Experimental investigation of Upgrading the Quality of Biogas using Corn Cob Derived Biochar from Cow Dung

By

Tariku Dessie Temare

A Thesis Submitted to the Department of Thermal and Aerospace Engineering
School of Mechanical, Chemical and Materials Engineering

Presented in Partial Fulfillment of the Requirement for the Degree of Master of science in Thermal Engineering

Office of Graduate Studies
Adama Science and Technology University

November 2020

Adama, Ethiopia

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DECLARATION

I hereby declare that this MSc. thesis entitled "*Experimental Investigation of Upgrading the Quality of Biogas Using Corn Cob Derived Biochar from Cow Dung"* in partial fulfillment of the requirement for the award of the degree of Master of Science in thermal engineering is my original work under the supervision of Dr. Dawit Gudeta, Assistant Professor of Thermal and Aerospace Engineering Department.

The matter embedded in this thesis has not been submitted for the award of a degree or diploma in any other university. All relevant resource information used in this paper has been duly acknowledged.

Tariku Dessie Temare	____________________	____________________
Candidate	Signature	Date

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

Dr. Dawit Gudeta	____________________	____________________
Advisor	Signature	Date

APPROVAL OF BOARD OF EXAMINERS

We, the undersigned, members of the Board of Examiners of the final open defense by Tariku Dessie Temare have read and evaluated his thesis entitled "*Experimental Investigation of Upgrading the Quality of Biogas Using Corn Cob Derived Biochar from Cow Dung*" and examined the candidate. This is, therefore, to certify that the thesis has been accepted in partial fulfillment of the requirement of the Degree of Master of science in Thermal Engineering.

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ABSTRACT

Today, energy is one of the fundamental needs of society and provides services in various forms. Anaerobic digestion (AD) is a mature technology to both manage waste and generate biogas for energy services. However, the raw biogas produced is often of low quality and the process is slow and operates over very long durations. Also, raw biogas is mainly a combination of carbon dioxide, methane, and unwanted gases that causes a reduction in energy efficiency from it. The deficiency with using biogas is due to the presence of CO_2 in biogas which is a non-combustible gas. The presence of CO_2 lowers the calorific value and the specific energy density of biogas. Furthermore, it reduces its flame speed and the extent of flammability in comparison to natural gas. So that alternative approaches are required to upgrade the biogas to methane-rich biogas by reducing the CO_2 and other contaminants such as H_2S within the digester. Biochar with its beneficial characteristics was applied to AD in this study. This work was aimed to study the effect of the utilization of biochar produced within slow pyrolysis at a temperature of 450℃ on the ability of enhanced methane production from mesophilic anaerobic digestions of cow dung (CD) through experimentation. To accomplish these aims, the AD experiments were conducted in plastic bottles of 1 L capacity used as a digester at mesophilic temperature (37℃ ± 1℃) with a working volume of 0.8L each and were fed on a batch basis. The biogas generation from control and digesters amended with corn cob derived biochar (CC-BC450) at four different concentrations (4, 6, 8, and 10 g/800 mL of media) labeled as ADM_0 (control), ADM_1, $ADM_{1.5}$, ADM_2, and $ADM_{2.5}$ were investigated. Each experimental condition was conducted in duplicate, with all digesters placed in a constant temperature water bath. To set the TS value to 8%, water was added to the prepared substrate samples. Five digesters with substrate samples, one digester without biochar and four digesters with the addition of biochar were prepared with inoculum. CC-BC450 was amended to AD in a way that a half of each CC-BC450 sample was added to the media through mixing for stability and half was added simply on the head space of the digester for adsorption. The experimental result showed that the cumulative methane production obtained from all digesters were (392.5 mL) for ADM_0, (444 mL) for ADM_1, (486 mL) for $ADM_{1.5}$, (647 mL) for ADM_2, and (540 mL) for $ADM_{2.5}$. Compared with the ADM_0 without any biochar, the cumulative methane production in the AD with (8, 10, 6, and 4 g/800 mL) CC-BC450 was increased to 39.33%, 27.31%, 19.23%, and 11.59% respectively.

