PAN AFRICAN UNIVERSITY

Institute of Water and Energy Sciences (Incl. Climate Change)

THE EFFECT OF BIOCHAR ON BIOGAS YIELD FROM ANAEROBIC DIGESTION OF FOOD WASTE AND BIOGAS UPGRADING

Done by: Colette Abimana

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Members of Jury:

President: Prof. Abdellatif Zerga

Supervisor: Dr. Wondwossen Bogale Eremed

External Examiner: Dr. Abdallah Khellaf

Internal Examiner: Dr. Abdallah Benyoucef

Academic Year: 2016-2017

DECLARATION

I Colette ABIMANA, hereby declare that the work represented in this thesis is my own contribution to the best of my knowledge. This work has never been submitted or presented to any other university or institution for academic purpose. I also declare that all information, material and results from other works presented in this thesis, have been fully cited and referenced in accordance with the academic rules and ethics. Therefore, I declare that the work presented in this thesis is my personal contribution for the fulfillment of the award for Master's degree in Energy Engineering.

Colette ABIMANA   Dr.-Ing. Wondwossen Bogale Eremed

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DEDICATION

I dedicate this work to:

The Almighty God;

My parents, sisters, brothers and other family members;

My lecturers and fellows classmates at PAUWES;

All my friends;

And to my country mates studying at PAUWES.

ABSTRACT

It has been shown that, the increase of greenhouse gases come from conversional energy resources, inadequate waste management technologies, deforestation grow rate and decrease of soil fertility are affecting worldwide environment. Therefore, anaerobic digestion technology had been integrated as one of the environmental friendly energy generation technologies and as biological techniques for waste management which use mainly organic materials (animal wastes, agriculture wastes, residential and industrial wastes) as feedstock and generate energy which is known as Biogas and fertilizer with almost zero emission of greenhouse gases. Biogas originates from mechanism of microorganism during the process of bio-degradation of organic materials under anaerobic conditions. However, anaerobic digestion still has some problems like inhibitions which affect its production. The low energy value of Biogas due to the presence of high quantity of carbon dioxide within Biogas and presence of impurities within the raw Biogas have become an obstacle for high energy application uses. There are several technologies of removing carbon dioxide and hydrogen sulphide from Biogas which have been used for many years ago.

The focus of this work was to minimize inhibitory problems and maximize the production of anaerobic digester using Biochar as an additive, and upgrade produced raw Biogas using sodium scrubbing and Biochar absorption as carbon dioxide and hydrogen sulphide removal in order to enriching Biogas and enable it for high energy application uses. Biochar is the porous carbonaceous solid produced from the thermochemical conversion of biomass in the absence or limited oxygen environment at a temperature ranging from 350 to 1000ºC. Recently, the use of Biochar in anaerobic digestion has been explored. However Biochar is mainly known as soil amendment or used for carbon sequestration.

During the experiment, anaerobic digestion of Ethiopian food wastes was conducted and Biochars were added at different concentration(15%; 25%; 50% and 85% based on dry matter of used substrates) as an additive material after being prepared in a laboratory of AAiT. Results has indicated that, the cumulative Biogas production was extremely low and poor in terms of CH_4 content where; in the 1st and 2nd experiment cumulative CH_4 yield was 2.24ml/g VS from R.Control and 5.77ml/g VS from R025 respectively as the highest production value compared to

415.496ml/g VS of the theoretical cumulative CH_4 yield. From the 3rd and 4th experiment where the food waste was co-digested with cow dung (for 1:2 and 1:1 ratio of cow dung to food waste) and Biochar added have produced very low cumulative Biogas and methane yield compared to the theoretical values. Upgrading of raw Biogas by removing CO_2 and H_2S was conducted and resulted in 81% as the highest CO_2 removal efficiency with 18.93% of CH_4 the lowest losses. Therefore, the effect of Biochar on anaerobic digestion of used food waste was not clear due to the quality of used food waste which has affected the system efficiency. Besides the upgrading of raw Biogas has not shown the high efficiency for CO_2 and H_2S removal instead high CH_4 losses was presented due to the lack of appropriates equipment for upgrading of Biogas which has become an obstacle to achieve the target percentage of methane in the final product.

__Key Words__: Biochar, Food Waste, Biogas production, Upgrading, Experiment

RÉSUMÉ

Il a été démontré que l'augmentation de serre gaz proviennent de ressources énergétiques conversional, technologies de la gestion des déchets inadéquates, déforestation croître taux et diminution de la fertilité du sol influent sur environnement dans le monde entier. Par conséquent, technologie de digestion anaérobie a été intégré comme une des technologies de production énergie environnement et techniques biologiques pour la gestion des déchets, qui utilisent des matériaux principalement organiques (déjections animales, les déchets de l'agriculture, les déchets résidentiels et industriels) comme matière première et produire de l'énergie qui est connu comme le biogaz et les engrais avec presque zéro émission de gaz à effet de serre. Biogaz provient du mécanisme du micro-organisme au cours du processus de biodégradation des matières organiques dans des conditions anaérobies. Cependant, la digestion anaérobie a encore quelques problèmes comme les inhibitions qui affectent sa production. La valeur de basse énergie du biogaz en raison de la présence d'une quantité élevée de dioxyde de carbone au sein de biogaz et de la présence d'impuretés dans le biogaz brut sont devenues un obstacle aux fins de l'application haute énergie. Il existe plusieurs technologies d'éliminer le dioxyde de carbone et d'hydrogène sulfuré de biogaz qui ont été utilisés pendant de nombreuses années il y a.

L'objectif de ce travail est de minimiser les problèmes inhibitrices et maximiser la production de digesteur anaérobie utilisant Biochar comme additif, et mise à niveau produit des biogaz brut à l'aide de sodium à récurer et absorption de Biochar comme suppression de sulfure dioxyde de carbone et d'hydrogène afin d'enrichir les biogaz et lui permettre aux fins de l'application haute énergie. Le biochar est solide poreux carboné provenant de la conversion thermochimique de la biomasse en l'absence ou l'environnement d'oxygène limité à une température allant de 350 à $1000^o C$. récemment, l'utilisation du Biochar dans la digestion anaérobie a été explorée. Cependant le Biochar est principalement connu comme amendement du sol ou utilisé pour le piégeage du carbone.

Pendant l'expérience, la digestion anaérobie de déchets alimentaires éthiopien a été menée et Biochars ont été ajoutés à différente concentration (15 % ; 25 %, 50 % et 85 % selon la matière sèche des substrats utilisés) comme matériau d'additif après en cours d'élaboration dans un laboratoire de AAiT. Résultats a indiqué que, la production de biogaz cumulative était extrêmement faible et pauvre en termes de contenu CH_4 où ; dans le 1st et 2nd expérience

cumulative CH_4 rendement était 2,24 ml/g VS de R.Control et 5,77 ml/g de R025 respectivement comme valeur de production la plus élevée par rapport à 415,496 ml/g VS du rendement théorique cumulé CH_4 . De la 3rd et 4ème expérience où les déchets alimentaires a été digérée conjointement avec la bouse de vache (pour 1 / 2 et 1:1 ratio de bouse de vache pour les déchets alimentaires) et Biochar ajoutés ont produit des biogaz cumulative très faible et le rendement de méthane par rapport aux valeurs théoriques. Valorisation du biogaz brut en enlevant le CO_2 et H_2S a été effectuée et conduit à 81 % comme la plus grande efficacité de retrait CO_2 avec 18,93 % de CH_4 les pertes le plus bas. Par conséquent, l'effet du Biochar sur la digestion anaérobie de déchets alimentaires utilisés n'était pas clair en raison de la qualité des déchets alimentaires usagées qui porte atteinte à l'efficacité du système. Sans compter que la valorisation du biogaz brut n'a pas démontré l'efficacité élevée de CO_2 et H_2S retrait plutôt CH_4 des pertes élevées a été présenté à cause de la manque de équipement approprie pour la mise à niveau du biogaz qui est devenue un obstacle pour atteindre le pourcentage cible de méthane dans le produit final.

Mots clés *: Le Biochar, déchets alimentaires, production de biogaz, la mise à niveau, expérience*

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ACRONYMS

AD	Anaerobic Digestion
^0C	Degree Celsius
AAiT	Addis Ababa Institute of Technology
AAU	Addis Ababa University
C:N	Carbon to nitrogen
CD	Cow Dung
CH_4	Methane
CO_2	Carbon dioxide
DAAD	Deutsche Academischer Austauschdienst- German Academic Exchange Services
DOC	Dissolved organic carbon
DTN	Dissolved total nitrogen
FW	Food Waste
G	Gram
GIZ	Deutsche Gesellschaft für Internationale Zusammenarbeit – Company specialized in international development
H	Hydrogen
H:C	Hydrogen to Carbon ratio
H_2S	Hydrogen Sulphide
HRT	hydraulic retention time
HTC	Hydrothermal Carbonization
IEA	International Energy Agency
KFW	Kreditanstalt für Wiederaufbau- German Government Development bank
L	Liter
MC	Moisture Content

M_T	Total mass or fresh weight
N	Nitrogen
NH_3	Free ammonia
NH_4^+	Ammonium ion
O	Oxygen
O:C	Oxygen to carbon ratio
PAUWES	Pan African University Institute of Water and Energy Science (including Climate Change)
Ppm	parts per million
PSA	Pressure Swing Adsorption
S	Sulphur
SO_2	Sulphur dioxide
SO_3	Sulphur trioxide
SRT	Solid retention time
TOC	Total Carbon Content
TS	Total Solid
VFA	Volatile fatty Acid
VS	Volatile Solid
WWTP	Waste Water Treatment Plant

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CHAPTER ONE

1.0. INTRODUCTION

1.1   General Introduction

According to the previous researches, it has been found that; the increase of greenhouse gases emitted, increase of water consumption, water pollution, decrease of soil fertility, inadequate waste management technologies, and deforestation grow rate are unsustainable resource use systems which influence worldwide and contribute on climate change (Sinervo, R. (2017); Kwak, D.H., et al. (2013) ; El-Fadel, M., Findikakis, A. N. & Leckie, J. O. (1997)). Therefore, anaerobic digestion technology has been established as one of sustainable biological recycling and recovery systems to minimize above issues (Mata-Alvarez, J., Mace, S. & Llabres, P. (2000)). Biogas originates from mechanism of bacteria during the process of bio-degradation of organic materials under anaerobic conditions.

Anaerobic digestion technology uses organic wastes as feedstocks to produce Biogas as fuel and digestate as fertilizer through anaerobic digestion conditions (Etuwe, C.N., Momoh, Y.O.L. and Iyagba, E.T. (2016)). Therefore quality of input substrate affects the production depending on their total solid, moisture content, volatile solids, carbon content and nitrogen content which vary from one substrate to another one. Biogas can be used for heat generation, electricity production and fuel as Biomethane for natural gas grid injection and transportation (Holm-Nielsen, J. B., et al. (2009); Shen, Y., et al. (2015); Yousef, A. M., et al. (2016)).

Organic wastes can be classified into five groups by considering their source of origin; urban wastes, industrial wastes, animal and human wastes, forest and agriculture wastes, fishery and poultry wastes. Biogas constitutes with 40-70% of methane, 25-45% of carbon dioxide and the rest are the impurities, which are hydrogen sulphide, ammonia, hydrogen, water vapors, nitrogen and other volatile compounds, where their concentrations depend on type of feedstocks used (**Appendix 1.)** and operating conditions (Rasi, S. (2009); Sinervo, R. (2017); Yousef, A. M., et al. (2016)). The presence of carbon dioxide in Biogas reduce the heat value and economic feasibility of Biogas. Therefore it is important to upgrade Biogas by removing unwanted constituents and remain with methane at a higher concentration and increase its heat value (Yousef, A. M., et al. (2016)). Low Biogas with 55% of methane has around 4700kCal or

20MJ/m^3 of calorific energy (Manonmani, P., et al. (2017)), while the upgraded Biogas with above 95% of methane has around 39.8MJ/m^3 of calorific energy value (Chaemchuen, S., et al. (2013)).

Anaerobic digestion process has shown some problems which inhibit the process and affect the production (Biogas and digestates). Recently, there had been researches on the use of inoculums, additive materials for immobilizing microorganisms and conductive materials in order to improve performance of anaerobic digestion by minimizing those inhibitions (Cai, J., et al. (2016)). Some of additives used are glass, polyethylene, carbon, activated carbon, and polyvinyl alcohol while, conductive iron oxides, semi-conductive iron oxides minerals and micrometer-size magnetite are conductive materials. However, the use of those additive media has shown some environmental and economic problems as they are persisted in anaerobic digestate which mainly used as fertilizer or require some addition system to separate them from digestate (Cai, J., et al. (2016); Yousef, A. M., et al. (2016)).

It is necessary to look for another way of solving those issues without creating environmental and economic problems. Therefore, adsorption have been identified as a method of removing organic compounds by using adsorbents such as zeolites, activated carbon, silica gel and bentonite which have been reported as removals of toxic chemicals from anaerobic digestion (Fagbohungbe, M.O., et al. (2016)). Recently, Biochar as one of activated carbon has been used in anaerobic digestion as an additive material, and it has been approved as an environmental friendly and low cost adsorbent.

Biochar is the porous carbonaceous solid produced from the thermochemical conversion of biomass in the absence or limited oxygen environment at a temperature ranging from 350 to 1000°C (Hewage, S. & Priyadarshani, R. (2016)). Biochar can be used as product itself, as an ingredient in a blended material and it has many applications such as an agent for soil improvement, improved resource use efficiency, energy production, waste management and mitigation of climate change, remove contaminants material in aqueous solutions as an adsorbent, including heavy metals, excessive nutrients and pharmaceuticals (Gurwick, N.P., et al. (2013), Sinervo, R. (2017); Sethupathi, S., et al. (2017) ; Woolf, D., et al. (2010)). Feedstocks used for Biochar production are woody biomass, crops residues, manures and grasses. Recently, it has been some discussions on the applications of Biochar in soil improvement, waste management, energy generation and as an additive substance in anaerobic digestion (Hewage, S.

& Priyadarshani, R. (2016); Sinervo, R. (2017)). Many of those discussions were focusing on the use of Biochar as soil amendment as its main application. However in the near past, few of those discussions had tried to look for some effects of Biochar as additive in anaerobic digestion process in terms of stability, mitigation of inhibition problems, Biogas and methane yield (Sinervo, R. (2017)).

1.2   Research Background

Anaerobic digestion technology has been used for long time as the most appropriate technology for waste management and energy generation. The first anaerobic digestion plant was built by 1897 in India followed by England and chine. After those two countries, the anaerobic digestion technology has been used all over the world where currently, it is well developed in Europe (Abbasi, T., Tauseef, S. M. & Abbasi, S. A. (2012)). Anaerobic digestion is regarded as a good technology for food waste treatment which facilitates for energy and resource recovery (Cai, J., et al. (2016)). However, anaerobic digestion has frequently faced some problems such as low methane yield and process instability. Therefore, the use of inoculum, some additive materials (such as glass, polyethylene, carbon, activated carbon, and polyvinyl alcohol) and support materials have been applied in order to improve stability and production of the anaerobic digestion of municipal solid wastes. Although, those additive materials have improved the stability and production of anaerobic digestion, they need to be removed from digestates in order to protect the environment. Therefore, the investment cost will increase due to the addition treatment for separating additive materials from digestates (Cai, J., et al. (2016)). For that reason recently, Biochar has been evaluated to be used as an additive material for anaerobic digestion as it does not require an additional treatment before using digestates as fertilizer or for regeneration (Cai, J., et al. (2016); Luo, C., et al. (2015)) but, there is no industry or biogas plant which is using biochar as an additive materials yet.

Depending on the application of biogas and the required energy, upgraded biogas is needed for high energy application such as vehicle fuels and a substitute of natural gas or injected in natural gas grid (Ryckebosch, et al. (2011)). Upgrading Biogas has two main parties; cleaning and CH_4 enrichment which include drying step too. Cleaning is about removing acidic gases and other impurities while enrichment (also known as upgrading) is about removing carbon dioxide from Biogas thus, the enhancement of calorific value of produced gas and drying the final product

(Yousef, A. M., et al. (2016); Zhao, Q., et al. (2010)). Upgrading of Biogas has been practiced main years ago in Europe, America and Asia.

While in Africa, it seems like up to now nothing has been done on this, however South Africa is constructing one Biogas upgrading plant and it was expected to produce Biomethane by the middle of 2017. In 2008 in Europe there were 79 Biogas upgrading plants, of which 35 were in Sweden, 15 were in Germany and 11 were in Switzerland. The upgraded Biogas were used as fuel for vehicles, and injected into natural gas grid (Holm-Nielsen, J.B., et al. (2009)). Generally, Biogas upgrading technology have had a significant growth in others continents except in Africa. According to Hoyer, K., et al. (2016), there were 428 Biogas upgrading plants within the IEA Bioenergy 37 Task member countries at the end of 2015.

1.3   Problem Statement

It has been found that, anaerobic digestion process is facing many problems which are affecting Biogas and methane yield as anaerobic digestion's productions and the quality of digestates (Fagbohungbe, M.O., et al. (2016)). However, the use of some chemicals such as additives and conductive materials has been applied in order to minimize those inhibitions factors and increase the production of anaerobic digestion process but they have shown some environmental and economic problems in the use of digestates. Currently, Biochar has been used as an additive although; the appropriate rate to be added in AD and for which conditional is still a matter. Which means that, the amount of biochar to be added may vary depend on type and quality of substrates used, inoculum and or some other factors. The energy content of Biogas is not enough to compete with natural gas due to the presence of carbon dioxide in Biogas at a high rate. In addition, methane as a worst greenhouse gas when it is emitted in the atmosphere, which may come from degradation of landfills, natural gas, coal and fuel oil exploitation with some other harmful gases are polluting the environment in general. Therefore, it is important to look for alternative fuel by using environmental friendly technology.

1.4   Objectives of Study

Biochar, which is known as soil amendment, useful for carbon sequestration and used in energy generation. The aim of this study is to find out the effect of Biochar added in anaerobic digester on Biogas yield which is mainly constituted by methane as the major components, and produce environmental friendly digestate. Anaerobic digestion use organic material to produce biogas

therefore, it will minimize solid waste from landfills and protect the environment from harmful gases . And also upgrade Biogas to Biomethane which can be used for cooking, substitute natural gas and, or vehicle fuel with high calorific value or high energy content.

Specific object:

- ➢ To improve anaerobic digestion process, minimize or mitigate anaerobic digestion inhibitions by adding Biochar.
- ➢ To find out the effect of Biochar on Biogas and methane yield
- ➢ To upgrade Biogas to Biomethane after removing CO2 and some impurities in the raw Biogas which was produced from anaerobic digestion of wet substrate
- ➢ To increase the energy value of Biogas in order to compete with natural gas and mitigate environmental problems caused by greenhouse gases emission.
- ➢ To produce digestate with high nutrients content.

Some researchers have focused on the effects of Biochar on Biogas production either experimentally or numerically. However, they are not many as it could be besides it is still hard to conclude about optimum concentration of Biochar which can be added in anaerobic digestion of organic matters in order to improve its efficiency. Therefore, many researches need to be done in this area for more clarification. Thus, in this work, detailed analysis was performed both experimentally and theoretically to find out the effects of Biochar on Biogas produced form anaerobic digestion of food waste and co-digestion of food waste and cow dung by adding different amounts of Biochar. Besides, this work suggested ways to further ways to clean and enrich Biogas production using Biochar which is considered as activated carbon and caustic solution (known as sodium scrubbing) were used for removing CO_2 and H_2S from raw Biogas produced during the experiment.

CHAPTER TWO

2.0. LITERATURE REVIEW

2.1   Environmental Impact of Solid Waste Landfilling

Disposal of solid wastes in landfills is practiced all over the world. Composition of solid waste depends on socio-economic conditions, location, waste collection and disposal methods, season, and sampling and sorting procedures. Solid waste is constituted by both organic and inorganic materials. From which most of organic materials are biodegradable, and they can be reduced to smaller compounds through aerobic and anaerobic bacteria which leads to the formation of gas and leachates. Disposal of solid wastes releases gas and leachates due to microbial decomposition, climatic conditions, refuse characteristics and landfilling operations. The released gas is constituted manly by carbon dioxide, methane, carbon monoxide, nitrogen, hydrogen, hydrogen sulphide, oxygen and trace compounds (El-Fadel, M., Findikakis, A. N. & Leckie, J. O.(1997); Reinhart, D. R., & A. Basel Al-Yousfi, A. (1996); Ryckebosch, et al. (2011)). Besides methane is a powerful greenhouse gas with a global warming potential that is far greater than of carbon dioxide (Howarth, R. W., Santoro, R. & Ingraffea, A. (2011); Chaemchuen, S., et al. (2013)).

 Landfills have shown many impact on the surrounding environment; health hazards, vegetable damage, ground water pollution, unpleased odors, landfill settlement, fire and explosion hazards, air pollution, and global warming (El-Fadel, M., Findikakis, N. A. & James O. Leckie, J. O. (1997)). Some measurements have been taken in terms of eliminating or minimizing impacts of landfill such as gas recovery, active gas pumping, installation of impermeable barriers before site operation, passive venting, hybrid system of impermeable barriers with passive systems (El-Fadel, M., Findikakis, N. A. & Leckie, J. O. (1997)), aerobic and anaerobic digestion systems. Anaerobic digestion has been approved as biological treatment of solid waste which is cost-effective due to its high energy efficiency recycling and recovery of organic waste with limited environmental impact compared to the other used technologies (Mata-Alvarez, J., Mace, S. & Llabres, P. (2000)).

