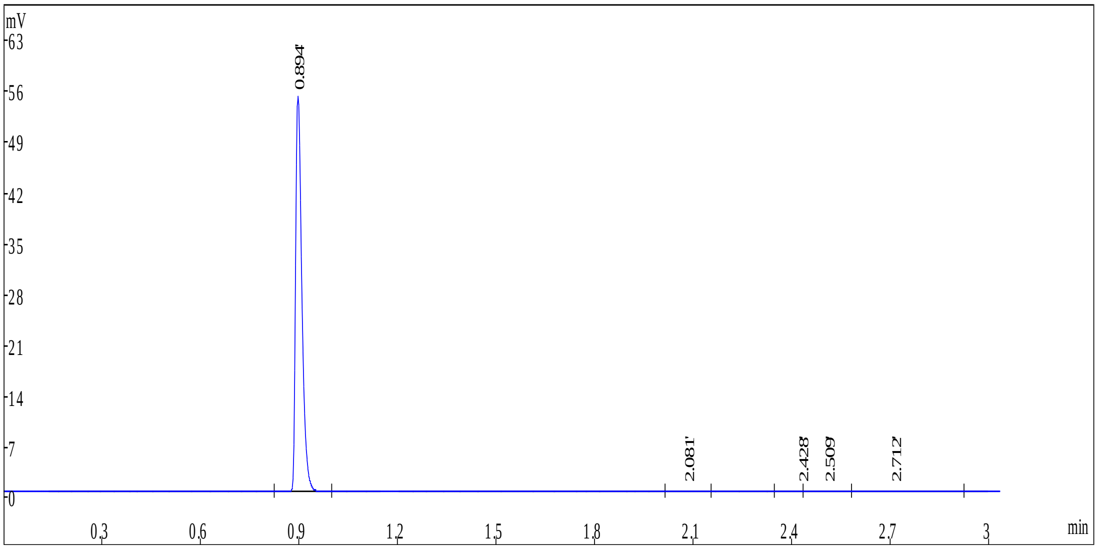
Printing time: Thu Jan 14 21:09:40 2021
Injection time: Wed Oct 14 16:17:51 2020
File opened: G:\Raw biogas 1(20201014 16;17;51).hw



```
--------------------------------------------
Rank   Time     Name   Area%      Area
--------------------------------------------
1      0.156          0.2481     113
2      0.892          99.13      45303
3      1.575          0.3695     169
4      2.857          0.2495     114
--------------------------------------------
Total                 100        45699
```

Raw biogas 2 Report

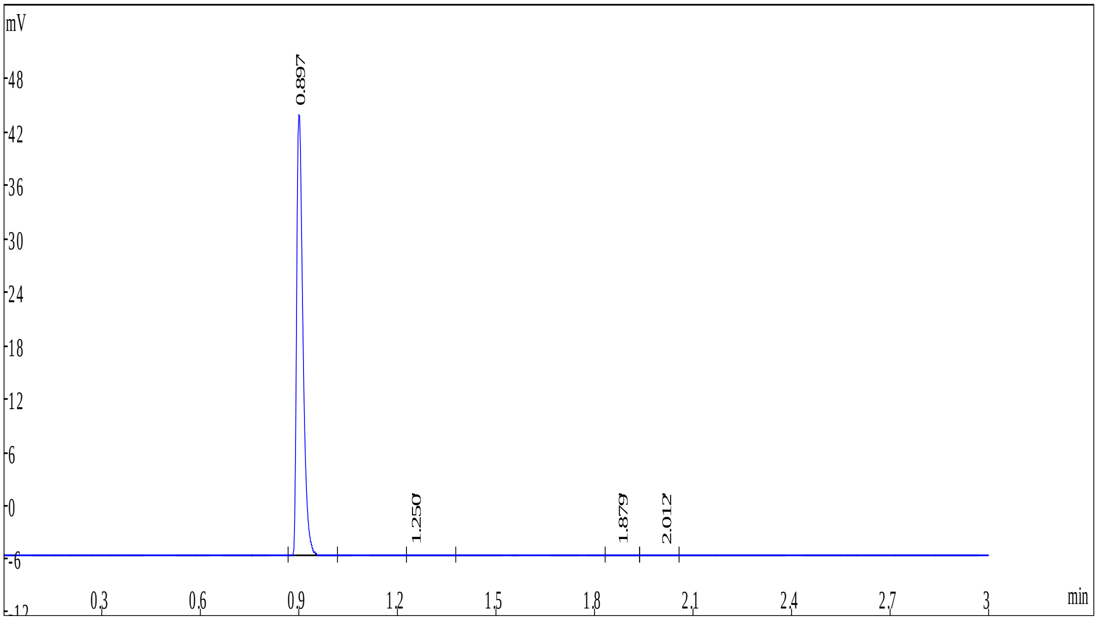
Printing time: Thu Jan 14 19:08:13 2021
Injection time: Thu Oct 15 14:59:16 2020
File opened: G:\Raw biogas 2 (20201015 14;59;16).hw



Rank	Time	Name	Area%	Area
1	0.894		97.87	61085
2	2.081		0.184	126
3	2.428		0.1962	134
4	2.509		0.4426	303
5	2.712		1.303	893
Total			100	62541

Raw biogas 3 Report

Printing time: Thu Jan 14 19:37:22 2021
Injection time: Mon Oct 19 15:27:26 2020
File opened: G:\Raw biogas 3(20201019 15;27;26).hw



```
---------------------------------------------
Rank   Time      Name   Area%      Area
---------------------------------------------
1      0.897            99.48      60359
2      1.250            0.1919      118
3      1.879            0.1645      101
4      2.012            0.164      101
---------------------------------------------
Total                  100       60679
```