Keywords: Anaerobic Digestion, Biogas Production, Slow pyrolysis, Biochar, Corn Cob

TABLE OF CONTENTS

CONTENTS **PAGE**

LIST OF TABLES

TABLES PAGE

LIST OF FIGURES

FIGURES PAGE

ABBREVIATIONS

AD	Anaerobic digestion
BC	Biochar
CC-BC350	Corn cob biochar made at 350 ºC
CC-BC450	Corn cob biochar made at 450 ºC
CC-BC550	Corn cob biochar made at 550 ºC
TS	Total Solids
VS	Volatile Solids
HRT	Hydraulic Retention Time
CD	Cow dung
gVS	Grams of volatile solids
MC	Moisture content
AC	Ash content
C/N	Carbon to Nitrogen ratio
VFAs	Volatile fatty acids
LHV	Lower heating value, KJ/kg
ASTM	American society for testing and materials
IBI	International biochar initiative
HTC	Hydrothermal carbonization
GAC	Granulated activated carbon
PAC	Powdered activated carbon
OLR	Organic loading rate
COD	Chemical oxygen demand
ADM	Mesophilic anaerobic digestion
APHA	American public health association
AS	Activated sludge
NA	Not analyzed
WDM	Water displacement method
GC	Gas Chromatography
BET	Brunauer-Emmett-Teller

NOMENCLATURES

D	Digester diameter	(m)
CT_{swt}	Concentration of TS in fresh discharge by weight	$(kg\,TS/kg\ \ discharge)$
D_H	Hydraulic chamber diameter	(m)
D_{pd}	Discharge per day	(kg/day)
f_1	Upper dome height	(m)
f_2	Sludge layer thickness	(m)
h	Distance between ground surface level and dome top	(m)
h_3	Hydraulic chamber height	(m)
H	Height of fermentation chamber [m]	(m)
H_1	Height of gas layer inside V_3	(m)
N	Number of biomass units or Cows	
R_1	Upper dome radius	(m)
R_2	Bottom radius	(m)
S_1	Area of upper dome	(m^2)
S_2	Area of sludge layer dome	(m^2)
T_d	Total discharge	(kg/day)
T_{ir}	Total influent required	(kg/day)
T_{sfc}	TS of favorable concentration	(%)
T_{sfd}	TS of fresh discharge	(kg/day)
V_1	Upper dome volume	(m^3)
V_2	Sludge layer volume	(m^3)
V_3	Fermentation chamber volume	(m^3)
V_c	Volume of the gas collecting chamber	(m^3)
V_f	Volume of the fermentation chamber	(m^3)
V_H	Volume of the hydraulic chamber	(m^3)
V	Total volume of bio-digester	(m^3)

Vs	Volume of the sludge layer	(m^3)
V_{gs}	volumetric gas storage production rate	(m^3/day)
V_{gs},TS	Volumetric gas storage production rate for TS	(m^3/day)
W_a	Daily water addition	(kg/day)
W_{vd}	Working volume of the digester	(m^3)
Y_{dg}	Volumetric gas yield by TS mass	(m^3/kgT_{sfd})
$Y_{dg,total}$	Total Volumetric gas yield	(m^3/kgT_{sfd})

CHAPTER ONE

INTRODUCTION

1.1 Background of the Study

Today, energy is one of the fundamental needs of society and provides services in various forms like power for transport, lighting, and heating, for cooking, water pumping, and some other services (Pedrasa et al., 2010). Due to an increasing number of populations, industrialization, the availability of contemporary agricultural machinery, and way of life, the energy demand is increasing at an alarming rate. To satisfy the energy need, a massive quantity of fossil fuels are utilized with an antagonistic impact on the environment (Mezmur and Bogale, 2019).

The Ethiopian energy sector continues to predominantly depend on conventional biomass energy and faces the difficulties of limited access to modern energy sources to fulfill the growing demand. Having access to modern energy sources is essential for economic development and livelihood improvement (Reddy, 2015). Access to modern energy supports both income generation activities and the national development agenda through improving education, reducing indoor air pollution, and ensuring environmental sustainability. While Ethiopia has seen dramatic economic growth in recent years, sustaining and continuing this growth into the future will require expansion of energy supply.

In Ethiopia, the current power generation for the electric grid depends almost entirely on hydropower. There are stark differences in the rate of electricity access in urban and rural areas.