2.2   Production of Biogas through Anaerobic digestion

Biogas is a combustible gas produced through anaerobic digestion process of organic materials or waste such as animal wastes, residential wastes, agriculture residuals, night soil, waste water, food wastes and industrial wastes (Ippolito, J.A., et al. (2012); Etuwe, C.N., Momoh, Y.O.L. & Iyagba, E.T. (2016)), and it can also be generated naturally, on which is important in biogeochemistry of carbon cycle (Gómez, E., Martin, J. & Michel, F.C. (2011)). Biogas generated naturally from degradation of landfills emit CH_4 and CO_2 in the atmosphere as greenhouse gases. In addition, CH_4 is a harmful greenhouse gas with about 22 times powerful compare to CO_2 (Chaemchuen, S., et al. (2013); Howarth, R. W., Santoro, R. & Ingraffea, A. (2011)), and it can destroy Ozone layer. Biogas production varies from one type of substrate to the other one. Therefore quality of input substrate can affect the production depending on their calorific values, moisture content, volatile solids, carbon content and nitrogen content which vary from one substrate to another one. Production of biogas within anaerobic digestion is a process occur through four phases in the presence of different microorganisms to facilitate each phase. Those phases are; hydrolysis, acidogenesis, acetogenesis and methanogenesis (Ippolito, J.A., et al. (2012); Etuwe, C.N., Momoh, Y.O.L. & Iyagba, E.T. (2016); Matheri, A.N., et al. (2016) ; Chaemchuen, S., et al. (2013); El-Fadel, M., Findikakis, N. A. & Leckie, J. O. (1997)).

Hydrolysis phase is about breaking down complex organic matter such as carbohydrates, proteins and fats by microorganisms into small and soluble organic molecules which are sugars, amino acids, and fatty acids. In acidogenesis, the products of hydrolysis are degraded by anaerobic bacteria into acetic acid, volatile fatty acids and H_2, with CO_2. In acetogenesis, acidogenesis products are reduced by acetogenic bacteria into acetic acid and CO_2 with H_2. In the last phase which is methanogenesis, acetogenesis products are converted by methanogenic bacteria into methane and carbon dioxide with some impurities with a very small concentration compare to the one of methane and carbon dioxide (Ippolito, J.A., et al. (2012); Etuwe, C.N., Momoh, Y.O.L. and Iyagba, E.T. (2016); Dobre, P., Matei, F. & Nicolae, F. (2014); Sorathia, H.S., et al. (2012)). Methanogenesis has two pathways, which are aceticlastic methanogenesis when methane is produced by reduction of CO_2 by H_2 while hydrogenotrophic methanogenesis is when methane is produced by reduction of acetic acid by water (Ippolito, J.A., et al. (2012)). Energetic value of Biogas is determined by methane content, as methane has a high calorific

value compare to other constituents of Biogas (Ippolito, J.A., et al. (2012); Dobre, P., Matei, F. & Nicolae, F. (2014)). All those phases are summarized in **Figure 1**.
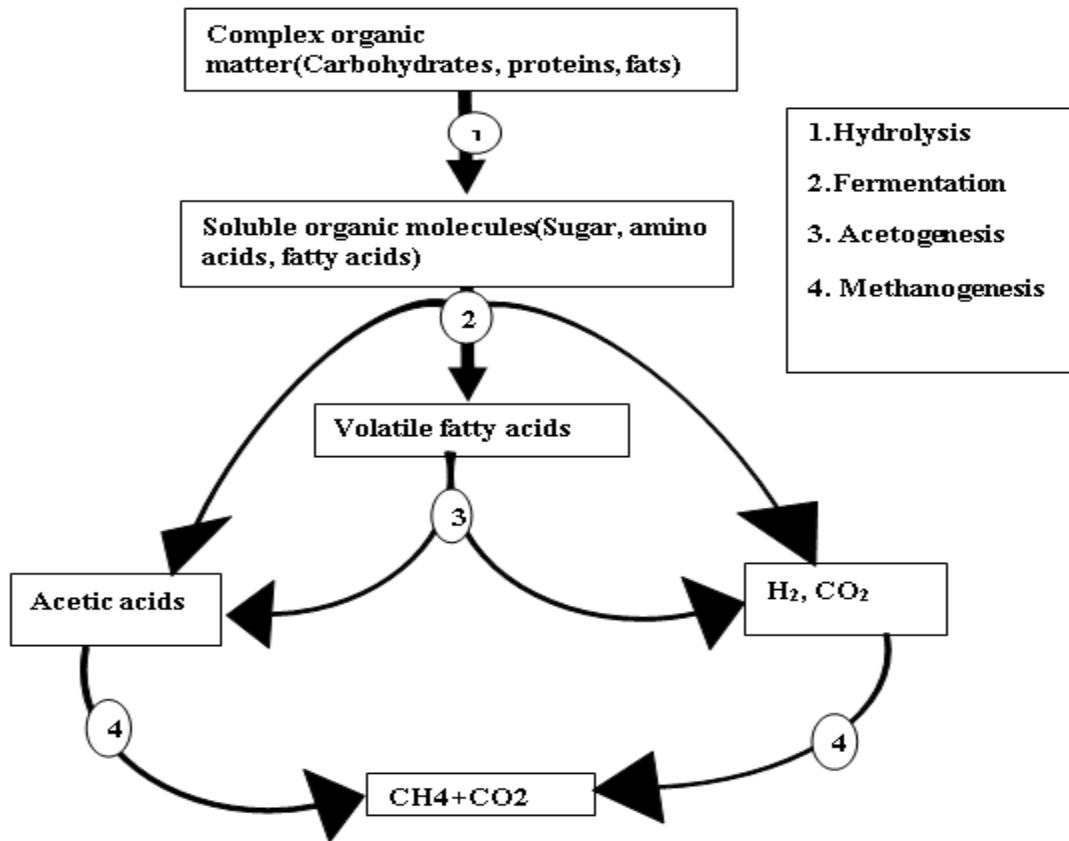
Figure 1. The phases of Biogas production through anaerobic digestion
(Source: Etuwe, C.N., Momoh, Y.O.L. & Iyagba, E.T. (2016); Sinervo, R., (2017) ; Matheri, A.N., et al. (2016))

2.3   Factors affecting production of Biogas

Anaerobic digestion requires appropriate conditions for microorganisms to maintain the process working properly. Hence, it is necessary to consider and care about each of those anaerobic condition parameters in order to prevent or minimize inhibition within digester (Ippolito, J.A., et al. (2012); Etuwe, C.N., Momoh, Y.O.L. & Iyagba, E.T. (2016); Sinervo, R. (2017)). A high attention must be taken for methanogenic bacteria, since they are very sensitive to the conditionals of environment and have a low growth rate (Dobre, P., Matei, F. & Nicolae, F. (2014)). Anaerobic digestion can be affected by different factors which are; temperature, substrate solid content, loading rate and mixing, retention time, pH-value, nutrients

concentration, and inhibitory factors (Etuwe, C.N., Momoh, Y.O.L. & Iyagba, E.T. (2016); Ippolito, J.A., et al. (2012); Dobre, P., Matei, F. & Nicolae, F. (2014) ; Sinervo, R. (2017)).

2.3.1   Temperature

In anaerobic digestion process, there are three ranges of temperature in which microorganisms operate differently in degradation of organic solids; 12-20°C as psychrophilic condition, 20-45°C as mesophilic condition and 45-60°C as thermophilic condition (Gómez, E., Martin, J. & Michel, F.C. (2011); Matheri, A.N., et al. (2016)). However, anaerobic digestion process mainly considers only two ranges of temperature (mesophilic and thermophilic condition) on which the process of anaerobic fermentation and methane forming bacteria perform well.

Anaerobic bacteria grow well in mesophilic and thermophilic condition, where, methanogenic bacteria are very sensitive to ambient condition (temperature) and their growth rate is higher in thermophilic condition (Sorathia, H.S., et al. (2012); Gómez, E., Martin, J. & Michel, F.C. (2011); Matheri, A.N., et al. (2016)). Thermophilic condition has a higher degradation rate of organic solids, better microbial activity which results in higher Biogas yields and limits the activation of pathogens, but it is not stable therefore, it can provoke inhibition in anaerobic digestion by increasing the fraction rate of free ammonia(NH_3) (Ippolito, J.A., et al. (2011)).

The rate of gas production increases with the increase in temperature but the percentage of methane reduces (Sorathia, H.S., et al. (2012)). Mesophilic conditions are most efficiency for stable and continuous methane production with minimum impurities(CO_2, N_2, H_2S and NH_3) (Dobre, P., Matei, F. & Nicolae, F. (2014)) and reduce inhibition of ammonia due to the lower production of free ammonia (Sinervo, R. (2017)). The production of Biogas is faster during summer and slow during winter means at low temperature (Sorathia, H.S., et al. (2012)).

2.3.2   Retention time

Retention time is also known as hydraulic retention time (HRT) or solid retention time (SRT) however, they are a bit different from each other. The hydraulic retention time represents how long substrate stays inside of the digester before being taken out as digestate (Ippolito, J.A., et al. (2012); Sorathia, H.S., et al. (2012)). While, solid retention time is the average time the activated organic solid spend in the digester and it depends on the rate of microorganism growth and substrate concentration (Gashaw, A. (2016)). Retention time depends on operating temperature, volume of digester and degradability of the used substrates in anaerobic digestion process.

Retention time should be long enough to prevent Biogas losses and it depend on degradation rate of substrate and volume of digester as it has been found that, within 0.66-1 range of diameter to depth ratio, Biogas production per unit volume of digester is high (Sorathia, H.S., et al. (2012)). Normally, under optimum condition 80-90% of the total Biogas production is produced within a period of 3 to 4 weeks. For longer retention time it is better to use a larger size digester for better performance in Biogas production (Sorathia, H.S., et al. (2012)).

2.3.3 Substrate solid content, loading rate and mixing

Organic materials must constitute of carbohydrates, proteins, fats, cellulose or hemicellulose as the main components to be used in anaerobic digestion (Sinervo, R. (2017)). Sometimes, substrates required pretreatment to enhance production of anaerobic digestion. Pretreatment breaks down the complex organic structure into simpler molecules which are more susceptible to bacteria degradation. Besides, pretreatment facilitated the heterogeneity of substrates which is in turn affected positively the final production of anaerobic digestion (Gashaw, A. (2016)). Degradation rate depends on substrate contents and type of substrate. Besides, high biodegradability of food wastes lead to the fast accumulation of organic acids, which inhibits methanogenesis phase. Based on total solid content within digester, digestion can be classify into two groups dry digestion with 25-45% and wet digestion with 2-15% of total solid content. For that, the wet digestion is used for substrates with high moisture content and is easy to manage compare to dry digestion which is used for substrates with high solid matter content in terms of process parameters (such as pH, temperature and TS). (Cai, J., et al. (2016); Dobre, P., Matei, F. & Nicolae, F. (2014); Sinervo, R., (2017) ; Owamah, H.I. & Izinyon, O.C. (2015)). The total solid content within feedstock is the major parameter for Biogas and methane production yield from anaerobic digestion process (Yi, J., et al. (2014)).

Loading rate is the amount of feedstock supply to the digester per day in continuous digester and once during the hydraulic retention time in batch digester. Therefore, it must be carried out at the same time to keep the total solid concentration ratio and rate of nutrients constant in the digester and avoid underloading and or overloading which can reduce Biogas production mainly for continuous digester (Sorathia, H.S., et al. (2012)). Substrate should not exceed the standards concentration for detergents, antibiotics, and antiseptics substances which are inhibitory substances for micro-organisms (Dobre, P., Matei, F. & Nicolae, F. (2014)). In a digester, water content depends on the organic materials used. Organic materials rich in cellulose and

hemicellulose with sufficient proteinaceous materials generate more gas, but complex polysaccharides are more favorable for methane production while only proteinaceous materials generate a little quantity of gas (Sorathia, H.S., et al. (2012)). Besides, high lignin content of substrate inhibits the initial phase of AD, which is hydrolysis (Owamah, H.I. & Izinyon, O.C. (2015)). Different substrates produce different amounts of Biogas and methane in the same conditions (more details are shown in **Appendix 1**.). Mixing is required to prevent sedimentation of dense matter, to release gas bubbles and to ensure the efficiency transfer of substrate for micro-organisms activity (Sinervo, R. (2017)).

2.3.4 Nutrients concentration

In anaerobic digestion process of organic material, there are some nutrients like nitrogen(N_2), carbon(C), phosphorous(P), sulfide(S), hydrogen(H), oxygen(O_2), calcium and magnesium etc required by microorganisms in order to grow and accelerate the process (Etuwe, C.N., Momoh, Y.O.L. & Iyagba, E.T. (2016); Sorathia, H.S., et al. (2012)). Carbon from carbohydrates produce energy and nitrogen from proteins contribute to the growth of microorganisms, which are responsible for anaerobic digestion process. Microorganisms consume approximately 30 of carbon times faster than nitrogen, therefore the optimum ratio of C:N for anaerobic digestion must vary from 15 to 30 (Matheri, A.N., et al. (2016); Mojapelo, N., et al. (2014)) with phosphorous 2% of feedstock ideally for maximum biological activity (Sorathia, H.S., et al. (2012)). Besides, Dioha, I. J., et al. (2013) has reported that the optimum C:N ratio for Biogas production to be between 25-30:1 for cow dung. While, Sinervo, R. (2017) reported that the C:N ratio to be range between 15 and 25 as recommended interval. However, all researchers did not report the same range but it seems like 15-30:1 can be the appropriate range for Biogas production. A higher or lower ratio will negatively affect the process and the quality of Biogas plant productions (methane and fertilizer) (Sorathia, H.S., et al. (2012); Matheri, A.N., et al. (2016)).

The increase of carbon leads to the formation of high CO2 content and low the pH while, the high nitrogen content increase the rate of ammonia and rises pH within digester (Gashaw, A. (2016)). Some organic materials contain all nutrients required by microorganisms while others do not, therefore, they may require some additional of nutrients or the use of co-digestion to fulfill the requirements (Sorathia, H.S., et al. (2012)). Co-digestion is the use of two or more different substrates in order to improve nutrients content required for anaerobic digestion and

enhance the production (Matheri, A.N., et al. (2016); Gashaw, A. (13 January, 2016)). Apart from the one needed for microorganisms growth, retaining nutrients in produced digestate, it has been a big issue for its applications such as agricultural because of the loss of nutrients during the AD process. Therefore, the use of some additional materials has been applied in order to reduce the losses however, some of those additives have presented the environmental problems and increased the operational cost of Biogas plant. Currently, Biochar has been approved as one of the cheapest and environmental friendly additive which can minimize these losses and retain nutrients during AD process and after the use of digestate (Fagbohungbe, M.O., et al. (2016)).

2.3.5 The pH value

The pH value shows the degree of acidity or alkalinity of a solution, where, pH value of 0 to 7 indicates acidic solution while the one of 7 to 14 indicates the alkaline solution. The pH value depends on the ratio of acidity and alkalinity and carbon dioxide in the digester (Sorathia, H.S., Rathod, P.P. & Sorathiya, A.S. (2012)). Anaerobic digestion process mostly for methanogenesis phase perform well for pH value range from 6.5 to 7.8 which is a neutral or mildly alkaline environment (Sorathia, H.S., Rathod, P.P. & Sorathiya, A.S. (2012); Gómez, E., Martin, J. & Michel, F.C. (2011); Matheri, A.N., et al. (2016); Budiyono, B. & Sumardiono, S. (2014); Manonmani, P., et al. (2017)) while for fermentation process is not sensitive to pH and works in wide range from 4 to 8 (Gómez, E., Martin, J. & Michel, F.C. (2011); Matheri, A.N., et al. (2016)).

The rate of methanogenesis reduces for too acidic or too alkaline environment (Sorathia, H.S., Rathod, P.P. & Sorathiya, A.S. (2012); Gómez, E., Martin, J. & Michel, F.C. (2011)). Mechanism of fermentation can affect the pH value by producing free hydrogen ions into the solution. The accumulation of ammonia lead to the increase in pH value while the accumulation of volatile fatty acid leads to the decrease in pH value (Sinervo, R. (2017)) and cause possible failure of anaerobic digestion process. To maintain the stability of pH in digester, buffers solutions such as; bicarbonate and ammonium bicarbonate in liquid phase and carbon dioxide in gas phase can be added (Sorathia, H.S., Rathod, P.P. & Sorathiya, A.S. (2012)).

2.3.6 Inhibitory factors

In the digester, there may be found some inhibitory substances such as ammonia, light metal ions, sulfide, heavy metals and organics which come from wastes as feedstocks and or formed during degradation processes (Gómez, E., Martin, J. & Michel, F.C. (2011)). The inhibition

depend on adaption of microorganisms, composition of substrates and concentration of inhibitors. Low concentration of inhibitors are required for microorganisms growth in anaerobic digestion process but at high concentration, they inhibit the process (Sinervo, R. (2017)).

Ammonia as the most inhibitor for methanogenic microorganisms, it comes from bacterial activity for degradation of nitrogenous materials and it is responsible for stability of a reactor. Free ammonia (NH_3) is the most toxic and it can causes proton imbalance and potassium deficiency, but it has been found that the concentration of about 200mg/L is helpful for microbial activity in anaerobic digester (Gómez, E., Martin, J. & Michel, F.C. (2011)). In a higher pH environment, free ammonia is higher than ammonium ion (NH_4^+) while in a lower pH environment, ammonium ion is higher than free ammonia and also their equilibrium depends on temperature where free ammonia is high at a high temperature. The inhibition leads to instability within a reactor, decrease of Biogas yield and a complete failure in anaerobic digestion process (Sinervo, R. (2017)).

Inhibition of volatile fatty acids (VFAs) and organic acid can occur when pH value decrease within a reactor and they come from the too intensive feeding of bioreactor, which leads to the depletion in the buffering capacity. Accumulation of VFAs contributes to the hydrolysis and can inhibit the process at a very high level. In additional, Sulphur compounds also can inhibit the anaerobic digestion process as a high amount of sulfides are toxic to many groups of bacteria. The same for some light and heavy metal ions at a higher concentration can become toxic to microorganisms within a digester (Sinervo, R. (2017)). Concentration of volatile acid measured by acetic acid in fermentation process greater than 2000 parts per million will inhibit the action of the methanogenic microorganisms (Sorathia, H.S., Rathod, P.P. & Sorathiya, A.S. (2012)).

In additional, it has been reported that the optimization of anaerobic digestion is important and required sometime depends on the type of substrate and its nutrients for example food waste which may not meet the requirements nutrients for Biogas production (Owamah, H.I. & Izinyon, O.C. (2015)). Therefore, some authors have proposed the use of co-digestion of two or more substrates in order to improve anaerobic production means Biogas or methane yield (Holm-Nielsen, J. B., et al. (2009); Owamah, H.I. & Izinyon, O.C. (2015)). In general, food waste contains a larger amount of easy degradable organic material and indigenous bacterial. However, due to its low C:N ratio it usually delays the AD process because of the excessive accumulation of intermediate products like volatile fatty acid (Owamah, H.I. & Izinyon, O.C. (2015)).

2.4 Preparation and properties of Biochar

Biochar is carbonaceous, porous, carbon stable and solid material generated from a thermochemical conversion of biomass in the absence or limited oxygen environment within a limited range of temperature 350ºC to 1000ºC (Sinervo, R. (2017); Yao, H., et al. (2013)). The term Biochar seems to be new but the same material had been used in the ancient human populations of Amazon to create dark soil call Terra Preta (Sinervo, R. (2017)). Biochar is a carbon material somehow similar to activated carbon (Sethupathi, S., et al. (2017); Yao, H., et al. (2013) . Biochar have chemical and physical properties, which depend on temperature, retention time, production techniques, heat transfer rate and type of feedstocks (Sinervo, R. (2017); Bogale, W. (2017) ; Sethupathi, S., et al. (2017); Yao, H., et al. (2013)). Biochar can be produced through pyrolysis, gasification (Bogale, W., 2017; Shen, Y., et al. (2015)), torrificaction, flash carbonization and hydrothermal carbonization processes even if pyrolysis is the most useful (Bogale, W. (2017)). Through pyrolysis, gasification and hydrothermal carbonization processes, Biochar, bio-oil and syngas are produced at once in those processes (Sinervo, R. (2017)).

Biochar has physical and chemical properties suitable for the safe and long- term storage of carbon in the environment and soil improvement. Properties of Biochar mainly depend on feedstocks, with chemical properties (such as porosity, concentrations of elemental constituents, pH and stability, and so on) having higher dependency than physical ones (such as density, and hardness) (Bogale, W. (2017); Shen, Y., et al. (2015)). Biochar can be produced from woody feedstocks rich in lignin have a high carbon and a low ash content compare to switchgrass and corn stove Biochar. Structure of carbon within feedstocks determine the final aromatic carbon groups in Biochar depending on operation temperature.

Biochar is constituted with carbon as main components, hydrogen, oxygen, nitrogen and Sulphur with small concentrations compare to the one of carbon (Bogale, W. (2017)). Stability of Biochar decrease with the increase in O:C ratio, this means that Biochar with the lowest ratio has the highest stability which is graphite, while Biochar with the highest ratio has the lowest stability which is biomass (Hewage, S. & Priyadarshani, R. (2016); Ippolito, J.A., et al. (2012)). Therefore, Biochar with O:C or H:C ratios less than 0.2 consists of graphene layers and is chemically stable. In general, H:C and O:C of Biochar decrease with increase of temperature. The extremely low ratio within Biochar implies its minimum polarity and maximum hydrophobicity, which lead to the capturing CO_2 in presence of water (Shen, Y., et al. (2016)).

Yield of pyrolysis products vary depend on; characteristics of feedstocks, pyrolysis processes adopted, temperature, retention time, and heating rate (Bogale, W. (2017)). Based on temperature and residence time, pyrolysis is divided into three methods; fast pyrolysis where residence time is in only seconds, slow pyrolysis and intermediate pyrolysis where residence time is from few minutes to several hours or even days. Concentration of productions (Biochar, bio-oil and syngas) differ from one method to another one as it is shown in **Table1**, and it has been concluded that the fast pyrolysis is appropriate for bio-oil production while slow pyrolysis is preferable for Biochar production (Sinervo, R. (2017); Bogale, W. (2017)).

By increasing pyrolysis temperature, Biochar yield decrease while bio-oil yield and syngas yield increase (Bogale, W. (2017)). Biochar is useful because of its surface area, pore size distribution and ion exchange capacity, which are the main properties of it. Pyrolysis at high temperature produces Biochars with high adsorption of organic contaminants by increasing surface area, micro porosity and hydrophobicity. While pyrolysis at low temperature produces Biochars with high ability to remove inorganic and polar compounds by increasing ion exchange capacity, electrostatic attraction and precipitation (Sinervo, R. (2017)).

Table 1. Products of pyrolysis and gasification processes

Process	Temperature(^{o}C)	Residence time	Products		
			Liquid(bio-oil)%	Solid(bio-char)%	Gas(syngas)%
Fast	300-1000	Short(<2 S)	75	12	13
Intermedia te	≈500	Moderate(10-20 S)	50	25	25
Slow	100-1000	Long(5-30 min)	30	35	35
Gasificatio n	>800	Moderate(10-20 S)	5	10	85

(*Sources: Sinervo, R. (2017); Bogale, W. (2017)*)

Hydrothermal carbonization known as liquid pyrolysis is a thermochemical conversional of biomass in the zero oxygen environment but performs under pressure around 20bar and in the presence of subcritical liquid phases and a temperature varies in 180-250°C. Most hydrothermal

carbonization processes use wet substrates as feedstocks and produce solids called hydrochar which have different chemical and physical properties with Biochar (Sinervo, R. (2017)). The use of hydrochar releases a larger amount of CO_2, N_2O and CH4 compare to Biochar therefore , hydrochar are not suitable materials in carbon sequestration process (Hewage, S. & Priyadarshani, R. (2016)).

2.5   Addition of Biochar in Anaerobic digestion

Recently, researches on the use of Biochar in anaerobic digester have been done although they are not many as in soil improvement application. Biochar is used in AD as an additive material not as feedstock. Additives are material that are fed at a low amount in AD to improve the process and increase production (such as CH4 yield, Biogas yield and quality of digestates). Additives can be trace minerals, micro- and macro-nutrients, buffering agents, compounds able to mitigate ammonia inhibition, and substances with high biomass immobilization capacity. From what has been done, the use of additives could increase Biogas yield by 20-30% compared to the production of control reactor (Sinervo, R. (2017)). It has been found that, the use of Biochar which is among of carbon-rich materials as an additive material in anaerobic digester increased the adsorption of inhibitors compounds (Sinervo, R. (2017); Cuetos, M.J., et al. (2017); Yao, H., et al. (2013)), the direct interspecies electron transfer(DIET), improved mobilization and promoted formation of biofilm, improved biogas production (Sinervo, R. (2017); Sunyoto, N.M., et al. (2016)), accelerated the syntrophic metabolism of ethanol (Sinervo, R. (2017)), enhanced faster decomposition of organic matter, temperature increased in the first days and carbon dioxide respiration rates increased (Janczak, D., et al. (2017)).

Adsorbents are chemically inert materials with adhesive properties which cause the accumulation of atoms, ions or molecules on their surface. With feedstocks containing high amounts of nitrogen, Biochar can be used to remove inhibitive ammonia and ammonium ions through adsorption and ion exchange on their reactive surfaces (Sinervo, R. (2017); Janczak, D., et al. (2017)). Cai, J., et al. (2016) used several Biochar concentrations in the range of 0.25–2.5 g/g TS waste and concluded that the amount of Biochar to be added depend on the amount of inoculum used. The use of pyrolytic Biochar enhanced the microbial activity, production and degradation of intermediate and volatile fatty acids but did not affect much methane production (Sinervo, R. (2017)). According to what has been done, the use of Biochar in AD has mitigated NH_4^+

inhibition of 6g/l of glucose solution at an NH_4^+ concentration of 7g/l during AD process (Lü, F., et al. (2016)).

Ability of Biochar to adsorb ammonium ions depends on surface of Biochar particles, contact time, increase of initial ammonium concentration, temperature and pH value (Sinervo, R. (2017); Cuetos, M.J., et al. (2017)) and it has been found that as the added Biochar rate increased also the emission of ammonia reduced by 30% and 44% for poultry and wheat straw with 5% and 10% of Biochar respectively and 10% for controlled digester means without Biochar (Janczak, D., et al. (2017)). Biochar produced through HTC released more nutrients in terms of DOC and DTN compare to pyrolytic Biochar at a higher difference. Therefore, nutrients released by Biochar can differ depending on type of feedstocks used, temperature and manufacturing techniques (Sinervo, R. (2017)). Besides, addition of Biochar as an adsorbent to anaerobic digestion reduce the lag-phase (Cuetos, M.J., et al. (2017)), organic matter increased as the added Biochar increased and lower organic matter loss was presented in a mixture with higher Biochar concentration (about 29% and 24% for poultry manure and wheat straw with addition of 5% and 10% of Biochar respectively) while, the higher organic matter loss was presented in a controlled digester at 50% without Biochar (Janczak, D., et al. (2017)).

According to what had been done by researchers on the effect of Biochar added in anaerobic digestion they has found that; by adding pyrolytic fruitwoods Biochar of 10g/l, methanogenic lag phase shortened by 30.3% and maximum methane production rate increased by 86.6% than for the controlled one (Luo, C., et al. (2015)), by adding pyrolytic rice husk Biochar of 1% (of dry matter), gas production increased by 31% and adding Biochar at a high concentration did not lead to a better Biogas production (Inthapanya, S., Preston, T.R. & Leng, R.A. (2012)). And also, addition of 8.3g/l, 16.6g/l, 25.1g/l and 33.3g/l of pyrolytic pine sawdust in two-phase anaerobic digestion of simulated carbohydrate food waste shortened lag phase by 21.4-35.7% for H2 and 41-45% for CH4 production, accelerated formation and degradation of VFA, buffered pH in hydrogen production, increased the maximum production rate by 32.4% for H_2 and 23-41.6% for CH_4 and increased production potential by 14.2-31% for H_2 and 1.9-9.6% for CH_4 production rate compared to the control one generally. However, maximum production of H_2 and CH_4 was presented for 8.3g/l added Biochar and minimum production was presented for 33.3g/l (Sunyoto, N.M., et al. (2016)) .

Additional of white oak Biochar (2.20 (named asWO250) and 4.40g/g (named as WO500) dry matter of sludge) and pinewoods Biochar (2.49 (as P250)and 4.97g/g (as P500) dry matter of sludge) separately in anaerobic digestion of substrate sludge(2.35g dry matter) with inoculum of 4.70g dry matter at mesophilic and thermophilic temperature produced cumulative Biogas volume varied in 465-537ml and 825-909ml for mesophilic and thermophilic condition respectively but they were slightly lower to the control (Shen, Y., et al. (2016)). However, CH_4 content in Biogas from digester with Biochar for both conditions was much more than from the control where, CH_4 content varied in 89.7-96.7% and 75.3-84.3% for mesophilic and thermophilic condition respectively while, for the control digester, the maximum values were 80% and 73% for mesophilic and thermophilic condition respectively (Shen, Y., et al. (2016)). According to Luo, C., et al. (2015), Biochar increased the methane yield at 86.6% and reduce acidification in AD.

 In additional, the increase of CH_4 yield compared to the controlled digester was 9.6%, 7%, 4.7%,and 3.9% for WO250, WO500, P250 and P500 respectively for mesophilic condition. While for thermophilic condition, CH_4 yield raised by 7.15, 5.7%, 9.5% and 6.8% for WO250, WO500, P250 and P500 respectively which show the higher increase for small amount of added Biochar (Shen, Y., et al. (2016)). The addition of Biochar in digester did not increase the total organic carbon instead, it enhanced the removal of total organic carbon up to 66.2% (pine Biochar) and 56.6%(white oak Biochar) for mesophilic and 32.4%(pine Biochar) and 31.6% (white oak Biochar) for thermophilic condition (Shen, Y., et al. (2016)). Besides, the concentration of NH_3-N increased in digester with Biochar at high concentration but the formation of free ammonia was reduced compared to the control digester (Shen, Y., et al. (2016)). Also by adding Biochar on anaerobic digestion of citrus peel at 1:3, 1:2, 1:1 and 2:1 citrus peel to Biochar ratios at 35^OC, the results showed the highest CH_4 yield (ml/g VS) for 1:3 which was followed by 1:1 while the lowest value was shown for 2:1 ratio. The same thing happened for CH_4 conversion efficiency (Fagbohungbe, M.O., et al. (2016)).

According to Y. Shen et al.(2015) with Biochar added for AD of WWTP at different concentration as follow 1.82, 2.55, 3.06 and 3.64g/g of TS of sludge, Biogas production was lower from digester with Biochar added and methane content within the produced Biogas was high (about 95% and above) compared to the control digester with no Biochar added. However, the increase of Biochar added reduced the maximum potential CH_4 production rate and reaction

rate constant but, additional of Biochar in AD increase the alkalinity means stability within the digester (Shen, Y., et al. (2015)). Besides, Biochar removed about 54.9% to 86.3% of CO_2 and concentration of H2S was <5ppm from digester with Biochar added while from the control digester, it was <99ppm in produced Biogas (Shen, Y., et al. (2015)). Meyer-Kohlstock, D., et al. (2016) have reported that by adding Biochar of 5% and 10% of total solid in bio-waste, Biogas and methane increased by 5% and 3% respectively compared to the control reactor.

According to Mumme, J., et al. (2014), pyrolytic Biochar had the ability to increase the bacterial and archaeal gene copy numbers and mitigate mild ammonia inhibition, but overall effects on the gas production were negligible with 0.4% of increment. However, they had found that the effect is not clear enough to make a conclusion after comparing what has been done in previous researches in this area. As conclusion for what has been done, addition of Biochar in anaerobic digestion has good impacts. However, there are still some confusion on the appropriate ratio to be added in AD and the type of effect in terms of AD production therefore, many researches must be done for more clarification.

2.6   Upgrading of Biogas to Biomethane

2.6.1   Impacts of presented impurities in raw Biogas

Impurities of raw Biogas are carbon dioxide (CO_2) which is the second main component of Biogas, H_2S, O_2, water, hydrocarbons, dust, siloxanes, Cl^-, F^-, and NH_3 however they may vary depends on the used feedstocks during anaerobic digestion (Ryckebosch, et al. (2011)). Presence of CO_2 in raw Biogas reduces its calorific value and increases its density. The presence of H_2S in raw Biogas leads to the formation of corrosion in compressors, gas storage tanks and engines and due to the combustion of raw Biogas SO_2 and SO_3 are formed. Besides, SO_2 and SO_3 are very toxic than H_2S and corrosive when they are reacted with water. Dust clogs compressors and gas storage tanks. High concentration of O_2 in Biogas causes an explosion. Hydrocarbons corrode engines due to the combustion of Biogas. Reaction of water with H_2S, NH_3, and CO_2 leads to the formation of acid and corrodes compressors, gas storage tanks and engines. Due to combustion of Biogas, siloxanes form SO_2 and monocrystalline quartz. Also, siloxanes abrade the surface of spark plugs, valves and cylinder heads. While, Cl^- and F^- corrode the combustion engine (Ryckebosch, et al. (2011)). Therefore, raw Biogas which has most of those impurities must be upgraded in order to prevent above issues.

2.6.2   Technologies for carbon dioxide removal

As it is known, calorific value of Biogas depends on methane content, there has been several techniques used for removing carbon dioxide from Biogas, some of them are; cryogenic separation, chemical scrubbing, pressure swing adsorption, membrane separation, high pressure water scrubbing, and organic physical scrubbing. Which are based on adsorption, absorption, cryogenic and membrane technologies in terms of their working principles (Yousef, A. M., et al. (2016); Holm-Nielsen, J.B., et al. (2009); Hoyer, K., et al. (2016); Barzagli, F., et al. (2014)). Methane loss from those technologies is low for chemical scrubbing with a value of 0.1% followed by cryogenic separation, then membrane separation while, the highest loss has been shown for pressure swing adsorption with an average value of 1.8% by comparing current used technologies (Yousef, A. M., et al. (2016)).

In addition, those technologies require additional energy to fulfil their tasks where the required energy differ from one technology to another one. Due to the additional of energy, it is necessary to calculate the energy efficiency for all technologies. In recent research, it has shown that cryogenic separation has a highest energy efficiency while pressure swing adsorption has the lowest as it is shown in **Appendix 2** (Yousef, A. M., et al. (2016)). Cryogenic separation seem to be the appropriate technology of enriching CH_4 as produced Biogas has a higher pressure compare to other technologies. However, high attention is required on the range of operating pressure in order to prevent CO_2 freeze-out in distillation column during the upgrading process (Yousef, A. M., et al. (2016)).

Among Biogas upgrading techniques, there are three technologies based on absorption; water scrubbing, organic physical scrubbing and chemical scrubbing. In water scrubbing, the absorbent is water. In organic physical scrubbing, the absorbent is organic solvents such as polyethylene glycol which has higher solubility with carbon dioxide than water. While in chemical scrubbing, the absorbent is amine solutions and it had shown that the methane loss is less than 0.1% by using chemical scrubbing (Petersson, A. & WeLLInGer, A. (2009)). **Table 2** compares some of the above technologies in terms of different parameters. Drying Biomethane can be done by using glycol scrubbing, silica gel activated charcoal or molecular sieves (Niesner, J., Jecha, D. & Stehlík, P. (2013)). The used steam must be treated after being used in order to protect the environment, this has to be done for all techniques of Biogas upgrading.

2.6.2.1   Water Scrubbing

Water scrubbing has been used for longtime in small and larger scale Biogas upgrading plants as CO_2 and H_2S removal. CO_2 and H_2S have a higher solubility in water than CH_4 and the absorption is a pure physical this means that there is no chemical reaction between water and CO_2 or H_2S, therefore regeneration is possible. Biogas is pressurized and fed to the bottom while water is fed on the top of the column, for that the absorption process is done in counter-currently (Yousef, A. M., et al. (2016); Zhao, Q., et al. (2010); Niesner, J., Jecha, D. & Stehlík, P. (2013)). At the end of water scrubbing, H_2S with less than $15cm^3/m^3$ goes with upgraded Biogas. Water scrubbing techniques is cheap when water is available or closer to the operation place. Water scrubbing can produce Biogas with greater than 97% of CH_4 while less than 2% of CH_4 is lost, and regeneration is possible (Ryckebosch, et al. (2011)). Disadvantage of water scrubbing is the big volume of water required for absorption process in order to avoid corrosion within the column (Yousef, A. M., et al. (2016); Zhao, Q., et al. (2010); Niesner, J., Jecha, D. & Stehlík, P. (2013)), operates at a high pressure with low temperature, and difficulty to maintain (Ryckebosch, et al. (2011)). Processes of water scrubbing technology are shown in **Figure 2**.
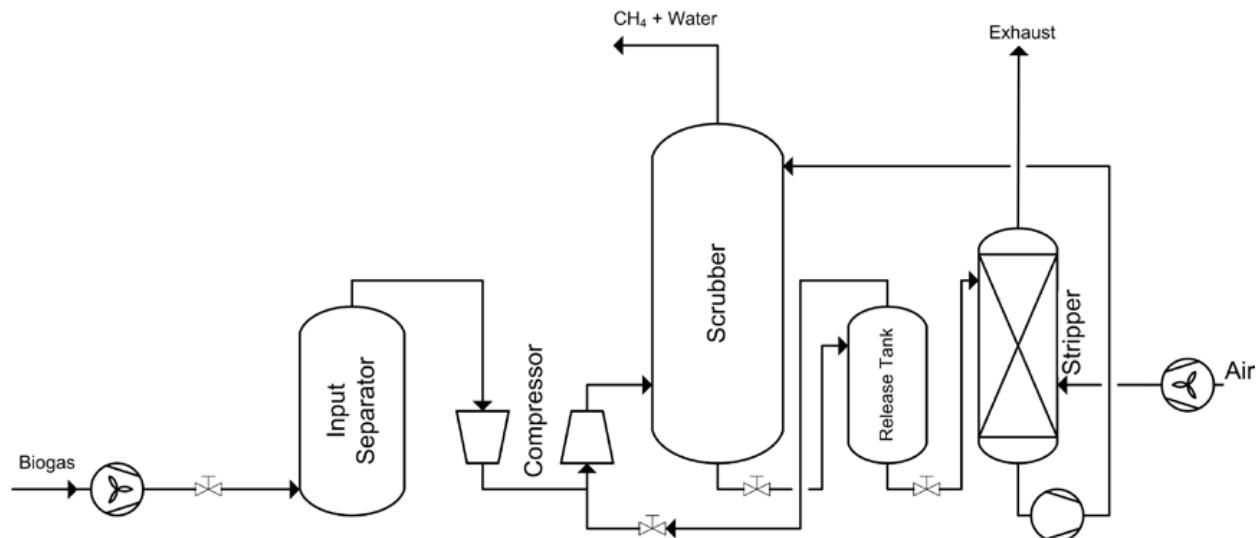
Figure 2. Schematic diagram of water scrubbing technology
Source: Zhao, Q., et al. (2010)

2.6.2.2   Organic physical scrubbing

Organic physical scrubbing known as physical absorption operate in similar way as water scrubbing but it use an organic solvent instead of water (Niesner, J., Jecha, D. & Stehlík, P. (2013)). Used solvents in physical scrubbing are amines with methanol, poly (ethylene glycol), or dimethyl ether and so on (Yeh, James T., Henry W. Pennline, and Kevin P. Resnik. (2001)). Carbon dioxide is absorbed by the solvent under pressure and CO_2 has shown a high solubility in the organic solvent compared to water (Niesner, J., Jecha, D. & Stehlík, P. (2013)). Methane loss during organic physical scrubbing has been found to be 1.5% which is high compared to other upgrading technologies excluding pressure swing adsorption (Yousef, A. M., et al. (2016)) while, the upgraded Biogas contents greater than 97% of CH_4, and regeneration is possible. However, organic physical scrubbing is expensive, operation is difficulty and reduced when glycol is diluted with water (Ryckebosch, et al. (2011)). Processes of organic physical scrubbing technology are shown in **Figure 3**.
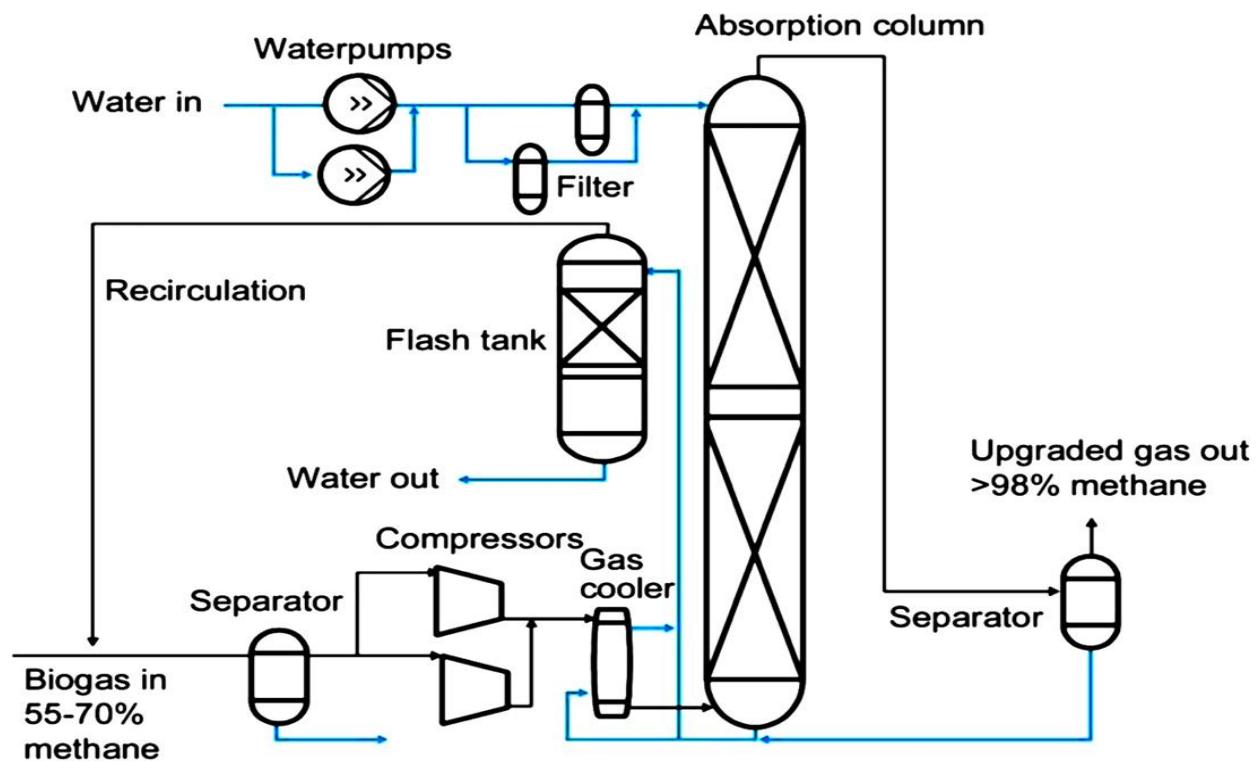
Figure 3. Schematic diagram of Physical Absorption process of CO2 without regeneration
Source: (Ryckebosch, et al., 2011)