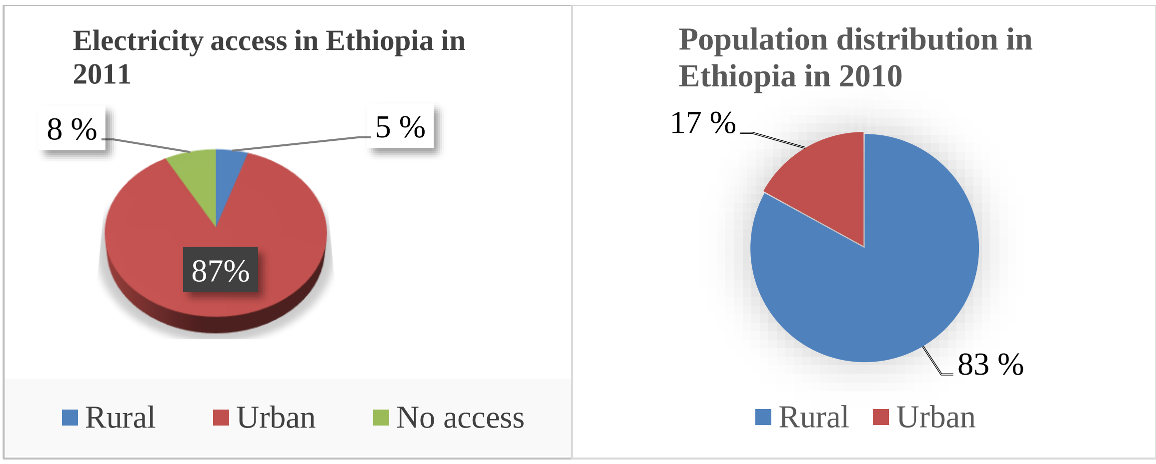

Figure 1.1: Electricity and population distribution (Mondal et al., 2018)

In rural areas of Ethiopia, the primary source of energy for cooking applications is biomass, which accounts for 91% of the energy consumed. About 7% of total primary energy is supplied by petroleum and electricity account for merely 2% of total energy use. The consumption of biomass accounts for over 98% of the total supply in the residential sector. Electricity is mostly used by urban households, small industries and due to the dependence on biomass for cooking, the increase in CO_2 emissions from 5.1 million tons in 2005 to 6.5 million tons have seen in 2010 (Mondal et al., 2018).

Considering all the continents 590–880 million tons of methane is released into the atmosphere through microbial activity each year. About 90% of the emitted methane derives from the decomposition of biomass and the remainder is of fossil origin (e.g. petrochemical processes) (E. Aravindaraj et al., 2017). The reactivity of methane was investigated and reported that, it has more than 20 times the global warming potential of carbon dioxide and that the concentration of it in the atmosphere is increasing by 1-2% per year(Kumar et al., 2004). In Ethiopia, where more than 83% of the population is living in a rural area and most of them are farmers. Thus, by using animal waste, and agricultural waste, it is possible to generate energy for rural communities.

Single-family biogas technology has enjoyed a period of rapid development, and the technology is continuing to mature, with more varieties. Biogas is produced when organic material is decomposed under anaerobic conditions in a digester. Biogas, a high-quality fuel, improves rural life by providing both heat and light. Single-family biogas technology provides rural inhabitants with a convenient and clean form of energy, along with useful by-products such as organic fertilizers. The effluent resulting from aging contain high extents of nitrogen, phosphate, potassium. These fertilizers can stimulate the growth of crops and promote root development, increase the brawniness of the stems, increase the size and yield of the plants, increase the size of individual grains, and accelerate the maturity of crops.

Environmental sanitation and health standards are increased as biogas digestion destroys harmful pathogens such as bacteria and parasites. Feces that have not gone through biogas digestion contain many parasite eggs and bacteria which are the main vectors for diseases in daily life. After digestion, the number of parasite eggs is reduced by at least 95% and the bacteria remaining in the feces will die quickly (Sun Jinshi, 2007).

Typically, impurities such as CO_2, H_2S, and NH_3 are produced during the AD. The impurities lower the caloric content of biogas and cause utility corrosion. Therefore, attempts to remove impurities from raw biogas are also needed. Biogas production shows an increasing trend in recent years. So, biogas upgrading had been researched extensively in recent years (Mezmur and Bogale, 2019). However, current costs for conventional upgrading technologies are too high to justify investments at the low biogas flows obtained from small scale biogas production (Bauer et al., 2013). To reduce this cost, simple and energy-efficient CO_2 and other contaminants reduction systems are required. One promising method in the reduction of biogas impurities is adsorption using biochar.