2.6.2.3   Chemical Absorption

Chemical absorption use the solute and solvent reacted by reversible bond to form the absorbent solution. Where, chemical solvents can be aqueous solutions of amine (such as mono-, di-, or tri-ethanolamine) or aqueous solutions of alkaline salts (such as Sodium, Potassium, and calcium hydroxide) (Niesner, J., Jecha, D. & Stehlík, P. (2013); Zhao, Q., et al. (2010)). While solute is the carbon dioxide which must be removed from raw Biogas in order to form Biomethane (Yeh, J. T., Henry, W. P., & Kevin P. R. (2001)). Chemical scrubbing has higher absorption efficiency, reaction rate, remove H_2S completely with 95-100% efficiency, generate Biogas with 99% of CH_4 and is able to operate at low pressure compare to water scrubbing and physical absorption. Regeneration of carbon dioxide is possible in chemical absorption by sending carbon dioxide-rich absorbent to the stripper and raise the temperature. However, high energy is required for treatment of waste chemicals after Biogas upgrading process which may affect the final cost of produced Biomethane, formation of foaming and poisoning can occur, and has high investment cost (Barzagli, F., et al. (2014); Niesner, J., Jecha, D. & Stehlík, P. (2013); Zhao, Q., et al. (2010); Ryckebosch, et al. (2011); Yeh, J. T., Pennline, H. W., & Resnik, K. P. (2001)). By comparing current upgrading techniques in terms of CH_4 losses, chemical scrubbing has the lowest value of 0.1% (Yousef, A. M., et al. (2016); Ryckebosch, et al. (2011)). Processes of chemical absorption technology are shown in **Figure 4**.
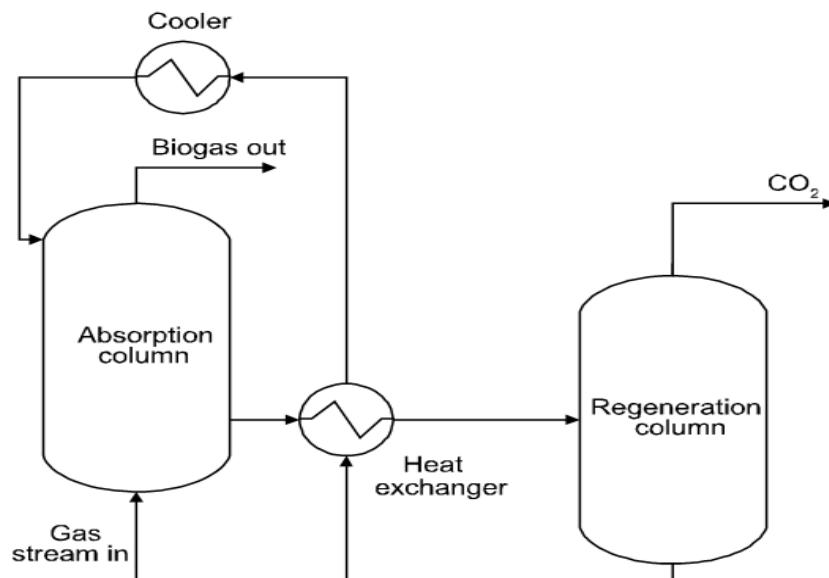
Figure 4. Schematic diagram of chemical absorption technology process
Source: (Zhao, Q., et al. (2010))

2.6.2.4   **Pressure Swing Adsorption**

Pressure swing adsorption is used to separate gases from a mixture of gases under high pressure and ambient temperature. Adsorbents can be activated carbon or zeolites, which used as molecular sieve. Working principle of pressure swing adsorption is based on the fact that under pressure, gases are attracted to the solid surface of adsorbent which means adsorbed (Zhao, Q., et al. (2010)). Therefore, the higher pressure implies that the adsorption is higher and the adsorption efficiency increased besides, as pressure is reduced regeneration will take place. However, level of increasing pressure depends on the type of adsorbent used in the process. The adsorption is based on the fact that, different gases are attracted at different level (less or more strongly) on solid surface of different adsorbents (Barzagli, F., et al. (2014); Niesner, J., Jecha, D. & Stehlík, P. (2013)).

It has been found that, the activated carbon impregnated by potassium iodide can catalytically reacts with O_2 and H_2S to form water and sulfur at 7 to 8bar and 50 to 70°C. Profits of using pressure swing adsorption are low power demand, low emission, and can remove O_2 and N_2 but not at a hundred percent. However, H_2S removal is required as additional step before or after starting PSA process (Zhao, Q., et al. (2010)), is expensive with high cost for both investment and operation (Ryckebosch, et al. (2011)). The losses of Methane during pressure swing adsorption has been found to be 1.8% and it has been reported as the highest loss compared to other upgrading technologies (Yousef, A. M., et al. (2016)) while, the upgraded Biogas contents 95-98% of CH_4 (Ryckebosch, et al. (2011)). In industries or Biogas plants, the use of more than two adsorber columns in parallel is advised in order to achieve a high purity of Biomethane (Niesner, J., Jecha, D. & Stehlík, P. (2013)). Processes of pressure swing adsorption technology are shown in **Figure 5**.
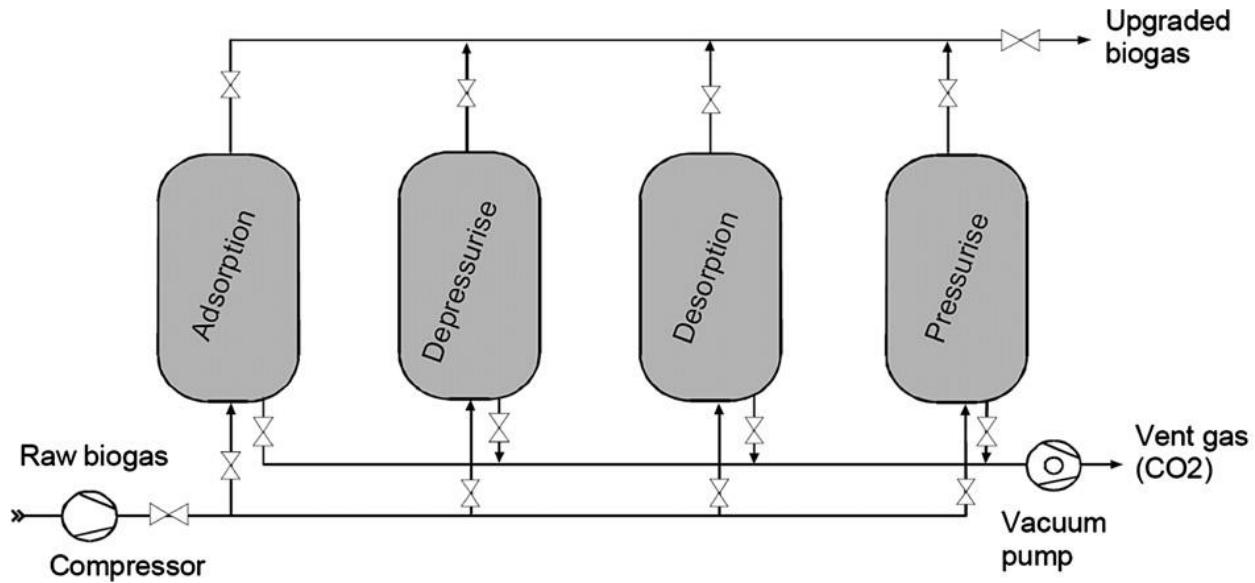
Figure 5. Schematic diagram of Pressure Swing Adsorption processes
Source: (Ryckebosch, et al. (2011)).

2.6.2.5   Membrane Separation

The working principle of membrane separation for gas is based on that, some gas components are passed through a thin membrane while, others are retained depending on their solubility within the membrane. The process occurs under high pressure in the range of 25 to 40bars (Zhao, Q., et al. (2010)). There are two types of membrane separation techniques; high pressure gas separation which separate CO_2 and H_2S from CH_4 and gas-liquid adsorption which uses a micro porous-hydrophobic membranes as an interface between gas and liquid of which CO_2 and H_2S are dissolved into the liquid while CH_4 is released (Zhao, Q., et al. (2010); Niesner, J., Jecha, D. & Stehlík, P. (2013)). The CO_2 removal efficiency of membrane is greater than 97% while, the H_2S removal efficiency is greater than 98%, H_2O is also removed and upgraded Biogas has greater than 96% of CH_4 (Ryckebosch, et al. (2011)).

By increasing the number or size of membrane module, the purity of upgraded Biogas is achieved however, losses of CH_4 may increase (Niesner, J., Jecha, D. & Stehlík, P. (2013)). In general, the CH_4 loss during membrane separation is slightly low with an average value of 0.5% (Yousef, A. M., et al. (2016)). Profits of using membrane separation techniques are that, the process is easy and compact, light in weight, low energy, maintenance requirements (Zhao, Q., et al. (2010); Niesner, J., Jecha, D. & Stehlík, P. (2013)), pure CO2 can be reached, technology is reliable and has low investment and operation cost (Ryckebosch, et al. (2011)). However,

maintenance is complex, and the cost of membrane is relatively high (Zhao, Q., et al. (2010); Niesner, J., Jecha, D. & Stehlík, P. (2013)). Processes of membrane separation technology are shown in **Figure 6**.
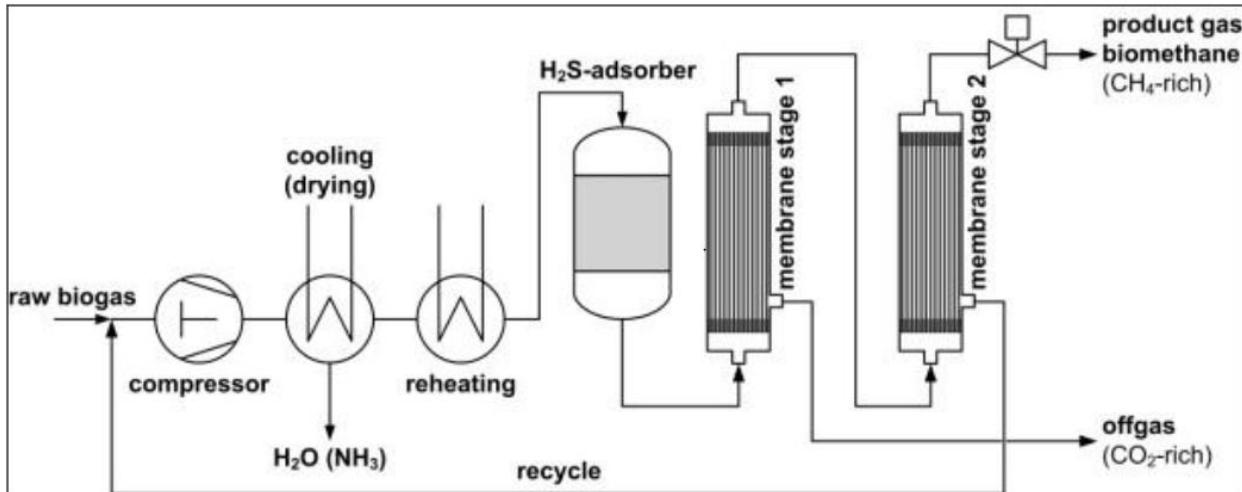
Figure 6. Schematic diagram of membrane separation technology
Source: (Ryckebosch, et al. (2011))

2.6.2.6   Cryogenic separation

Working principle of cryogenic separation is based on the fact that different impurities within Biogas are liquified at different temperature and pressure condition. This process operates at low temperature around $-100^{o}C$ and high pressure almost about 40bars. Profits of using cryogenic separation technique are the high purity of CH_4 is achieved with around 99%, and can be used for larger scale of farm however, it require many additional equipment (such as compressors, heat exchanger, and turbine) which increase the cost for implementation and operation (Zhao, Q., et al. 2010). Upgraded Biogas contains 90-98% of CH_4 and some amount of CO_2 is still presented (Ryckebosch, et al. (2011)). Processes of cryogenic separation technology are shown in **Figure 7**.
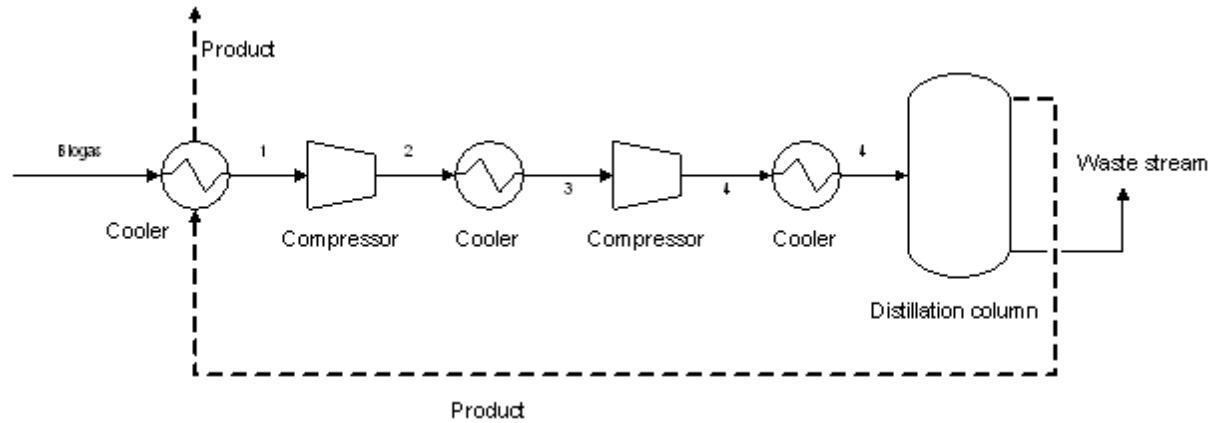
Figure 7. Schematic diagram of cryogenic separation technology

Source: (Zhao, Q., et al. (2010))

Table 2. Comparison between different parameters for some Biogas upgrading techniques

Parameter	Pressure swing adsorption	Water scrubbing	Organic physical scrubbing	Chemical scrubbing
Pre-cleaning needed[a]	Yes	No	No	Yes
Working pressure(bar)	4-7	4-7	4-7	No
Methane loss[b]	<3%/6-10%[f]	<1%/<2%[g]	2-4%	<0.1%
Methane content in upgraded gas[c]	>96%	>97%	>96%	99%
Electricity consumption[d](kWh/Nm^3)	0.25	<0.25	0.24-0.33	<0.15
Hat requirement(°C)	No	No	55-80	160
Controllability compered to nominal load	+/-10-15%	50-100%	10-100%	50-100%
Refences[e]	>20	>20	2	3

Note that; [a] Refers to raw Biogas with less than 500 mg/m^3 of H2S. For higher concentrations, pre-cleaning is recommended also for the other techniques. [b] The methane loss is dependent on operating conditions. [c] The quality of Biomethane is a function of operational parameters. [d] Given in kWh/Nm^3 of raw Biogas, compressed to 7 bar(g). [e] Number of references reviewed.

Some are pilot plants. [f] <3 % CarboTech, / 6–10 % QuestAir. [g] < 1 % Malmberg / <2 % Flotech (Petersson, A. & WeLLInGer, A. (2009))

According to Barzagli, F., et al. (2014), the use of single or blended amines as absorbents of CO_2 and H_2S for upgrading air by selecting amines as 2-amino-2- methyl-1-propanol (AMP), 2-(tert-butylamino) ethanol (TBMEA), 2-(isopropylamino) ethanol (IPMEA), and Nmethyl-2,2'iminodiethanol (MDEA), the absorption efficiency or CO_2 capturing depended on the CO_2 content presented in the air or Biogas (as they had considered air as Biogas based on their compositions) and were ranged from 13% to 100% for CO_2. The mixture of EG/PrOH (as a solvent) had shown a higher absorption efficiency than BEGMME solution, this depends on the high reactivity of EG/PrOH towards CO_2 compared to BEGMME solution. MDEA was unable to react with CO_2 in the absence of water as a solvent while AMP reacted well in both solvents, as it is shown in **Appendix 3** (Barzagli, F., et al. (2014)). Besides, it had been reported that by using 10% of aqueous solution of mono-ethanolamine for CO_2 removal in Biogas with 40% of CO_2 reduced up to 0.5-1% of volume at low pressure (Zhao, Q., et al. (2010)).

In additional to the known upgrading technologies, Yousef, A. M., et al. (2016) has reported that, by using a low-temperature CO_2 removal technique under high pressure they achieved 99.7% removed CO_2 with 0.19% CH_4 loss. Besides energy efficiency was 95.5% which was higher compared to the known techniques where the highest is 94.4% and 90.2% as the lowest (**Appendix 2**).

2.6.3 Biogas cleaning

The main importance of cleaning is to prevent corrosion and mechanical wear of the upgrading equipment by removing or minimizing the content of all impurities from raw Biogas produced through anaerobic digestion. Therefore it must be done before the starting or at the earlier part of upgrading process.

2.6.3.1   Removal of water

Biogas comes from digester contain water vapor which can lead to corrosion of gas pipelines. Water vapor can be removed by increasing pressure or decreasing temperature, absorption in glycol solutions or hygroscopic salts, adsorption by using SiO_2, activated carbon or molecular sieves, and silica gel, cooling by burying gas pipeline in the soil, and compression (Petersson, A. & WeLLInGer, A. (2009)). Absorption technique for removal of water has a high efficiency at

dew point of -5till and -15^0C. During absorption of water, dust is also removed and technique does not have toxics. However, it is expensive and operate at a high pressure and temperature of 200^0C for regeneration. Adsorption technique has a high water removal efficiency at dew point of -10till and -20^0C, low operation cost and regeneration is possible. However, Adsorption technique is expensive, operation pressure ranges in 6-10bars, and dust and oil must be removed before. While cooling techniques which is also considered as pretreatment technique removes water, dust and oil, and it is a simple techniques. Although, freezing can occur at -18^0C (Ryckebosch, et al. (2011)).

2.6.3.2   Removal of Hydrogen Sulphide (H_2S)

H_2S can be removed by precipitation of Iron Chloride ($FeCl_2$, $FeCl_3$) or Iron (II) Sulfate ($FeSO_4$) in digester as absorbents for chemical absorption, adsorption on activated carbon, water scrubbing, Sodium Hydroxide scrubbing, (chemical absorption for a very larger gas volume or a higher concentration of H_2S), and biological treatment (Petersson, A. & WeLLInGer, A. (2009); Hoyer, K., et al. (2016)). The adsorption of H_2S on activated carbon is performed by adding small dose of oxygen or impregnated activated carbon in order to oxidized the adsorbed gas to Sulphur or to bind it strongly to the surface of activated carbon. Adsorption on activated carbon (impregnated with KI 1-5%) can produce Biogas with H_2S content of less than $3cm^3/m^3$ (Ryckebosch, et al. (2011)).

Adsorption on activated carbon has high purification rate, high loading capacity, operates at a low temperature, and is a compact technique. However, CH_4 is lost during the removal of H_2S, H_2O and O_2 are needed to remove H_2S, regeneration is possible at temperature of 450^oC, and the technique is expensive (Niesner, J., Jecha, D. & Stehlík, P. (2013); Ryckebosch, et al. (2011)). However, this technique is applied when H_2S is low within the raw Biogas or applied at the end of Biogas upgrading process (Niesner, J., Jecha, D. & Stehlík, P. (2013)). Besides, the use of some of those adsorbents and absorbents have been proven expensive because of the raw materials used in their preparation, this affected the feasibility of plant in terms of economy (Sun, L., Wan, S. & Luo, W. (2013)).

Chemical absorption has a high removal efficiency of 95-100%, for some of chemical absorbents regeneration is possible while for the other it is impossible and requires a small volume of operation with low CH_4 losses. However, chemical absorption technique is expensive and more difficult. The use of sodium hydroxide scrubbing for H_2S removal requires low electricity, small

volume and pumping compared to absorption in water with low CH_4 losses (Ryckebosch, et al. (2011)). H_2S removal efficiency of sodium hydroxide scrubbing is high with greater than 95% can be achieved. However, NaOH solution is more difficulty and expensive technique, and regeneration is impossible. Sodium hydroxide solution can also be used for CO2 removal (Zhao, Q., et al.(2010)).

2.6.3.3   Removal of other impurities

Oxygen and Nitrogen can be removed by adsorption with activated carbon or PSA, molecule sieves or membrane but, they are expensive and need high attention to prevent explosion. While ammonia is removed when the gas is dried or upgraded, by activated carbon, and some upgrading techniques can also remove NH_3 (Petersson, A. & WeLLInGer, A. (2009); Hoyer, K., et al. (2016); Ryckebosch, et al. (2011)). The Oxygen content of 0-4% is harmless while 6-12% cause the explosion when it is reacted with Biogas with 60% of CH_4 depending on the temperature. Siloxanes can be removed by; absorption in strong acid, absorption with organic solvents, adsorption on activated carbon, adsorption on silica gel and cryogenic separation technologies. Hydrocarbons, which results from landfill Biogas is removed by activated carbon and regeneration is possible at 200^0C (Ryckebosch, et al. (2011)).

According to the previous researches on the use of Biochar in Biogas upgrading as an adsorbent of CO_2, H_2S and CH_4, it has been found that by using different types of Biochar, CO_2 and H_2S were adsorbed where, adsorption capacity was higher for H_2S than for CO_2. While CH4 was not adsorbed by Biochar depending on their porous 'size, which were big than the required size for adsorb CH_4. Besides, the presence of CO_2 inhibited H_2S adsorption because of the competitive adsorption and reaction between CO_2 and H_2S on the surface of activated carbon on which Biochar is considered as one of them (Sethupathi, S., et al. (2017)). From what had been done by Zhao, Q., et al. (2010) on CO_2 removal using amines solution with different concentrations, they had achieved 100% CO_2 removal in 1minute with 10% or 20% of MEA however, after 7 or 13mins concentration of CO_2 rose again which means that, the saturation point amine solution with CO_2 was achieved. They also used MDEA and found that the high CO_2 removal efficiency were shown for MEA solution (Zhao, Q., et al. (2010)). By using NaOH solution for CO_2 and H_2S removal, and 94% of CH_4 was achieved from 60% in raw gas but CO_2 and H_2S were also presented therefore, they concluded that NaOH system is not appropriately for Biogas upgrading depending on the final use (Zhao, Q., et al.(2010)).

2.6.4 Standards for chemical composition of Biomethane

Generally, the quality of Biogas varies depend on energy demand of end uses. Quality standards of pipeline requires 100mg/m^3 for water content. The water content in raw Biogas depends on the temperature of Biogas where, the lower temperature leads to the lower water content with raw Biogas (Ryckebosch, et al. (2011)). There is no international technical standards for Biogas injection therefore, some countries has developed theirs national technical standards and procedures for injection of Biogas to the natural gas grid. **Table 3** listed the main requirements standards for Biogas injection for four European countries which are Germany, Sweden, France and Switzerland. Germany has two types of gas standards; limited injection and unlimited injection (when the concentration of cited H-gas is maintained). Switzerland also has two standards of gas injection (Persson, M., Jönsson, O. & Wellinger, A. (2006)).

Table 3. National standards for gas injection of different countries

Country	Parameter	Unit	Demand in standard	Type of gas
Sweden	Lower Wobbe index	MJ/nm^3	43.9-47.3[1]	
	MON(motor octane number)		>130 (calculated according to ISO 15403)	
	Water dew point	^{0}C	<t[2]-5	
	$CO_2+O_2+N_2$	vol-%	<5	
	O_2	vol-%	<1	
	Total sulpur	mg/nm^3	<23	
	NH_3	mg/nm^3	20	
Switzerland	Methane content	vol-%	>96	Unlimited gas injection
	Gas relative humidity	phi	<60%	
	Dust		Technically free	
	CO_2	vol-%	<6	
	O_2	vol-%	<0.5	
	H_2	vol-%	<5	

	H$_2$S	mg/nm^3	<5	
	S	mg/nm^3	<30	
	Methane content	vol-%	>50	**Limited gas injection**
	Gas relative humidity	phi	<60%	
	Dust		Technically free	
	CO2	vol-%	<6	
	O2	vol-%	<0.5	
	H2	vol-%	<5	
	H2S	mg/nm^3	<5	
	S	mg/nm^3	<30	
Germany	Higher Wobbe index	MJ/nm^3	43.1-56.5[3] in H gas[4] grids	**Gas injection according to G260/262**
			37.8-46.8[5] in L gas[6] grids	
	Relative density		0.55-0.75	
	Dust		Technically free	
	Water dew point	^{0}C	<t[7]	
	CO$_2$	vol-%	<6	
	O$_2$	vol-%	<3 (in dry distribution grids)	
	S	mg/nm^3	<30	
France	Higher heating value	MJ/nm^3	H gas: 38.52 to 46.08	**Gas injection**
			L gas: 34.2 to 37.8	
	Higher Wobbe index	MJ/nm^3	H gas: 48.24 to 56.52	
			L gas: 42.48 to 46.8	
	Hydrocarbon dew point	^{0}C	<-5 from1 to 80 bar	
	Water dew point	^{0}C	<-5 at MOP downstream from	

		injection point (Gergwater correlation)
CO_2	vol-%	<2
Dust	mg/nm^3	<5
Total sulphur	mg/nm^3	<100 instant content
		<75 annual average
O_2	ppmv	<100
Hg	mg/nm^3	<10 (Natural gas)
		<50 (Liquefied Natural gas)
Cl	mg/nm^3	<1
F	mg/nm^3	<10
H_2	%	<6
CO	%	<2

Note that from the **Table 3**, [1]corresponds to 95-99% methane content, t^2 and t^7 equal to the ambient temperature, [3]corresponds to >97.5% methane content, [4]is the high heat value gas, [5]corresponds to 87-97.5% methane content and [6]is the low heating value gas (Persson, M., Jönsson, O. & Wellinger, A. (2006)).

CHAPTER THREE

3.0.   MATERIALS AND METHODOLOGY

3.1   Preparation of Biochar and Elemental Analysis

Preparation of Biochar from sawdust and wood chips of eucalyptus tree has been done by using pyrolysis process at 650°C and was held for 35 minutes by using a furnace in chemical engineering laboratory of Addis Ababa Institute of Technology. Produced Biochar were cooled at room temperature and crashed into very small size parties in order to facilitate degradation of substrate easily. Determination of elemental analysis (such as C, H, N, O, and S) of Biochar was conducted using EA 1112 Flash CHNS/O- analyzer in a duplicate way then the average was calculated, with carrier gas flow rate of 120 ml/min, reference flow rate 100 ml/min, oxygen flow rate 250 ml/min; furnace temperature of 900°C and oven temperature of 75°C. The pH of Biochar was measured using a digital pH meter after mixing 100ml of distilled water with 10g of Biochar, and then the mixture was shaken with speed of 150rpm for 1hour at room temperature by using Shaking machine of SHKA4450-1CE model. The moisture content was calculated by the weight loss after heating the Biochar at 105°C for 24 hours in an Oven given by equation (**1**)**.** The volatile solid matter was determined as the weight loss after heating in a covered crucible at 950°C for 6 min using the furnace (LTH 407GN, LHT 04/17 SN262014), given by equation (**2**)**.** The total organic carbon was determined as the residue remained after heating Biochar at 950°C in an closed crucible given by equation (**4**). All measurements were done in duplicate manner from that average value were calculated.

3.2   Collection of Substrate, Inoculum and Preparation

Substrates which is the mixture of food wastes (breads, Injera, vegetables, meat, pasta and Irish potatoes) were collected from dormitory' restaurant of Addis Ababa institute of technology. Injera is made of teff, contains 15% of proteins, 3% of and 82% of carbohydrates and high calorific material (Gashaw, A., Teshita, A. & Ethiopia, B.H. (2014)). Substrate was prepared before being used by removing inorganic materials such as bones, metals and other indigestible materials. After that, the food waste was prepared in order to form an homogeneous subatrates. The homogeneity process was divided into two stages; the first one was chopping using the electronic food processor and the second one was blending using a food liquidizer.

The inoculum was collected from the outlet of digester of a café husk Biogas pilot plant which is an experiment of a Phd. student and is located in Addis Ababa University Institute of Science (Arat Kilo). The inoculum was mainly liquid with total solid matter less than 6%. Therefore, it can be called wet sludge (with <15% of dry matter) or taken as water with the pH of 7.6. The food waste was preserved in fridge and inoculum was preserved at room temperature until to the day of feeding. Cow dung were collected from Biofarm and Bio-economy Africa (known as Bio-economy Africa) located in Addis Ababa, Ethiopia. Collected cow dung was fresh and was preserved in fridge up to the feeding day and used as it was without additional preparation.

Figure 8. a) was the crushed Biochar while, b) was crushed food waste before being liquidized

3.3   Elemental and proximate Analysis and Calculations for substrate

Determination of moisture content of food waste, which was the weight loss after heating sample of food waste at 105°C for 24hours as it is given by equation (1) by using an 202-0A Electric Thermostatic Heated Dry. Total solid was determined as the remaining quantity after the removal of moisture content and is given by equation (3). Volatile solid matter was determined as the weight loss after heating the remaining quantity (from the determination of moisture content) known as dried matter at 950°C for 6minuntes in a closed crucible and is given by equation (2) by using a furnace (LTH 407GN, LHT 04/17 SN262014). And then, the total organic carbon was determined as the remaining quantity from determination of volatile solid matter and is given by equation (4).

The same furnace was used for determination of ash content by heating the dried matter at 600ºC for 2hours in an open crucible and the output or the remaining mass was considered as ash content. The same procedures were followed for determination of proximate analysis of cow dung and some of them also has been done for inoculum. All of those measurements were done in a duplicate manner and the average was taken in chemical laboratories of Addis Ababa University Institute of Technology. Determination of elemental compositions (C, O H, N, and S) of substrate based on dried matter was conducted using EA1112 Flash CHNS/O-Analyzer, with carrier gas flow rate of 120 ml/min, reference flow rate 100 ml/min, oxygen flow rate 250 ml/min; furnace temperature of 900ºC and oven temperature of 75 °C in chemistry laboratory of Addis Ababa Institute of Science (Arat Kilo). All measurements were conducted in duplicate manner and average values were taken.

$$MC(\%) = \frac{M_T - M_d}{M_T} \times 100 \tag{1}$$

$$VS(\%) = \frac{M_d - M_b}{M_T} \times 100 \tag{2}$$

$$TS(\%) = \frac{M_d}{M_d} \times 100 \tag{3}$$

$$TOC(\%) = \frac{M_b}{M_d} \times 100 \tag{4}$$

$$AC(\%) = \frac{M_{b.opened}}{M_d} \times 100 \tag{5}$$

Where, MC was the moisture content(%), VS was the volatile solid matter(%), TS was the total solid matter(%), TOC was the total organic carbon(%), M_T was the total mass of substrate(g), M_d was the dried matter of substrate(g), M_b was the mass of burned substrate after evaporation of volatile solid matter(g) in a closed crucible, and $M_{b.opened}$ was the remaining mass after burning the dried matter at 600ºC in an open crucible. Above equations for VS, TOC and AC are in terms of total mass but they can also be calculated in terms of dry matter or total solid by dividing with mass of dried matter instead of total solid. Results are shown in **Table 8**.

3.4   Anaerobic digestion process

3.4.1   First lab experiment setup of AD of food waste

During the first experiment which was a batch digestion of food waste as substrate; measurements and calculations of the amount for substrate, inoculum and Biochar to be mixed as the feedstocks were done and then mixed all in the same flask until it became an homogeneous mixture. Feedstocks were mixed in flasks of 500ml by adding 100g or ml of substrate(food waste), 200ml of inoculum, 30ml of tap water and different amount of Biochar 15%, 25%, 50% and 85% based on dry matter were added to different flasks as reactors in duplicate way. Therefore, the total number of reactors were 12; 8 reactors in which Biochar were added, 2 reactors for control and 2 reactors for inoculum. For which the total solid in 10 reactors (the one for inoculum were excluded) was 11.7% calculated from substrate only (food waste, and inoculum). However, only 8.5% (calculated from food waste) was considered for Biogas production and calculation of theoretical methane yield. Samples were measured by using a digital balance and a graduated beaker. In the first digester, there was no Biochar added, which means that, only substrate and inoculum were mixed with water. On the other side, Biochar was added with different percentage in reactors and pH of the mixture was measured using the digital pH-meter. The pH (the acidity and alkalinity) within reactors was adjusted to 7 by adding the appropriate amount of hydrochloric acid (HCl) and or sodium hydroxide (NaOH) (Matheri, A.N., et al. (2016); Owamah, H.I. & Izinyon, O.C. (2015)). **Table 4** show the characteristics of feeding substrate.

Flasks were incubated in a water bath at $38 \pm 1℃$. The inoculum to substrate ratio was constant in all flasks with a ratio of 2:1 based on the total mass of substrate used. For each reactor was attached a gas collecting bag for gas collection at ambient temperature and pressure (**Figure 9**). The volume of Biogas produced was measured using a 50ml high performance gastight syringe manually as it has been done previously (Kwak, D.H., et al. (2013); Shen, Y., et al. (2015)) once in two or three days. Constituents of generated Biogas from each digester were analyzed before and after cleaning (removal of H_2S) and Biogas upgrading (removal of CO_2) using a Chromatography instrument called BIOGAS 5000 (G500729) which is a portable Biogas analyzer equipped with infrared and electrochemical detector. **Figure 10** is representing the whole process form production of Biogas up to the upgrading process.

Table 4.Feeding substrate characteristic for the batch digestion in the first experiment

Reactor	Inoculum		Food Waste		Biochar added		Added Water (ml)	Total volume Occupied (ml)	Total solid in reactor(g)
	Volume (ml)	TS(g)	Total mass(g)	TS(g)	% of TS for FW	Mass (g)			
R.Inoc	200	10.58	0	0	0	0	0	200	10.58
R.Control	200	10.58	100	28.17	0	0	30	330	38.75
R015	200	10.58	100	28.17	15	4	30	334	42.75
R025	200	10.58	100	28.17	25	7	30	337	45.75
R050	200	10.58	100	28.17	50	14	30	344	52.65
R085	200	10.58	100	28.17	85	23	30	353	61.58

Note that, R.Inoc was a reactor for inoculum; R.Control was a reactor for food waste no Biochar added; R015 was a reactor with 15% added Biochar; R025 was a reactor with 25% of Biochar added; R050 was a reactor with 50% of Biochar added; R085 was a reactor with 85% of Biochar added.

3.4.2 Second lab experiment setup of AD of food waste

In this experiment, the same procedures were applied. Inoculum to substrate ratio was 2:1 by adding 100g of food waste and 200ml of inoculum, the same amount of Biochar (15%, 25%, 50% and 85%) were also added as in the first round but no additional water was added. The pH was adjusted at 7 within all reactors. There was 11reactors of which 1 for inoculum, 2 for control (means no Biochar added), and 8 of which different amount of Biochar were added. Therefore, the minimum total solid in 10 reactors (the one for inoculum was excluded) was 12.9% calculated from substrate only (food waste, and inoculum). However, only 9.3% (calculated from food waste) was considered for Biogas production.   **Table 5** show the characteristics of feeding substrate. Reactors were incubated in a water bath at $38 \pm 1°C$. Production were measured in the same way as in the first experiment.

Table 5. Feeding substrate characteristic for the batch digestion in the second experiment

Reactor	Inoculum		Food Waste		Biochar added		Total volume (ml)	Total solid in reactor(g)
	Volume (ml)	TS(g)	Total mass(g)	TS(g)	% of TS for FW	Mass (g)		
R.Inoc	200	10.58	0	0	0	0	200	10.58
R.Control	200	10.58	100	28.17	0	0	300	38.75
R015	200	10.58	100	28.17	15	4	304	42.75
R025	200	10.58	100	28.17	25	7	307	45.75
R050	200	10.58	100	28.17	50	14	314	52.65
R085	200	10.58	100	28.17	85	23	323	61.58

Note that, R.Inoc was a reactor for inoculum; R.Control was a reactor for food waste no Biochar added; R015 was a reactor with 15% added Biochar; R025 was a reactor with 25% of Biochar added; R050 was a reactor with 50% of Biochar added; R085 was a reactor with 85% of Biochar added.

3.4.3   Third lab experiment setup Co-digestion

In this experiment, co-digestion of food waste and cow dung was used as substrates. Where, the amount of food waste was 100g mixed with 50g of cow dung and 200ml of inoculum was added. Therefore, the inoculum to substrate ratio was 4:3 in terms of volume or total mass and cow dung to food waste ratio was 1:2. From that, the percentage of the total solid within reactors (except the one for inoculum) was 13.11% and calculated from only substrate(food waste, cow dung and inoculum). Biochar were added at different rate (15, 25,50 and 85%). However, only 10.0% (calculated from food waste and cow dung) was considered for Biogas production. The total number of reactors was 12; 2 reactors for inoculum alone (200ml), 2 for a mixture of food waste and cow dung with no Biochar added (R.FW&CD), and 8 reactors on which Biochar were added at different rate. **Table 6** show the characteristics of feeding substrate. The pH was adjusted between 7 and 7.2 within all reactors. Reactors were incubated in a water bath at 37 ± 1℃. The measurement of productions was done in the same way as it is in previous rounds.

Table 6. Feeding substrate characteristic for the batch digestion in the third experiment

Reactor	Inoculum		Food Waste		Cow Dung		Biochar added		Total volume (ml or g)	TS in reactor(g)
	Volume (ml)	TS(g)	MT (g)	TS(g)	MT (g)	TS (g)	% of TS	Mass (g)		
R.Inoc	200	10.58	0	0	0	0	0	0	200	10.58
R.FW &CD	200	10.58	100	28.17	50	7.14	0	0	350	45.89
R015	200	10.58	100	28.17	50	7.14	15	6.9	356.9	52.73
R025	200	10.58	100	28.17	50	7.14	25	11.5	361.5	57.30
R050	200	10.58	100	28.17	50	7.14	50	22.9	372.9	68.62
R085	200	10.58	100	28.17	50	7.14	85	39.0	389.0	84.60

Note that, R.Inoc was a reactor for inoculum; R.FW&CD was a reactor for sole substrates (food waste with cow dung); R015 was a reactor with 15% added Biochar; R025 was a reactor with 25% of Biochar added; R050 was a reactor with 50% of Biochar added; R085 was a reactor with 85% of Biochar added.

3.4.4 Fourth lab experiment setup Co-digestion

In the fourth experiment, it was a co-digestion of food waste and cow dung, which were used as substrates. By mixing 50g of food waste with 50g of cow dung, 150ml of inoculum was added in all reactors with the inoculum to substrate ratio of 3:2 in terms of volume or total mass and 50ml of water was added. Cow dung to food waste ratio was 1:1.Therefore, minimum value of the total solid within all 8reactors was 9.66%, and 7.3 to 7.14% in the control which was calculated from food waste, cow dung, inoculum and added water. However, only 7.0% (calculated from food waste and cow dung in 8reactors) and 4.7% (in the R.CD) was considered for Biogas production. The same amount of Biochar (15, 25, 50 and 85%) were added in the same way as in previous experiments. The total number of reactor was 10; 2 for cow dung (100g) alone (in one of them, water was added instead of inoculum), and 8 reactors on which Biochar was added. **Table 7** show the characteristics of feeding substrate. The pH was adjusted between

7 and 7.2 in all reactors. Reactors were incubated in water bath at $37 \pm 1℃$. Production were measured in the same way as in the first experiment.

Table 7. Feeding substrate characteristic for the batch digestion in the fourth experiment

Reactor	Inoculum		Food Waste		Cow Dung		Biochar added		Added Water (ml)	Total volume (ml or g)	TS in reactor (g)
	Volume (ml)	TS(g)	MT(g)	TS(g)	MT (g)	TS (g)	% of TS	Mass (g)			
R.CD	150	7.93	0	0	100	14.28	0	0	50	300	22.0
R015	150	7.93	50	14.0	50	7.14	15	4.3	50	304.3	33.2
R025	150	7.93	50	14.0	50	7.14	25	7.2	50	307.2	36.1
R050	150	7.93	50	14.0	50	7.14	50	14.5	50	314.5	43.3
R085	150	7.93	50	14.0	50	7.14	85	24.6	50	324.6	53.4

Note that, R.CD was a reactor for cow dung no Biochar added; R015was a reactor with 15% added Biochar; R025 was a reactor with 25% of Biochar added; R050 was a reactor with 50% of Biochar added; R085 was a reactor with 85% of Biochar added.