Biochar is a charcoal product produced from plant-derived biomass that is subjected to thermal treatment in the partial or total absence of oxygen. The thermal treatment changes the microstructure of the particles to form an aromatic-aliphatic region and a crystalline region, which are made up of different pore sizes based on their internal diameter. These pores are responsible for the adsorptive behavior of biochar for compounds such as phosphate, nitrate, nitrite, ammonium, metals, pesticides, and carbon dioxide. The sorption mechanisms of a biochar material are similar to other adsorbents (activated carbon, zeolite, and bentonite (Zhang et al., 2012). Different types of biochar have been used in the study of the reduction of biogas impurities such as H_2S and ammonia. However, up to now, there are limited studies on the reduction of biogas impurities such as carbon dioxide. In this study through various considerations, increasing methane yield from anaerobic digestion of cow dung with corn cob derived biochar was proposed and has been tested.

1.2 Statement of the Problem

According to the present scenario of Ethiopia, most regions of the country particularly rural areas don't have access to electricity and there is no balance between demand and supply for those regions having access to electricity. Due to this reason, most people use conventional fuel such as firewood leading to depletion of conventional fuel, deforestation, indoor air pollution, and greenhouse gas emission. Also, 90% of methane is emitted into the atmosphere from the decomposition of biomass and contributes to global warming due to difficulties associated with the burning of organic wastes (E. Aravindaraj et al., 2017). Biochemical conversion of biowastes to biogas through AD has received increasing attention in recent years.

Raw biogas is mainly a combination of carbon dioxide, methane, and unwanted gases that causes a reduction in energy efficiency from it. The barrier that limits biogas utilization is due to the presence of CO_2 in biogas which is a non-combustible gas. The presence of CO_2 lowers the calorific value and the specific energy density of biogas. Furthermore, CO_2 reduces its flame speed and the extent of flammability in comparison to natural gas. So that alternative approaches are required to upgrade the biogas to methane-rich biogas by reducing the CO_2 and other contaminants within the digester. In this study addition of biochar prepared from locally available feedstock is used to upgrade the quality of biogas and increase its heating value by reducing pollutants like carbon dioxide, hydrogen sulfide and to avoid inhibitory stages during the processes, enhancing the quality of generated biogas to achieve higher methane concentration with fewer contaminants, and increasing system stability to potentially enable processing of the substrate.

1.3 The Objective of the Study

1.3.1 General objective

The general objective of this study is to upgrade the quality of biogas using corn cob derived biochar from the digestion of cow dung for household cooking applications in rural areas.

1.3.2 Specific objectives

The specific objectives are to:

- Estimating biogas fuel required for household consumption having ten members
- Sizing the digester depending on the amount of biogas.
- Development of laboratory-scale biogas production unit on a batch basis.
- Characterization of the substrate and establish mixture for feed.
- Produce biogas using a laboratory-scale biogas production unit and measuring methane production.
- Investigate the effect of biochar in gas yield and in reducing pollutants.

1.4 Scope of the Study

The scope of this study was aimed at the production of biochar, utilization of biochar in AD and to investigate the effects of biochar addition concentrations on the gas yield and gas production rate as well as gas quality in mesophilic anaerobic digestion of cow dung within a lab-scale batch operation.

1.5 Limitations of the Study

The limitations of this study are: -

The lack of accessibility of laboratory equipment such as BET, GC, and water bath.

Pilot-scale biogas production is not conducted due to cost insufficiency.

1.6 Significance of the Study

This research significantly reduces the costs associated with biogas upgrading could improve the overall economics of energy production from waste relative to other commercial upgrading methods, reducing the barrier to entry and opening it up to smaller-scale waste treatment facilities. AD usually creates biogas that is mainly a combination of carbon dioxide and methane, and extra steps are required to upgrade the biogas to renewable natural gas by removing the CO_2 and other contaminants.

However, adding biochar directly to the anaerobic digester sequesters the CO_2 and may create a biogas stream that is more than 90% methane and less hydrogen sulfide, thus reducing the need for upgrading steps. The biochar is used to improve the operating conditions for anaerobic digestion, and it is nutrient-rich, so the effluent left after the process is completed can serve as a high-quality fertilizer. This approach would also offer improved process economics, reduced barriers to entry, and reduced greenhouse gas emissions over the production of fertilizers. More importantly, the reduction of upgrading steps alone could make many smaller biogas projects profitable.

1.7 Research Focus

The core of this research problem under study can be best pronounced by testifying the following research questions: -

- Why most farmers in Ethiopia did not produce and use biogas?
- What are the reasons for biogas production?
- Most of the time biogas users use biogas for cooking. Why only for short period?
- Does the addition of biochar improve methane yield?
- Which concentrations of biochar with the substrate produces the highest methane?
- What are the major factors affecting methane yield?
- Does variation in the amount of biochar added to the digestion process affect biogas production? These research questions have been addressed in the following chapters.

1.8 Organization of the Study

There are seven chapters in this thesis as presented in Figure 1.2. using a schematic map.

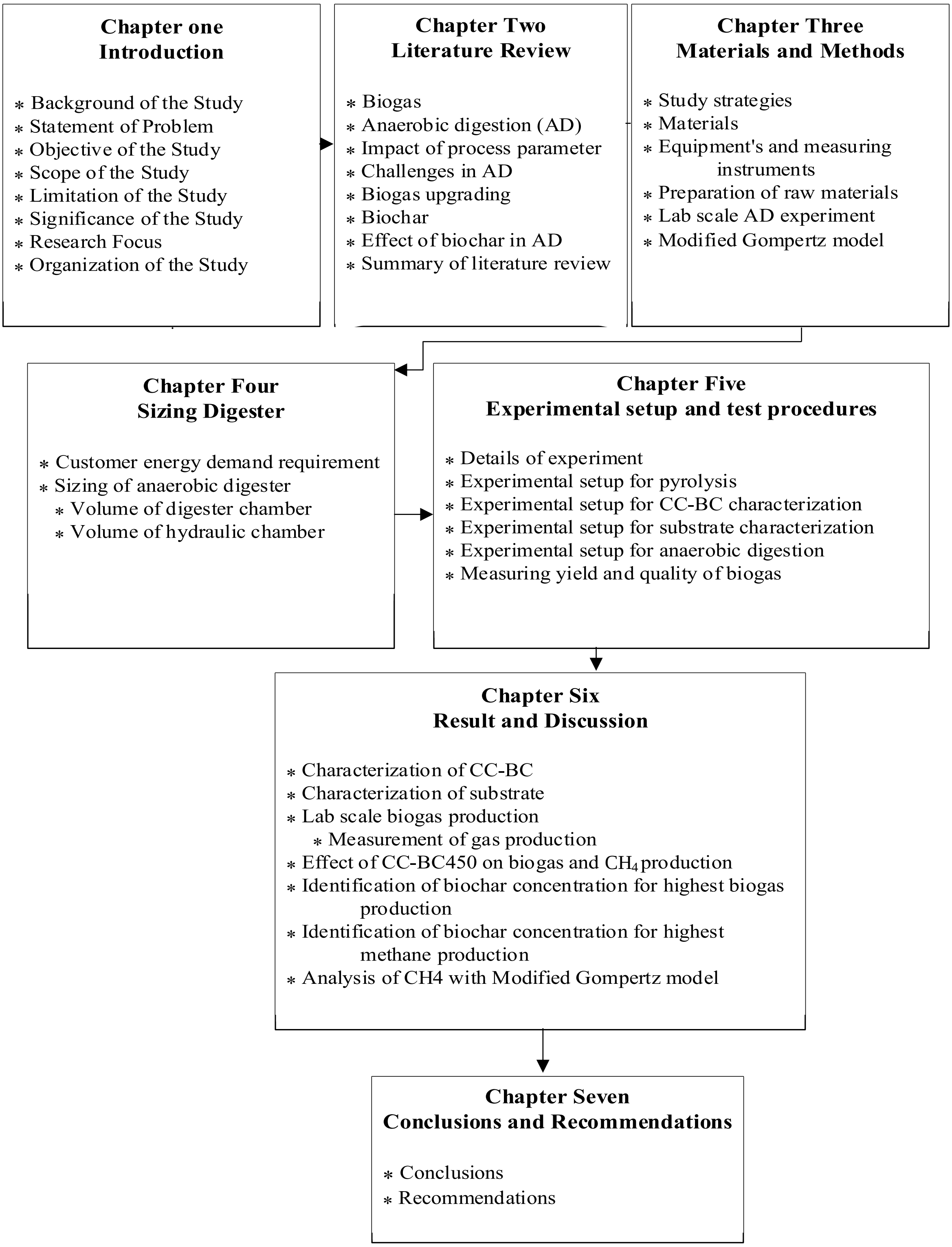

Figure 1.2: Thesis map

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

This chapter reviews the fundamentals and state of knowledge relating to AD. Existing studies of biogas technology, factors affecting biogas production, and biochar utilization in AD are reviewed and, in the end, the gaps of the studies are depicted.