Figure 9. Set-up of lab experiment for biogas production through Anaerobic digestion

3.5   Upgrading of Biogas

During upgrading of raw Biogas, unwanted gases such as carbon dioxide and hydrogen sulphide were removed using Biochar adsorption as adsorbent, NaOH absorption also called Sodium scrubbing. Sodium scrubbing was prepared by mixing 2 moles of NaOH with 1L of distilled water in order to form the concentrated solution, solution was put in bottle, from which the raw Biogas was passed through for removing of CO_2 and H_2S. The solution of Biochar with distilled

water has also applied as absorbent solution during the experiment, by mixing 30g of crushed Biochar with 500ml of distilled water and the form solution was put in a bottle. In Biochar adsorption, pieces of Biochar were put in a bottle from which raw Biogas was passed in order to remove CO_2 and H_2S. Upgraded Biogas was collected in bag (urine bag used at the hospital) to be analyzed. Constituents of final product were analyzed after cleaning (removal of H_2S) and Biogas upgrading (removal of CO_2) using a Chromatography instrument called BIOGAS 5000 (G500729) which is a portable Biogas analyzer equipped with infrared and electrochemical detector.
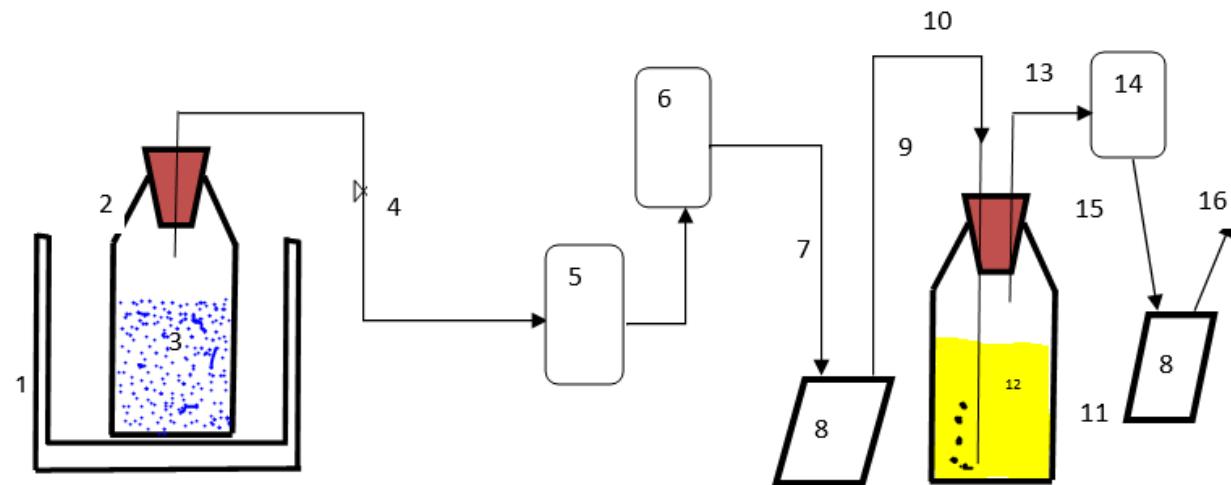
Figure 10. Schematic diagram of experimental processes (AD process and Analysis and Upgrading of Biogas)

Where, [1] was the water bath, [2] was a reactor or digester, [3] was the feedstock, [4] was a valve, [5] was a biogas collecting bag, [6] was bag collecting measured biogas, [7] was the inlet pipe for raw biogas, [8] was the Chromatograph instrument (gas analyzer), [9] was the outlet of analyzed raw biogas, [10] was the inlet of raw biogas, [11] was flask, [12] was a mixture of adsorbent with distilled water and dots were bubbles of biogas , [13] was the upgraded biogas pipe, [14] was the upgraded biogas collecting bag, [15] was the inlet of upgraded biogas to the Biogas analyzer and [16] was the outlet of analyzed upgraded biogas.

3.6   Theoretical cumulative methane production

Theoretical cumulative methane production was calculated using the elemental composition of feedstock. From which those elements C, H, O, N and S based on total solid were considered to create the stoichiometric equation of feedstock, which is given by equation (6) for single substrate, and this equation is known as the Buswell equation. Then from the stoichiometric

equation (Eq. 6), the equation for theoretical methane was derived equation (7). However this equation did not considered non-biodegradable materials and biodegradable came from the addition material in order to improve the process within digesters (Fagbohungbe, M.O., et al. (2016); Nielfa, A., Cano, R. & Fdz-Polanco, M. (2015)). The theoretical methane was calculated in ml/g VS added.

$$C_aH_bO_cN_dS_e + fH_2O \rightarrow jCH_4 + kCO_2 + nNH_3 + iH_2S \quad (6)$$
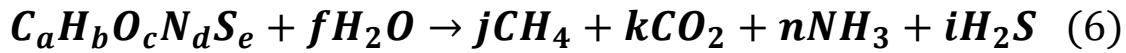
Where, a is the number of atoms of carbon, b is the number of atoms of hydrogen, c is the number of atoms of oxygen, d is the number of atoms of nitrogen, and e is the number of atoms of Sulphur.

$$f = a - \frac{c}{2} + \frac{3d}{4} + \frac{e}{2} - \frac{b}{4} \quad , \qquad\qquad j = \frac{a}{2} - \frac{c}{4} - \frac{3d}{8} - \frac{e}{4} + \frac{b}{8} \quad ,$$

$$k = \frac{a}{2} + \frac{c}{4} + \frac{3d}{8} + \frac{e}{4} - \frac{b}{8} \quad , \qquad\qquad n = d \, , \qquad\qquad i = e$$

Then after, by replacing f, k, j, n and i with their equivalences in equation (6), the theoretical cumulative methane production (T_{CH_4}) was calculated as it is shown by equation (7) for simple substrate.

$$T_{CH_4} = \frac{22400 \left(\frac{a}{2} - \frac{c}{4} - \frac{3d}{8} - \frac{e}{4} + \frac{b}{8} \right)}{12a + b + 16c + 14d + 32e} \qquad (7)$$

Theoretical methane for co-digestion of food waste and cow dung (when elemental analysis was done separately) was calculated by equation 9 which was derived from equation 8.

$$C_aH_bO_cN_dS_e + C_gH_lO_hN_mS_p + f_2H_2O \rightarrow j_2CH_4 + k_2CO_2 + n_2NH_3 + i_2H_2S \quad (8)$$
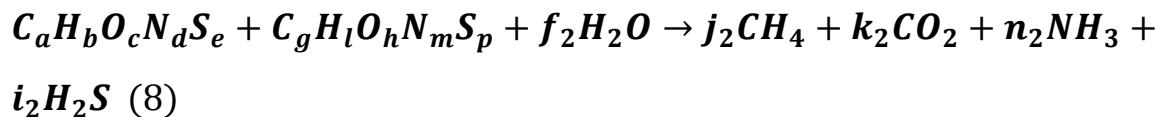
Where, a and g are the number of atoms of carbon, b and l are the number of atoms of hydrogen, c and h are the number of atoms of oxygen, d and m are the number of atoms of nitrogen, while, e and p the number of atoms of Sulphur for food waste and cow dung respectively.

Where,

$$j_2 = \frac{b}{8} + \frac{l}{8} + \frac{a}{2} + \frac{g}{2} - \frac{c}{4} - \frac{h}{4} - \frac{3d}{8} - \frac{3m}{8} - \frac{e}{4} - \frac{p}{4} \; ;$$

$$n_2 = d + m \; ; \qquad i_2 = p + e \; ;$$

$$f_2 = a + g - \frac{b}{4} - \frac{l}{4} - \frac{c}{2} - \frac{h}{2} + \frac{3d}{4} + \frac{3m}{4} + \frac{e}{2} + \frac{p}{2} \; ;$$

$$k_2 = \frac{a}{2} + \frac{g}{2} - \frac{b}{8} - \frac{l}{8} + \frac{h}{4} + \frac{3d}{8} + \frac{3m}{8} + \frac{e}{4} + \frac{c}{4} + \frac{p}{4}$$

Then after, by replacing f_2, k_2, j_2, n_2 and i_2 with their equivalences in equation (8), the theoretical cumulative methane production (T_{CH_4}) was calculated as it is shown by equation (9) for co-digestion of food waste and cow dung.

$$T_{CH_4} = \frac{22400 \times \left(\frac{b}{8} + \frac{l}{8} + \frac{a}{2} + \frac{g}{2} - \frac{c}{4} - \frac{h}{4} - \frac{3d}{8} - \frac{3m}{8} - \frac{e}{4} - \frac{p}{4} \right)}{VS_{FW} + VS_{CD}} \quad (9)$$

Where, VS_{FW} and VS_{CD} are the amount of volatile matter for food waste and cow dung used in experiment respectively and T_{CH_4} is in ml/g VS.

3.7 Efficiency of methane conversion

The efficiency of methane conversion (E_{CH_4}) is the percentage of the actual methane production to the theoretical methane production ratio (Fagbohungbe, M.O., et al. (2016)). Which is expressed in the equation (10). The actual methane production is calculated by subtracting methane production from digestion of inoculum alone.

$$E_{CH_4} = \frac{Actual\ Methane\ production(ml)}{Theoretical\ Mehane(ml)} \times 100 \qquad (10)$$

CHAPTER FOUR

4.0. RESULTS AND DISCUSSION

Data analysis were done by analyzing elemental and proximate analysis results for food wastes, cow dung and Biochars, comparing the production from all those reactors based on the concentration of Biochar for each experiment separately and results from upgrading of Biogas were also analyzed. Experimental values were also compared with the theoretical value of the cumulative methane yield.

4.1   Proximate and Elemental Analysis Results

4.1.1 Analysis of food waste

The proximate analysis of used substrate (food waste) has shown that the moisture content of food waste was high with 71.81% of the total mass of food waste used. Total solid was 28.17% from which 81.89% of TS was the volatile solid and 17.98% of TS was total organic carbon of the total used mass. In general, the production of Biogas depends on the VS, which means that, higher VS content in the feedstocks leads to the higher Biogas yield (Omar, R., et al. (2008)) . Therefore, the presented value of VS in food waste was promising for Biogas generation as it was high. While, the ash content was 8% of TS as it is shown in **Table 8.** The relationship between the amount of carbon and nitrogen present in organic materials is expressed by the carbon to nitrogen (C:N) ratio. A suitable C:N ratio plays an important role for the proper proliferation of the bacteria for the degradation process (Yen, H.W. & Brune, D.E. (2007)). According to the results of elemental analysis of food waste shown in **Table 8**, carbon content was 45.17 and nitrogen was 2.78% of total solid. Therefore, carbon to nitrogen ratio calculated was 16.25 in the food waste.

4.1.2 Analysis of Biochar

Proximate analysis of pyrolytic Biochar gave 0.74% as moisture content, 99.25% as TS which shown that Biochar was mainly solid as it was prepared in a furnace at a high temperature hence, water was evaporated during preparation. TS was constituted by 20.55% of VS and 79.43% of TOC. However VS of Biochar was high, it did not contribute to Biogas production as other additives. From elemental analysis of Biochar, 88.96% of dried Biochar was C while 0.36% was N, results are shown in **Table 8.** Hence, the C:N ratio in Biochar gave 247.03. However, Biochar

was not degraded during AD process or contribute in production of Biogas as it was used as an additive but, it might increase the C:N ratio in digester during the AD process. The atomic H:C and O:C ratios are used to estimate the degree of aromaticity and maturation of charcoal.

From elemental analysis results of Biochar, H:C ratio was equal to 0.0260 while O:C ratio was 0.0947. Biochar with O:C or H:C ratios less than 0.2 is mainly consists of graphene layers and is chemically stable. The extremely low ratio of Biochar implies its minimum polarity and maximum hydrophobicity, which lead to the capturing CO_2 in presence of water (Shen, Y., et al. (2016)). The O:C and H:C ratios are lower than 0.2, which have shown a high degree of aromaticity, presence of graphene layers and chemical stability of the used Biochar. The measurement for pH of Biochar has shown the high alkalinity value of 9.01. Biochar results were different from what has been founded by Sun, L et al. (2013) on Biochar produced from eucalyptus at 600ºC (Sun, L., et al. (2013)), where the differences were mainly based on temperature difference as characteristics of Biochar differ for different temperature.

4.1.3   Analysis of Cow Dung

The proximate analysis of used cow dung has shown that the moisture content of food waste was very high with 85.46% of the total mass of cow dung used, this was because the used cow dung was fresh. Total solid was 14.28% from which 70.22% of TS was the volatile solid and 29.78% of TS was total organic carbon of the total used mass. Therefore, the value of VS presented in the cow dung was promising for Biogas generation as it was high. Besides, the ash content was 13.96% of TS as it is shown in **Table 8**. This analysis shown that the cow dung has higher moisture content and ash content compared to the used food waste. According to the results of elemental analysis of cow dung shown in **Table 8**, carbon content was 43.95% and nitrogen was 1.14% of total solid. Therefore, the calculated C:N ratio for cow dung was 38.55. Which was higher compared to the one of food waste and the advised ratio in AD. H in cow dung was high compared to the one of food waste and Biochar as it had higher moisture content too. The O content was proportionally high with 46.82% of total solid. Which might be a result of undigested carbohydrates of the feed in the cow stomach (Omar, R., et al. (2008)) .

Table 8. Results for Proximate and Elemental analysis of food waste and Biochar

Parameter	Unite	Food Waste	Biochar	Cow dung	Inoculum
Moisture content	%	71.81	0.74	85.46	94.71
Total Solid	%	28.17	99.25	14.28	5.29
Volatile Solid	%	81.89	20.55	70.22	68.40
Total Organic Carbon	%	17.98	79.43	29.78	31.5
Ash content	%	8	-	13.96	29.17
pH value	-	-	9.01	-	7.6
Carbon	%	45.17	88.93	43.95	-
Hydrogen	%	3.72	2.31	7.75	-
Oxygen	%	48.14	8.42	46.82	-
Nitrogen	%	2.78	0.36	1.14	-
Sulfur	%	0.19	0	0.34	-

4.2   Effect of Biochar on Biogas and Methane Production

4.2.1 First lab experiment for anaerobic digestion of food waste

In this experiment, food waste (Ethiopian food wastes) was used as substrates inoculated with the inoculum of coffee husk which was collected at the outlet of digester of a Biogas pilot plant from which was feed with coffee husk. The used inoculum was having 5.29% of TS therefore, it was considered as waste water and was used to dilute the substrate in a reactor with 30ml of addition water . Biochar was added as additive material at different percentage 15%, 25%, 50% and 85% based on dry matter of FW. During the experiment, 6reactors were used in duplicate manner; R.Inoc, R.Control, R015, R025, R050 and R085. Biogas was produced only once means on the next day after feeding reactors and incubated them at 38^0C, where the Biogas production was decreasing from R050, R085, R.Control, R015, R025 and R.Inoc respectively. The highest Biogas yield was produced by R050 with 1825ml which is equal to 79.11ml/g VS while, the lowest was from R.Inoc with 125ml which is equal to 17.27ml/g VS. The comparison of

produced Biogas by those reactors was in this order; R050 > R085 = R.Control > R015 > R025, shown in **Table 9**. Experimental results of Biogas was very low compared to the planned production.

The analysis of produced Biogas has given the highest CH_4 content of 3.4% from R015 followed by 2.95% from R.Control and the lowest value was 2.1% from R085 while R025 and R050 had produced Biogas with the same CH_4 content in terms of percentage. The concentration of CH_4 was extremely very low from all reactors compared to the theoretical value. From which methane yield was high in R.Control with 2.24ml/g VS while the lowest was 0.95ml/g VS, shown in **Table 9** while, theoretical CH_4 was calculated and found 415.496ml/g VS. By considering the highest cumulative CH_4 production which is 2.24ml/g VS, the efficiency was 0.54% which is extremely very low, and it was useless to calculate the efficiency as the production was almost zero too. Methane yield from R.Inoc was not known because its methane concentration was not analyzed due to the insufficient production of Biogas compared to the minimum volume required by the used Biogas analyzer which is 1000ml. The reason of failure was assumed to be the used of inoculum which was not fresh and has leaded to the delay of digestion. After 14days, feedstocks were removed from reactors as they were not producing and refed reactors using fresh inoculum in the 2nd lab experiment. However, this could be a results of high biodegradability of food wastes, as they lead to the fast accumulation of organic acids, which inhibits methanogenesis phase (Cai, J., et al. (2016)). For more details on experimental results see **Appendix 4** and **5**.

Table 9. Biogas production and Methane yield from First lab experiment

Reactor	Experimental Biogas production(ml)	Experimental Biogas production (ml/g VS)	Methane(%)	Methane(ml/g VS)
R.Inoc	125	17.27	--	--
R.Control	1750	75.86	2.95	2.24
R015	1300	56.36	3.4	1.92
R025	1000	43.35	2.2	0.95
R050	1825	79.11	2.2	1.74
R085	1750	75.86	2.1	1.59

4.2.2   Second Lab Experiment for anaerobic digestion of food waste

During the second lab experiment, food wastes were used as substrates again, fresh inoculum was added to speed up the AD process and different amounts of Biochar (0, 15%, 25%, 50% and 85% based on dry matter) were added as in the first experiment. In this experiment 5reactors were used in duplicate manner; R.Control, R015, R025, R050 and R085 while for inoculum there was only one reactor (R.Inoc). Reactors were incubated at 38^0C using a water bath for 14days. During that period, Biogas was produced only once means on the second day after feeding reactors, where the Biogas production was decreasing from R025, R050, R.Control, R015, R085 to R.Inoc respectively. The highest Biogas yield was produced by R025 with 2000ml which was equal to 86.70ml/g VS, and the lowest was from R085 with 1125ml which was equal to 48.77ml/g VS, while R.Inoc did not produce shown in **Table 10**. The comparison of produced Biogas by those reactors was in this order; R025 > R050 = R.Control > R015 > R085. Experimental results of Biogas was very low compared to the planned production.

The analysis of produced raw Biogas has shown that the highest value was 7.1% from R015 followed by 6.65% from R025, 5.55% from R.Control, and 3.2% from R085 while, the lowest value was 2.55% from R050. From which methane yield was high in R025 with 5.77ml/g VS while the lowest was 1.56ml/g VS from R085, shown in **Table 10**. The CH_4 content in the produced from all reactors was extremely low compared to the standards value of CH_4 which is normally varied in this range 40-70% (Yousef, A. M., et al. (2016); Zhao, Q., et al. (2010)). Cumulative methane production was extremely low compared to the calculated theoretical cumulative CH_4 yield of 415.496ml/g VS. By considering the highest cumulative CH_4 production which is 5.77ml/g VS, the efficiency was 1.39% which is extremely very low. Which could be a results of high biodegradability of food wastes, as they lead to the fast accumulation of organic acids, which inhibits methanogenesis phase (Cai, J., et al. (2016)).

Although the inoculum was fresh, results were similar to the first lab experiment results. Therefore, the assumed reason of failure of AD in the first lab experiment was wrong instead, the main reason was the quality of used substrate (Ethiopian food wastes) which was not good enough to produce good quality of Biogas when is used alone as it has been reported by Gashaw, A., Teshita, A. & Ethiopia, B.H. (2014)**.** Gashaw, A., Teshita, A. & Ethiopia, B.H. (2014) have reported that, the degradation of Injera by anaerobic digestion bacteria produces large amounts of

organic acids and lowers the reactor pH which in turn limits the generation of methane. Which was due to the chemical composition of Injera (which is 15% of proteins, 3% of and 82% of carbohydrates) and is the main component of Ethiopian food wastes. After 14days, feedstocks were removed from reactors as they were not producing and reactors were refed again using co-digestion of food waste and cow dung. For more details on experimental results see **Appendix 6** and **7**.

Table 10. Biogas production and CH$_4$ From 2nd Lab Experiment

Reactor	Experimental Biogas production(ml)	Experimental Biogas production (ml/g of VS)	Methane(%)	Methane(ml/g of VS)
R.Inoc	0	0.00	--	--
R.Control	1825	79.11	5.55	4.39
R015	1635	70.88	7.1	5.03
R025	2000	86.70	6.65	5.77
R05	1825	79.11	2.55	2.02
R085	1125	48.77	3.2	1.56

4.2.3   Third Lab Experiment for co-digestion

In the third lab experiment, substrates were food wastes and cow dung which means co-digestion. The rate of cow dung to food waste was 1:3. Inoculum were used , and Biochars (0, 15%, 25%, 50%, and 85%) were added as in the 1st and 2nd lab experiments. During this experiment 6reactors were used in duplicate manner; R.Inoc, R.FW&CD, R015, R025, R050 and R085 and incubated at 37^{0}C. One of R050 was blowed-up on the first day therefore, the cumulative production of R050 was low compared to the other reactors. Biogas was produced on the first day of incubation but measurements were taken on the second day because of some inconveniences. During 15days of incubation, the R085 has shown the highest cumulative Biogas production with 54.89ml/g VS compared to other reactors except for R.Inoc which has produced 55.84ml/g VS (**Figure 11**). The increase in Biogas production were not that much in all reactors where the highest increase was 23.65ml/g VS for R.Inoc and the lowest was 5.47ml/g

VS by comparing the first and the last production. While, the highest increase was 9.88ml/g VS from R.FW&CD followed by R050 with 9.31, R025 with 8.37ml/g VS, R085 with 6.16ml/g VS and the lowest was 5.47ml/g VS from R015, shown in **Figure 11**. In reality , the R.Inoc cannot produce higher than other reactors with feedstock therefore, the process was inhibited again by high rate of Ethiopian food waste.

The analysis of produced Biogas was done once during the period of 15days due to the insufficiency production of Biogas and has showed that the CH4 content was very low and almost similar to the previous results (from 1st and 2nd lab experiments). The highest CH4 content was 5.4% from R025 followed by 5.3% from R015 , 5.1% from R.FW&CD, 2.8% from R085 and 1.4% from R050 which has blowed-up, shown in **Table 11**. Cumulative Biogas production of R015 and R025 were almost equal the same for methane content (**Appendix 8 and Table 11**). The CH_4 content in the produced from all reactors was extremely low compared to the standards value of CH_4 which is normally varied in this range 40-70% (Yousef, A. M., et al. (2016)). Produced cumulative CH_4 yield was extremely lower compared to the theoretic cumulative CH4 yield calculated, which was 457.240ml/g VS. Therefore, it was useless to calculate the efficiency for the produced cumulative methane yield from this experiment.
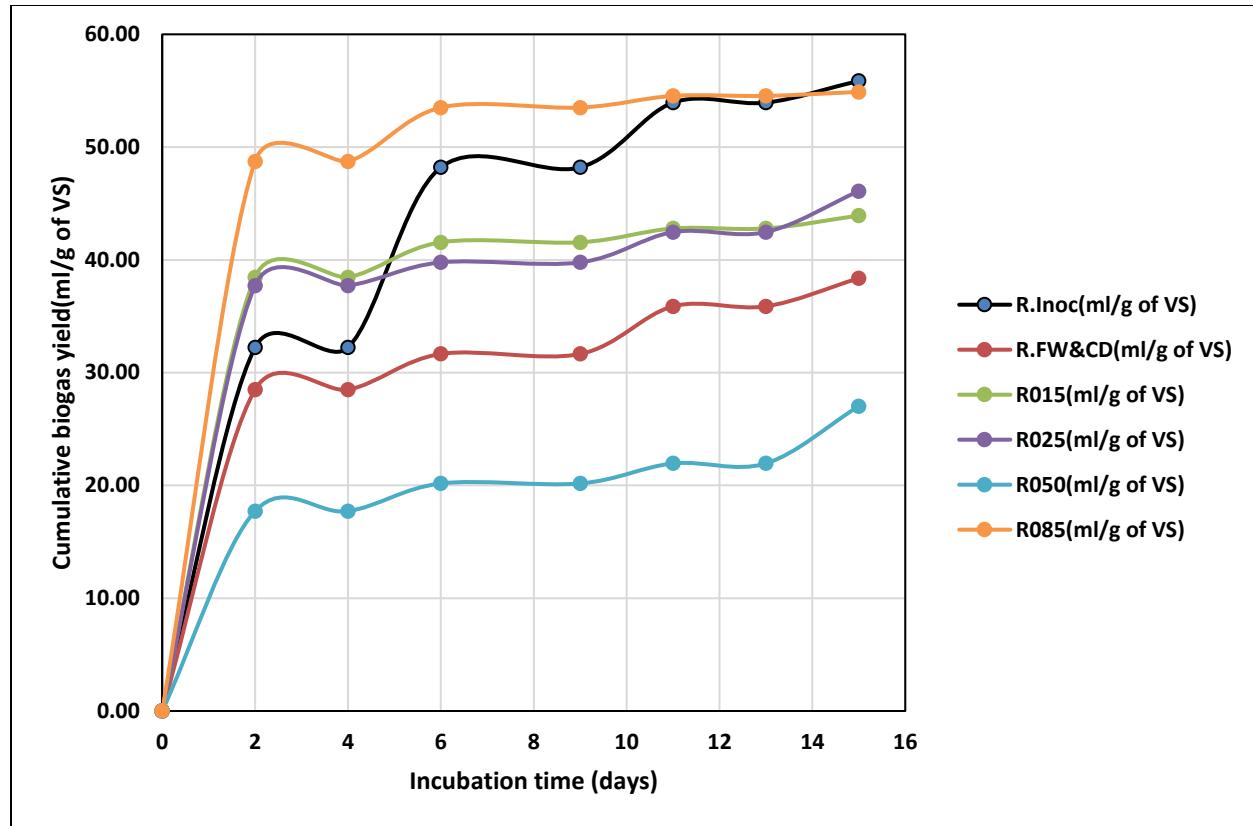
Figure 11. Experimental results of cumulative Biogas yield from 3ʳᵈ Lab Experiment

Table 11. Methane content (%) from produced Biogas during the third lab experiment

Incubation time(day)	R.Inoc	R.FW&DC	R015	R025	R050	R085
2	4.2	5.1	5.3	5.4	1.4	2.8

4.2.4 Fourth Lab Experiment co-digestion

In the fourth lab experiment, used substrates was a co-digestion of food wastes and cow dung. The rate of cow dung to food waste was 1:1. Inoculum were used with additional water (50ml) in order to form wet digestion, and Biochar with different rate (0, 15%, 25%, 50%, and 85%) were added as in previous lab experiments. During this experiment 5reactors were used in duplicate manner; R.CD, R015, R025, R050 and R085 and were incubated at 37^0C. In one of R.CD , inoculum was not used because it got finish before R.CD was fed. Therefore, the cumulative production of R.CD was not that much as it was supposed to be during 14days as the substrates

were not inoculated which delayed the anaerobic digestion process of one of R.CD. Biogas was produced on the first day of incubation from all reactors and were measured. On the 1stday after incubation Biogas production was increased in this order R.CD < R085 < R050< R015 < R025. On the third day, there was no Biogas production from all reactors.

On the 5th day, Biogas was produced from all reactors except R025 which has produced almost nothing followed by R015 while, the highest production R085 followed by R.CD. The production of Biogas from R025 was not really increasing during the incubation period of 14days compared to other reactors. R015 and R050 have produced almost similar Biogas yield during incubation period. Cumulative Biogas production was almost equal on 8th day for all reactors except R025. After 8th day, cumulative Biogas production was increasing for R.CD and R085 however, cumulative Biogas production was high for R.CD compared to R085. During 14days of incubation, the R085 has shown the highest cumulative Biogas production with 201.31ml/g VS compared to other reactors except for R.CD which has produced 214.62ml/g VS. In summarized way, cumulative Biogas yield was R.CD > R085 > R015 > R050 > R025 during incubation period of 14days, shown in **Figure 13** and **Appendix 9**. The Biogas production was not that much as it was expected from all reactors.

The analysis of produced Biogas was done during the period of 14days however, for some reactors it was impossible due to the insufficiency production of Biogas compared to the required flow rate of the used Biogas analyzer in this experiment. The analysis has shown that, the CH4 content was very low and similar to the previous results (from 1st, 2nd and 3rd lab experiments) for Biogas produced by R015, R025, R050 and R085 which was not the case for R.CD **(Appendix 10)**. On the 1st day after the feeding day, the Biogas analysis was done for all reactors and results have shown the highest CH$_4$ content was 4.55% from R015 followed by 3.85% from R025 , 3.45% from R050, 3.2% from R.CD and 2.8% from R085 which was the lowest CH4 content, shown in **Appendix 10**.   On the next days, analysis was done for some reactors accordingly. On the 5th day, Biogas from R085 and R.CD were analyzed and shown this 0.1% and 22.5% of CH$_4$ content respectively. On 8th day, Biogas from R050 and R.CD were analyzed and results were shown as 0% and 41.1% of CH4 content respectively. On 10th day, analysis was conducted for R015, R085 and R.CD from which results were 3%, 0% and 56.5% of CH$_4$ content respectively. On 12th day, Biogas from R085 and R.CD were analyzed and resulted 0% and 43.3% of CH$_4$ content respectively. On 14th day, analysis was conducted for R015, R050 and

R.CD from which have resulted this 0%, 0% and 29.2% of CH_4 content respectively (**Appendix 10**). **Figure 12** represents cumulative methane yield from R.CD.

The CH_4 content in the produced from all reactors (R.CD is excluded) was extremely low compared to the standards value of CH_4 which is normally varied in this range 40-70% (Yousef, A. M., et al. (2016); Zhao, Q., et al. (2010)). Cumulative methane production from R.CD was 790.53ml which was equal to 78.84ml/g VS while, the highest methane production rate was 220.63ml/day (**Appendix 10**). The cumulative CH_4 produced by R.CD was very low compared to 649.265ml/g VS the calculated theoretical cumulative CH_4 yield. Therefore, the efficiency of methane production from R.CD was found to be 12.14% in 14days of incubation which differs to the retention time. Reactors on which cow dung and food waste were co-digested have not produced Biogas with good CH_4 content instead CO2 and impurities were at high rate. Besides, CH4 content was reducing as the incubation time increased and concentration of biochar increased. The produced cumulative CH_4 yield by reactors with co-digestion of food waste and cow dung was extremely low compared to 486.649ml/g VS the calculated theoretical value of CH_4. According to results of analysis, CH_4 has decreased as the amount of Biochar increased. However, AD experiment did not produce as it was expected therefore; it was not easy to conclude on the effect of Biochar and the appropriate rate to be added in AD as an additive material.
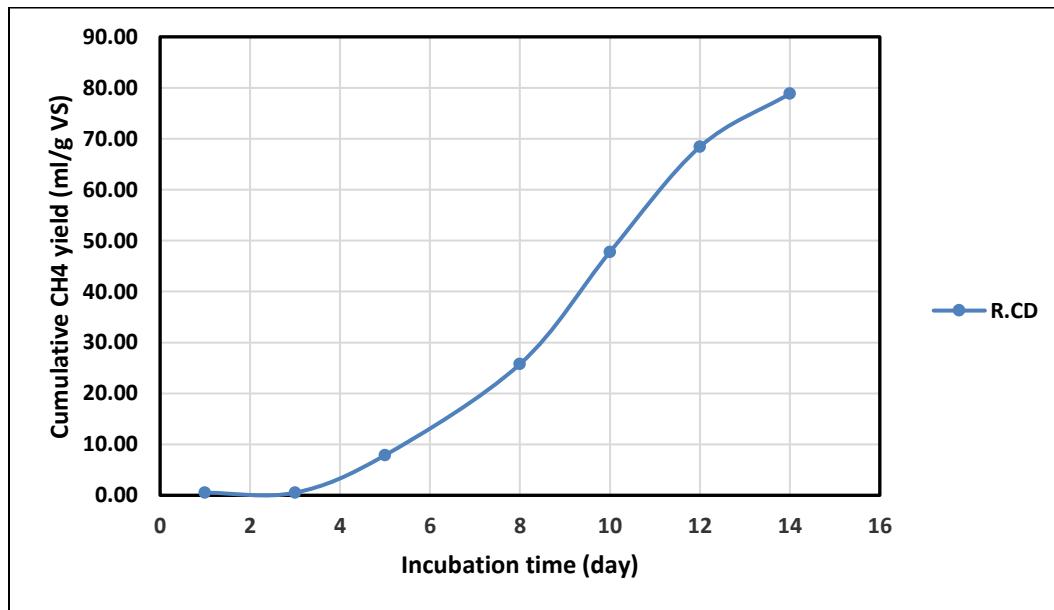
Figure 12. Experimental results of cumulative methane production from R.CD
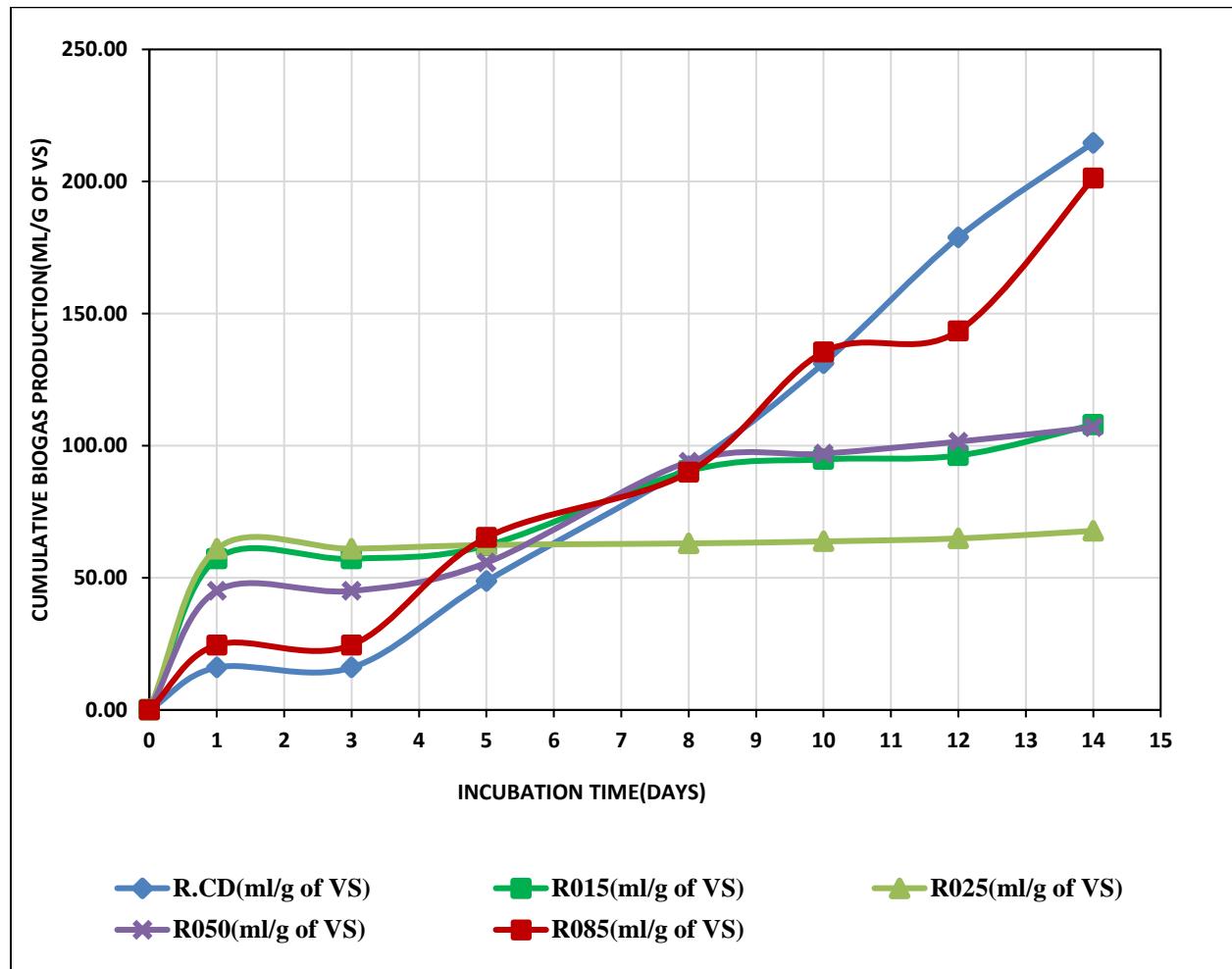
Figure 13. Experimental results of cumulative Biogas yield from 4th Lab Experiment

The CH_4 content in the produced Biogas from all reactors (R.CD was excluded) was extremely low compared to the standards value of CH_4 which is normally varied in this range 40-70% which has reported by Yousef, A. M., et al. (2016); Dobre, P., Matei, F. & Nicolae, F. (2014)) , 45-75% reported by Zhao, Q., et al. (2010) or 40-75% reported by Gashaw, A. (2016) and (Ryckebosch, et al. (2011)). Therefore as conclusion for the results, the produced Biogas was not really the normal Biogas as it does not have the same quality of Biogas in terms of methane content due to the quality of used feedstocks which was the ethiopian food waste mainly constituted by injera.

4.3   Upgrading of Biogas

The upgrading of raw Biogas to Biomethane from which unwanted components such as carbon dioxide and hydrogen sulphide were removed using Biochar adsorption as adsorbent, NaOH absorption also called Sodium scrubbing and Biochar absorption. The CO_2 absorption efficiency of Sodium scrubbing was 81%, the H_2S removal efficiency was 12.36% while, the O_2 has increased by 22.28%. However, the CH_4 losses through sodium scrubbing was high with 18.93% which was due to unappropriated appliances used for upgrading as there was no compressors (to lower or increase pressure), pumps in order to make the process efficiently.   The solution of Biochar has absorbed 29.15% of CO_2, reduced H_2S to the lower value than 1000ppm depending on the initial value and the O_2 increased for more than 100% while, the CH_4 losses was 27.9% in Biochar solution. The use of Biochar as an adsorbent has resulted to 57.76% CO_2 adsorption, less than 1000ppm of H_2S, and the O_2 increased by 100% while, the loss in CH_4 was 51.72% which was extremely high losses and led the method to be the worst for Biogas upgrading.

Used methods has led to the extremely high losses of methane, low CO_2 and H_2S removal efficiency compared to what has been achieved in the previous researches through cryogenic separation, chemical scrubbing, pressure swing adsorption, membrane separation, high pressure water scrubbing, and organic physical scrubbing technologies (Yousef, A. M., et al. 2016; Ryckebosch, et al. (2011)). However, main reasons were first of all the quality of produced biogas which was not normal and the used appliances which were not appropriate for Biogas upgrading for adsorption technology. Therefore, sodium scrubbing has shown high efficiency for CO_2 removal, with low CH_4 losses and O_2 increment compared to Biochar absorption and adsorption. However, it was not the case for H_2S removal. The use of Biochar in Biogas upgrading has shown affinity with H_2S compared to CO_2 removal. The big challenge for Biogas upgrading during this work, it was the extremely poor raw Biogas with unbelievable CO_2 content which was around 80% in most of reactors while, in the normal case CO_2 content in raw Biogas ranges in 15-60% which has been reported by Ryckebosch, et al. (2011). Besides availability of required appliances, it was impossible because of lack of maintenance therefore the experiment was so complicated and inefficiency.

CHAPTER FIVE

5.0. CONCLUSION AND RECOMMENDATION

5.1   Conclusion

The analysis of Biochar from eucalyptus has indicated that, Biochar can be classified as activated carbon as 88.9% of Biochar was carbon content with moisture content was below 1% of total mass. The experimental results for anaerobic digestion of Ethiopian food waste mainly constitute of Injera has indicated an extremely very low and poor Biogas production with lower than 10% methane content from all experiments. The addition of Biochar (at different rate) in anaerobic digestion of Ethiopian food waste has not shown a clear effect on both Biogas and methane due to the quality of used substrates which did not produce Biogas even when was digester as sole substrates due to the high biodegradability of food wastes, as it leads to the fast accumulation of organic acids, which inhibits methanogenesis phase and their biological and or chemical components which have inhibited the anaerobic digestion process. Besides, Biochar cannot change the quality of feedstocks but it enhances the process which in turn may increase the production and shortened the retention time.

Almost the same thing happened when the food waste was co-digested with cow dung at two different ratio 1:2 and 1:1with addition of biochar, where reactors have produced a very low Biogas with extremely low methane content which was reducing as the incubation time was increased and the concentration of biochar increased within a reactor. From the experiment, carbon dioxide and hydrogen sulphide content were high compared to what is acceptable in Biogas, where carbon dioxide content around 80% and around or even above 1000ppm for hydrogen sulphide. The experiment was done four times and has produced results which look almost similar with the lag phase which was less than one day. Therefore, the produced Biogas was not really the normal Biogas as it has not had the same quality of Biogas in terms of methane content. Reactor from which cow dung was digested (R.CD) has shown an increment in methane production. For that it was clear that the used food waste collected from dormitory of AAiT was not good enough for Biogas production through anaerobic digestion due to biological and or chemical components of the used food waste which has inhibited its anaerobic digestion process.

Used methods for CO_2 and H_2S removal have shown low CO_2 and H_2S removal efficiency and high CH_4 losses compared to the known upgrading technologies mainly used in Europe, America and Asia. However, the quality of produced biogas and the availability of appropriate appliances were the main reasons of failure.

5.2   Recommendation

Man researches must be done on Ethiopian food waste (Injera) for more clarification in terms of nutrients (biological and or chemical components). As it has been shown in literature review that, the use of Biochar as an additive material for anaerobic digestion has been applied. However, the optimum concentration of Biochar to be added is still a matter which needs to be clarified therefore; many researches are welcomed in this field. It is not easy to find literatures on the Kinetic Modelling of Anaerobic digestion from food waste when Biochar was added to see the effects of Biochar on Biogas Yield therefore; future researchers are welcomed to work on this. Evaluation of the effect of added biochar on digestates in terms of nutrients is also needed. In additional, effect of light on anaerobic digestion productions must be studied.

For those who can find enough appliances for upgrading can try to use Biochar as an adsorbent or absorbent material for CO_2 and H_2S removal and see what will happen. Apart from recommendation which directly related to the experiment, Pan African University Institute of Water and Energy Science (including Climate Change) PAUWES must have its own laboratories in order to prevent an kind of delay which may happen for those who want to conduct a laboratory work on their master thesis or personal research, for better and quality education as PAUWES has engineers who need practical more than theoretical work. This will help them to be innovative and enable them to find solutions for Africa from which they are get scholarships.

References

Abbasi, T., Tauseef, S. M., & Abbasi, S. A. (2012). A brief history of anaerobic digestion and "Biogas". In *Biogas Energy* (pp. 11-23). Springer New York.

Barzagli, F., et al. (2014). Novel non-aqueous amine solvents for Biogas upgrading. *Energy & Fuels*, *28*(8), pp.5252-5258.

Bogale, W. (2017). Preparation of Charcoal Using Flower Waste. *Journal of Power and Energy Engineering*, *5*(02), p.1. Available on : https://doi.org/10.4236/jpee.2017.52001

Budiyono, B. & Sumardiono, S. (2014). Effect of total solid content to Biogas production rate from vinasse. *International Journal of Engineering*, *27*(2), pp.177-184.

Cai, J., et al. (2016). Effects and optimization of the use of Biochar in anaerobic digestion of food wastes. *Waste Management & Research*, *34*(5), 409-416.

Chaemchuen, S., et al. (2013). Metal–organic frameworks for upgrading Biogas via CO_2 adsorption to Biogas green energy. *Chemical Society Reviews*, *42*(24), pp.9304-9332.

Cuetos, M.J., et al. (2017). Enhancing anaerobic digestion of poultry blood using activated carbon. *Journal of advanced research*, *8*(3), pp.297-307.

Dioha, I.J., et al. (2013). Effect of carbon to nitrogen ratio on Biogas production. *International Research Journal of Natural Sciences*, *1*(3), pp.1-10.

Dobre, P., Matei, F. & Nicolae, F. (2014). Main factors affecting Biogas production: An overview. *Romanian Biotechnological Letters*, *19*(3), pp.9283-9296.

El-Fadel, M., Findikakis, A.N. & Leckie, J.O. (1997). Environmental impacts of solid waste landfilling. *Journal of environmental management*, *50*(1), pp.1-25.

Etuwe, C.N., Momoh, Y.O.L. & Iyagba, E.T. (2016). Development of Mathematical Models and Application of the Modified Gompertz Model for Designing Batch Biogas Reactors. *Waste and Biomass Valorization*, *7*(3), pp.543-550.