2.2 Biogas

Biogas originates from biogenic material and is a sort of biofuels, regularly alluded to as a gas delivered by bacteria fermentation of organic material under anaerobic conditions (without oxygen). As seen by Buren (1983), biogas is a combustible gas delivered by microorganisms when organic materials are fermented in a certain range of temperatures, moisture contents, and acidities, under airtight condition. Biogas is viewed as an inexhaustible source of energy since the raw materials are continually recovered (Maria Berglund, 2016).

2.2.1 Biogas composition

The principal constituents of raw biogas delivered by the anaerobic digestion are methane and carbon dioxide with various quantities of contaminants, for example, ammonia (NH_3), water vapor, hydrogen sulfide, carbon monoxide, and hydrocarbons. These contaminant's presence and quantities depend largely on the biogas source, which could be anaerobic digestion of numerous substrates and landfill decompositions.

The composition of gas fluctuates with the raw material used. Methane has a large share within the biogas composition with (40–75)%, followed by CO_2 with (25–55)% (Kadam and Panwar, 2017). The main components of biogas are methane (50–75%) and carbon dioxide (25–50%) (Maghanaki et al., 2013). Biogas contains methane (60–70%), carbon dioxide (30–40%), and trace gases such as hydrogen sulfide (H_2S). The CH_4 in biogas can be exploited as a renewable energy source for the production of heat and electricity, or use as a vehicle fuel (Awe et al., 2017).

Table 2-1: Composition of biogas and natural gas (Kadam and Panwar, 2017)

Composition, (%)	**Biogas**	**Natural Gas**
Methane	40–75	87–97
Carbon dioxide	25–55	0.1–1.0
Hydrogen sulfide (ppm)	50–5000	NA
Ammonia	0–1	NA
Water	0–10	NA
Nitrogen	0–5	0.2–5.5
Oxygen	0–2	0.01–0.1
Hydrogen	0–1	0.02

The removal of the contaminants especially H_2S and CO_2 will significantly improve the quality of the biogas for its further uses.

Table 2-2: Impact of Carbon dioxide and other trace elements on biogas utilization

Trace elements	**Biogas**	**Impact on biogas utilization**
Carbon dioxide, (%)	30–40	Decreasing calorific value, anti-knock properties of engines, and corrosion.
Nitrogen, (%)	0–5	Decreasing calorific value, anti-knock properties of engines, and corrosion.
Hydrogen sulfide, (ppm)	0–4000	Corrosion, emission, and health hazards.
Ammonia, (ppm)	100	Emission, anti-knock properties of engines, and corrosion when dissolved.

2.2.2 Biogas characteristics

Biogas is about 20% lighter than air and has an ignition temperature in the range of 500℃ to 750℃. It is an odorless and colorless gas that burns with a clear blue flame like that of LPG gas. The estimated calorific value of 1 m^3 is about 22 MJ if burns with 60% efficiency (Raja and Wazir, 2017). The lower heating value of biogas ranges from 15 to 30 MJ/Nm^3 and is lower than that of natural gas, which is around 36 MJ/Nm^3 (Awe et al., 2017). Each cubic-meter of biogas has the same thermal output as 0.6–0.7 kg of diesel or the heating capacity of 2.3 kg of coal which can heat 65 liters of water from 20℃ to boiling. Alternatively, 1 m^3 of biogas can light a biogas lamp (equivalent to a 60 W light bulb) for 6 to 7 hours or keep an internal combustion engine of 1 horsepower running for 2 hours or produce 1.25 kWh of electricity (Sun Jinshi, 2007).

Table 2-3: Characteristics of biogas from AD

Parameters	Unit	Biogas from AD		
Lower heating value	MJ/Nm^3	23	22	-
	KWh/Nm^3	6.5	-	5.0–7.5
	MJ/kg	20	-	-
Density	Kg/Nm^3	1.1	-	1.2
Ignition point	°C		500–750	700
References		(Awe et al., 2017)	(Raja and Wazir, 2017)	Demirbas, and Balat, M. (2009)

2.2.3 Sources and potential feedstock's for biogas production

Biogas can be produced from any organic waste with suitable VS content through AD under certain process parameters. All sorts of biomass can be utilized as substrates for biogas generation as long as they contain carbohydrates, proteins, fats, cellulose, and hemicelluloses as primary components.