Fagbohungbe, M.O., et al. (2016). The challenges of anaerobic digestion and the role of Biochar in optimizing anaerobic digestion. *Waste Management*. www.elsevier.com/ locate/wasman

Fagbohungbe, M.O., et al. (2016). Impact of Biochar on the anaerobic digestion of citrus peel waste. *Bioresource technology*, *216*, pp.142-149. www.elsevier.com/locate/biortech

Gashaw, A. (2016). Co-digestion of municipal organic wastes with night soil and cow dung for Biogas production: A Review. *African Journal of Biotechnology*, *15*(2), pp.32-44.

Gashaw, A., Teshita, A. & Ethiopia, B.H. (2014). Co-digestion of Ethiopian food waste with cow dung for Biogas production.

Gómez, E., Martin, J. & Michel, F.C. (2011). Effects of organic loading rate on reactor performance and archaeal community structure in mesophilic anaerobic digesters treating municipal sewage sludge. *Waste Management & Research*, *29*(11), pp.1117-1123.

Gurwick, N.P., et al. (2013). A systematic review of Biochar research, with a focus on its stability in situ and its promise as a climate mitigation strategy. *PloS one*, *8*(9), p.e75932.

Hewage, S. & Priyadarshani, R. (2016). Effect of charred digestate (Biochar) and digestate on soil organic carbon and nutrients in temperate bioenergy crop production systems.

Holm-Nielsen, J.B., et al. (2009). The future of anaerobic digestion and Biogas utilization. *Bioresource technology*, *100*(22), pp.5478-5484.

Howarth, R.W., Santoro, R. & Ingraffea, A. (2011). Methane and the greenhouse-gas footprint of natural gas from shale formations. *Climatic Change*, *106*(4), p.679.

Hoyer, K., et al. (2016). Biogas Upgrading-Technical Review.

Inthapanya, S., Preston, T.R. & Leng, R.A. (2012). Biochar increases Biogas production in a batch digester charged with cattle manure. *Livest. Res. Rural Dev*, *24*.

Ippolito, J.A., Laird, D.A. & Busscher, W.J. (2012). Environmental benefits of Biochar. *Journal of environmental quality*, *41*(4), pp.967-972.

Janczak, D., et al. (2017). Biochar to reduce ammonia emissions in gaseous and liquid phase during composting of poultry manure with wheat straw. *Waste Management*. http://dx.doi.org/10.1016/j.wasman.2017.04.033

Kwak, D.H., et al. (2013). Evaluation of Methane Yield on Mesophilic-Dry Anaerobic Digestion of Piggery Manure Mixed with Chaff for Agricultural Area. *Advances in Chemical Engineering and Science*, *3*(04), p.227. http://dx.doi.org/10.4236/aces.2013.34029

Lü, F., et al. (2016). Biochar alleviates combined stress of ammonium and acids by firstly enriching Methanosaeta and then Methanosarcina. *Water research*, *90*, pp.34-43.

Luo, C., et al. (2015). Application of eco-compatible Biochar in anaerobic digestion to relieve acid stress and promote the selective colonization of functional microbes. *Water research*, *68*, pp.710-718.

Manonmani, P., et al. (2017). Biogas Production Potential of Food Waste. *IJEAB: Open Access Bi-Monthly International Journal: Infogain Publication*, *2*(Issue-2). http://dx.doi.org/10.22161/ijeab/2.2.18

Mata-Alvarez, J., Mace, S. & Llabres, P. (2000). Anaerobic digestion of organic solid wastes. An overview of research achievements and perspectives. *Bioresource technology*, *74*(1), pp.3-16.

Matheri, A.N., et al. (2016). Modelling the Kinetics of Biogas Production from Co-digestion of Pig Waste and Grass Clippings. In *24th World Congress on Engineering (WCE 2016) London-UK*

Meyer-Kohlstock, D., et al. (2016). Biochar as additive in Biogas-production from bio-waste. *Energies*, *9*(4), p.247. www.mdpi.com/journal/energies

Mojapelo, N., et al. (2014). Bio-methane Potential of the Organic Fraction of Municipal Solid Waste. *Academic edu*.

Mumme, J., et al. (2014). Use of Biochars in anaerobic digestion. *Bioresource technology*, *164*, pp.189-197.

Nielfa, A., Cano, R. & Fdz-Polanco, M. (2015). Theoretical methane production generated by the co-digestion of organic fraction municipal solid waste and biological sludge. *Biotechnology Reports*, *5*, pp.14-21.

Niesner, J., Jecha, D. & Stehlík, P. (2013). Biogas upgrading technologies: state of art review in European region. *Chem Eng Trans*, *35*, pp.517-522.

Omar, R., et al. (2008, November). Anaerobic treatment of cattle manure for Biogas production. In *Proceedings Philadelphia, Annual meeting of American Institute of Chemical Engineers* (pp. 1-10).

Owamah, H.I. & Izinyon, O.C., 2015. Optimal combination of food waste and maize husk for enhancement of Biogas production: Experimental and modelling study. *Environmental Technology & Innovation*, *4*, pp.311-318. Available on: www.elsevier.com/locate/eti

Persson, M., Jönsson, O. & Wellinger, A. (2006, December). Biogas upgrading to vehicle fuel standards and grid injection. In *IEA Bioenergy task* (Vol. 37, pp. 1-34).

Petersson, A. & WeLLInGer, A. (2009). Biogas upgrading technologies–developments and innovations. *IEA Bioenergy*, *20*, pp.1-19.

Rasi, S. (2009). *Biogas composition and upgrading to Biomethane*. University of Jyväskylä.

Reinhart, D.R. & Basel Al-Yousfi, A. (1996). The impact of leachate recirculation on municipal solid waste landfill operating characteristics. *Waste Management & Research*, *14*(4), pp.337-346.

Ryckebosch, E., et al. (2011). Techniques for transformation of Biogas to Biomethane. *science direct,* pp. 1633-1645.

Sethupathi, S., et al. (2017). Biochars as Potential Adsorbers of CH4, CO2 and H2S. *Sustainability*, *9*(1), p.121.Avilable on: www.mdpi.com/journal/sustainability

Shen, Y., et al. (2016). Towards a sustainable paradigm of waste-to-energy process: Enhanced anaerobic digestion of sludge with woody Biochar. *Journal of Cleaner Production*, *135*, pp.1054-1064. www.elsevier.com/locate/jclepro

Shen, Y., et al. (2015). Producing pipeline-quality Biomethane via anaerobic digestion of sludge amended with corn stover Biochar with in-situ CO 2 removal. *Applied Energy*, *158*, pp.300-309.

Sinervo, R. (2017). Effects of Biochar addition on anaerobic digestion and comparison of different Biochar qualities.

Sorathia, H.S., Rathod, P.P. & Sorathiya, A.S. (2012). Biogas generation and factors affecting the Bio-gas generation–a review study'. *International Journal of Advanced Engineering Technology*, *3*(2) ,ISSN 0976-3945.

Sun, L., Wan, S. & Luo, W. (2013). Biochars prepared from anaerobic digestion residue, palm bark, and eucalyptus for adsorption of cationic methylene blue dye: characterization, equilibrium, and kinetic studies. *Bioresource technology*, *140*, pp.406-413. www.elsevier.com/locate/biortech

Sunyoto, N.M., et al. (2016). Effect of Biochar addition on hydrogen and methane production in two-phase anaerobic digestion of aqueous carbohydrates food waste. *Bioresource technology*, *219*, pp.29-36. www.elsevier.com/locate/biortech

Woolf, D., et al. (2010). Sustainable Biochar to mitigate global climate change. *Nature communications*, *1*, p.1.

Yao, H., et al. (2013). Adsorption of fluoroquinolone antibiotics by wastewater sludge Biochar: role of the sludge source. *Water, Air, & Soil Pollution*, *224*(1), p.1370.

Yeh, J.T., Pennline, H.W. & Resnik, K.P. (2001). Study of CO2 absorption and desorption in a packed column. *Energy & fuels*, *15*(2), pp.274-278.

Yen, H.W. & Brune, D.E. (2007). Anaerobic co-digestion of algal sludge and waste paper to produce methane. *Bioresource technology*, *98*(1), pp.130-134.

Yi, J., et al. (2014). Effect of increasing total solids contents on anaerobic digestion of food waste under mesophilic conditions: performance and microbial characteristics analysis. *PloS one*, *9*(7), p.e102548. Available on: www.plosone.org

Yousef, A.M., et al. (2016). Upgrading Biogas by a low-temperature CO 2 removal technique. *Alexandria Engineering Journal*, *55*(2), pp.1143-1150.

Zhao, Q., et al (2010). Purification technologies for Biogas generated by anaerobic digestion. *Compressed Biomethane, CSANR, Ed*.

Appendix

Appendix 1. Specific Biogas production potential and methane content for different substrates.

Substrate	Average dry matter (DM) content (S.U.%)	Biogas potential (l/kg S.U.)	Methane content (%)
Wheat straws	86.5	367	78.5
Barley straws	84	380	77
Lucerne	22.5	445	77.7
Grass	16	557	84
Corn silage	34	108	52
Corn stalks	86	309	--
Dried leaves	12.5	260	58
Beet leaves	13.5	501	84.8
Poultry wastes	27.5	520	68
Cattle manure	14	260-280	50-60
Horse dung	27.5	200-300	66
Sheep dung	25	320	65
Pig manure	13.5	480	60

(Source: Dobre, P., Matei, F. and Nicolae, F.(2014))

Appendix 2. The comparison between the proposed Techniques of upgrading in terms of Energy efficiency.
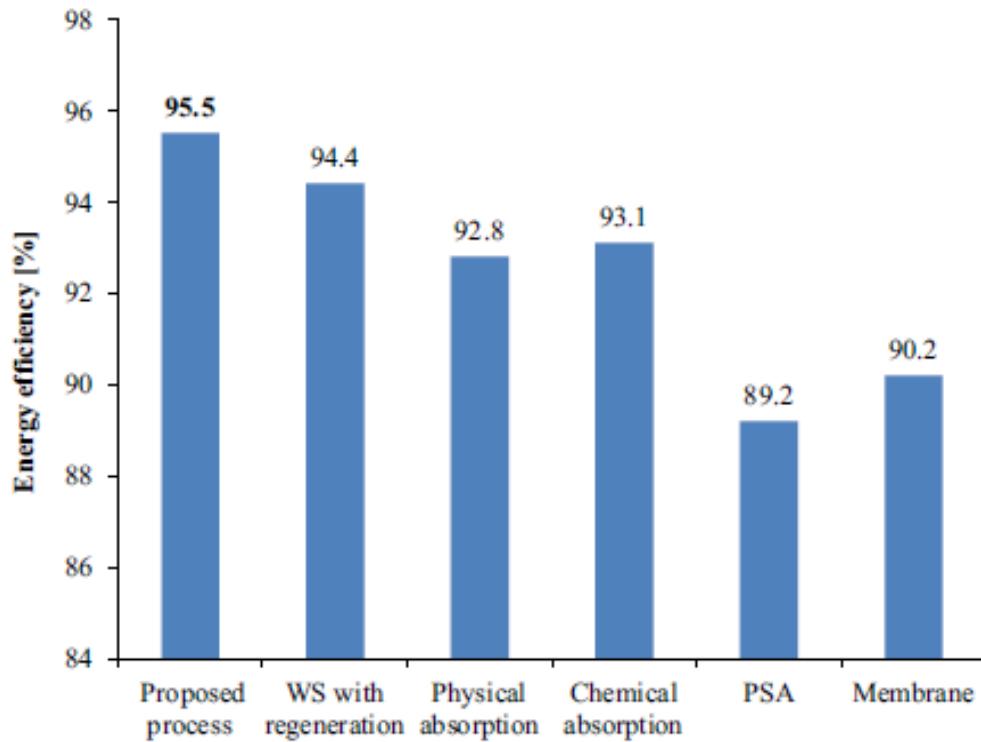
The diagram compared upgrading technologies in terms of energy efficiency. Compared technologies were; the cryogenic separation and the conventional technologies, namely water scrubbing with regeneration (WS with regeneration), physical absorption, chemical absorption, pressure swing adsorption (PSA) (Yousef, A. M., et al. (2016)).

Appendix 3. Variation of the CO$_2$ Absorption efficiency of different amines in different solution as a function of time.
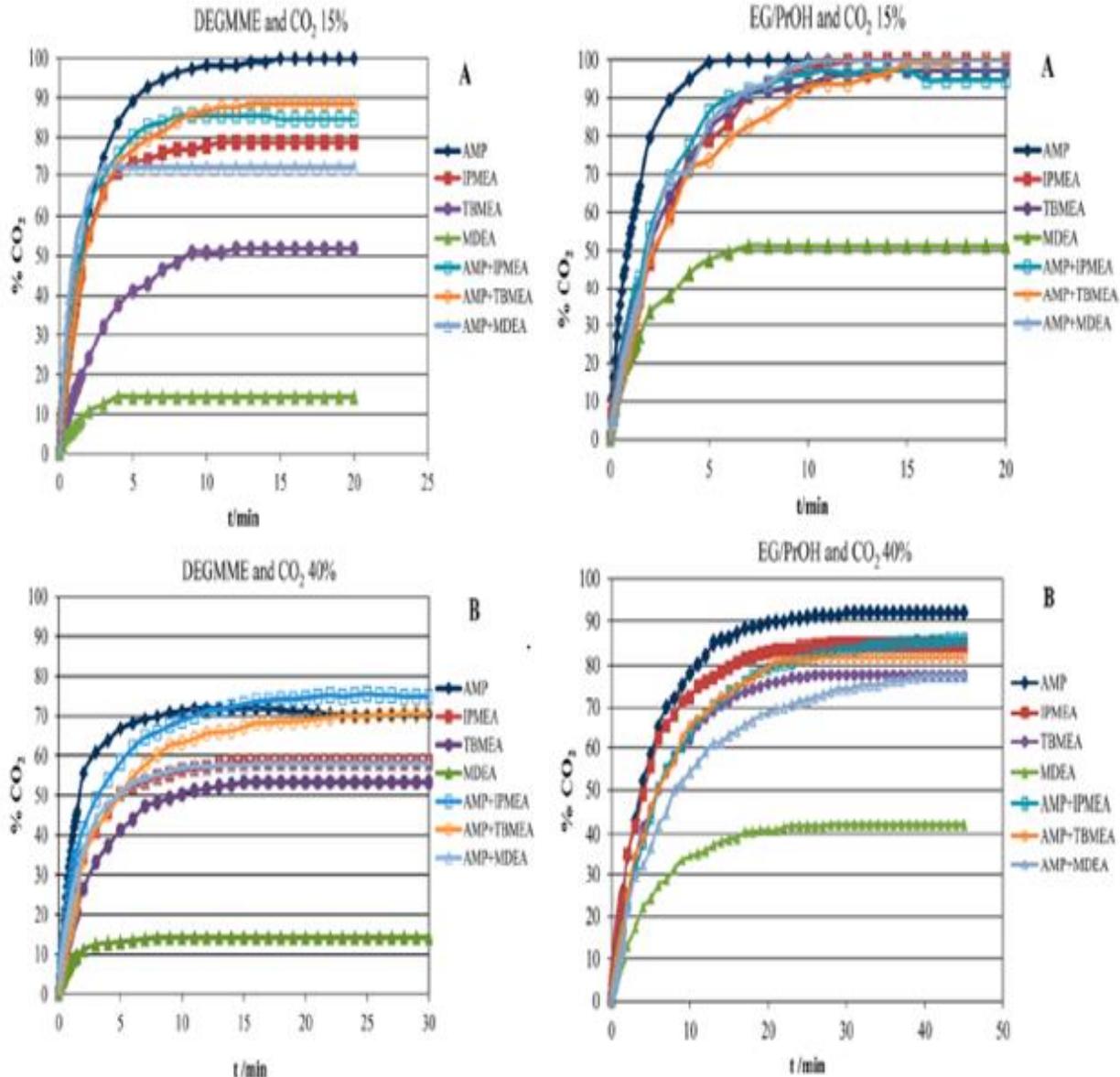
Note that, the above figures are for variation of the CO$_2$ (15% and 40%) Absorption efficiency of different amines in different solution (DEGMME solutions- left figures A and B, and EG/PrOH solutions-right figures A and B) as a function of time (**Barzagli, F., et al. (2014)**).

Appendix 4. Experimental results of Biogas for 1st Lab experiment

Reactor	Experimental biogas production(ml)		
	1st	**2nd**	**Average**
R.Inoc	50	200	125
R.Control	1600	1900	1750
R015	2000	600	1300
R025	2000	0	1000
R05	2000	1650	1825
R085	2000	1500	1750

Appendix 5. Analysis of raw Biogas produced for the 1st lab experiment

Parameter	**R.Control**	**R015**	**R025**	**R050**	**R085**
CH4(%)	2.95	3.4	2.2	2.2	2.1
CO2(%)	67.75	84.2	85.5	92.8	90.55
O2(%)	5	3.2	3	1.8	1.75
H2S(ppm)	>>1000	741	>>1000	977	937
Balance(%)	24.3	9.25	9.3	3.65	5.55

Appendix 6. Biogas Production from 2nd Lab experiment

Reactor	Experimental biogas production(ml)		
	1st	**2nd**	**Average**
R.Inoc	0	0	0
R.Control	2000	1650	1825
R015	2000	1270	1635

R025	2000	2000	2000
R05	1900	1750	1825
R085	2000	250	1125

Appendix 7. Analysis of raw Biogas produced from 2nd Lab Experiment

Parameter	R.Control	R015	R025	R.050	R.085
CH4(%)	5.55	7.1	6.65	2.55	2.55
CO2(%)	80.75	86.3	84	78	78
O2(%)	1.8	2	2.6	1.1	1.1
H2S(ppm)	905	589	258	…..	……
Balance(%)	11.95	4.55	6.65	18.4	18.4

Appendix 8. Experimental results of Biogas from 3rd Lab Experiment

Retention time (Days)		0	2	4	6	9	11	13	15
R.Inoc	Biogas yield(ml)	0.00	233.00	0.00	115.50	0.00	41.50	0.00	14.00
	Cumulative Biogas yield(ml/g of VS)	0.00	32.23	32.23	48.20	48.20	53.94	53.94	55.88
R.FW&CW	Biogas yield(ml)	0.00	800.00	0.00	89.00	0.00	118.50	0.00	70.00
	Cumulative Biogas yield(ml/g of VS)	0.00	28.49	28.49	31.66	31.66	35.88	35.88	38.37
R015	Biogas yield (ml)	0.00	1080.00	0.00	87.00	0.00	34.50	0.00	32.00

		0.00	38.46	38.46	41.56	41.56	42.79	42.79	43.93
	Cumulative Biogas yield (ml/g of VS)	0.00	38.46	38.46	41.56	41.56	42.79	42.79	43.93
R025	Biogas yield (ml)	0.00	1059.50	0.00	57.50	0.00	75.50	0.00	102.00
	Cumulative Biogas yield (ml/g of VS)	0.00	37.73	37.73	39.78	39.78	42.47	42.47	46.10
R050	Biogas yield (ml)	0.00	497.50	0.00	69.00	0.00	50.00	0.00	142.50
	Cumulative Biogas yield (ml/g of VS)	0.00	17.72	17.72	20.17	20.17	21.95	21.95	27.03
R085	Biogas yield (ml)	0.00	1368.50	0.00	134.00	0.00	29.00	0.00	10.00
	Cumulative Biogas yield (ml/g of VS)	0.00	48.73	48.73	53.51	53.51	54.54	54.54	54.89

Appendix 9. Experimental results of Biogas from 3rd Lab Experiment

Day		*0*	*1*	*3*	*5*	*8*	*10*	*12*	*14*
R.CW	Biogas yield(ml)	0.00	161.00	0.00	327.50	436.50	390.50	478.00	358.50
	Cumulative biogas yield(ml/g of VS)	0.00	16.06	16.06	48.72	92.25	131.20	178.87	214.62
R015	Biogas yield (ml)	0.00	942.50	0.00	82.50	465.00	72.50	24.00	192.50
	Cumulative biogas yield (ml/g	0.00	57.20	57.20	62.21	90.43	94.83	96.29	107.97

	of VS)							
R025	Biogas yield (ml)	0.00	1005.50	0.00	23.00	10.00	12.50	18.50	47.50
	Cumulative biogas yield (ml/g of VS)	0.00	61.02	61.02	62.42	63.03	63.79	64.91	67.79
R050	Biogas yield (ml)	0.00	742.00	0.00	176.00	629.50	50.50	75.00	89.50
	Cumulative biogas yield (ml/g of VS)	0.00	45.03	45.03	55.71	93.92	96.98	101.54	106.97
R085	Biogas yield (ml)	0.00	405.00	0.00	670.00	407.00	750.00	131.00	954.00
	Cumulative biogas yield (ml/g of VS)	0.00	24.58	24.58	65.24	89.94	135.46	143.41	201.31

Appendix 10. Experimental results of CH₄ production for the fourth lab experiment

Incubation time(day)	R.CD			R015	R025	R050	R085
	Average (%)	Average(ml)	Cumulative CH$_4$ (ml/g VS)				
1	3.2	5.15	0.51	4.55	3.85	3.45	2.8
3	--	--	0.51	--	--	--	--
5	22.5	73.69	7.86	--	--	--	0.1
8	41.1	179.40	25.75	--	--	0	--
10	56.5	220.63	47.76	3	--	--	0
12	43.3	206.97	68.40	--	--	--	0
14	29.2	104.68	78.84	0		0	--

Note that : (–) means that the analysis was note done because of insufficient Biogas production.

Appendix 11. Some of used instruments in this experiment