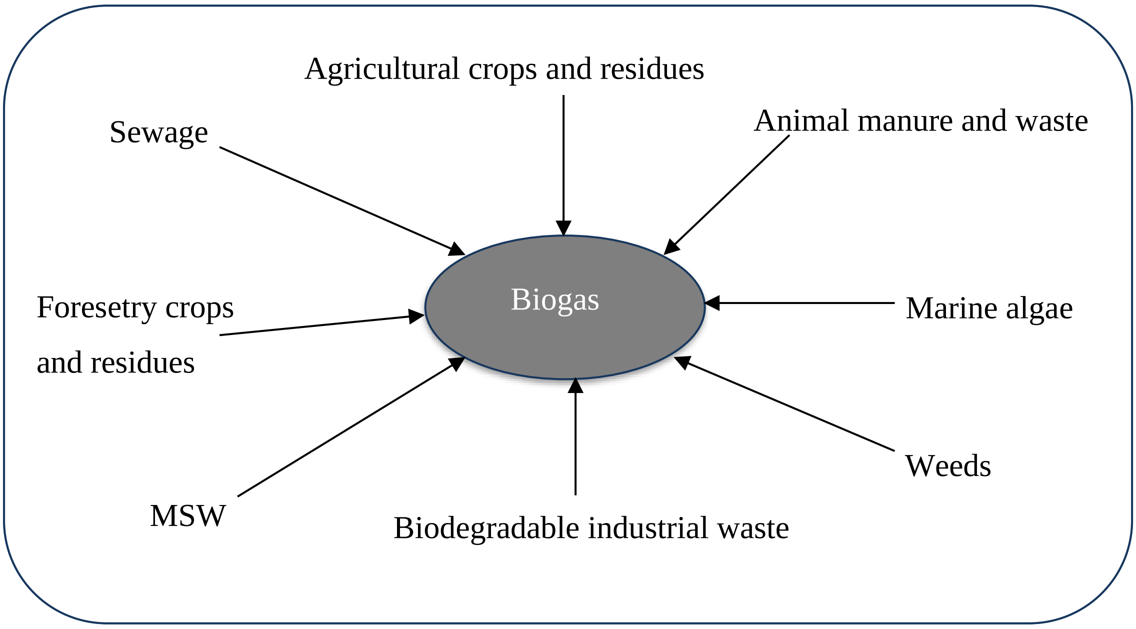

Figure 2.1: Examples of substrates anaerobically digested to generate biogas

The composition of biogas and the methane yield relies upon the feedstock type, the digestion system, and the retention time. Only strong lignified organic substances, e.g., wood, are not suitable due to the slowly anaerobic degradation. The digestion of raw material with high-fat content can provide a higher gas yield and a higher proportion of methane than the digestion of raw material rich in carbohydrates (Maria Berglund, 2016). The most widely recognized farming biomass that is utilized as substrate (feedstock) in biogas digesters is CD, because of its natural content of anaerobic bacteria, high energy content, high water content, and high availability (Deublein and A. Steinhauser, 2011).

2.3 Anaerobic Digestion

Anaerobic digestion is a simple technology broadly utilized for handling biodegradable, organic waste for biogas production. AD has been considered as waste-to-energy technology and is widely used in the treatment of different organic wastes, for example, organic fraction of municipal solid waste, sewage sludge, food waste, animal manure, etc. (Abubakar and Ismail, 2012).

2.3.1 The biochemical process of anaerobic digestion

The biogas production process involves multiple related biochemical processes with microorganisms in the absence of air that work together to achieve the degradation of organic matter into methane and carbon dioxide. The four anaerobic processes of hydrolysis, acidogenesis, acetogenesis, and methanogenesis run simultaneously in the AD.

The first stage is hydrolysis, in which the complicated components and molecules are converted into simpler molecules and components. In this state, the complicated carbohydrates, lipids, and proteins are transformed into simpler sugar molecules and/or amino acids, and further fatty acids. Small amounts of biogas are formed and gas generation increases until it reaches its peak during the fourth step of methanogenesis. Figure 2.2 shows a simplified diagram of the biochemical process of AD (Sunyoto, 2019).

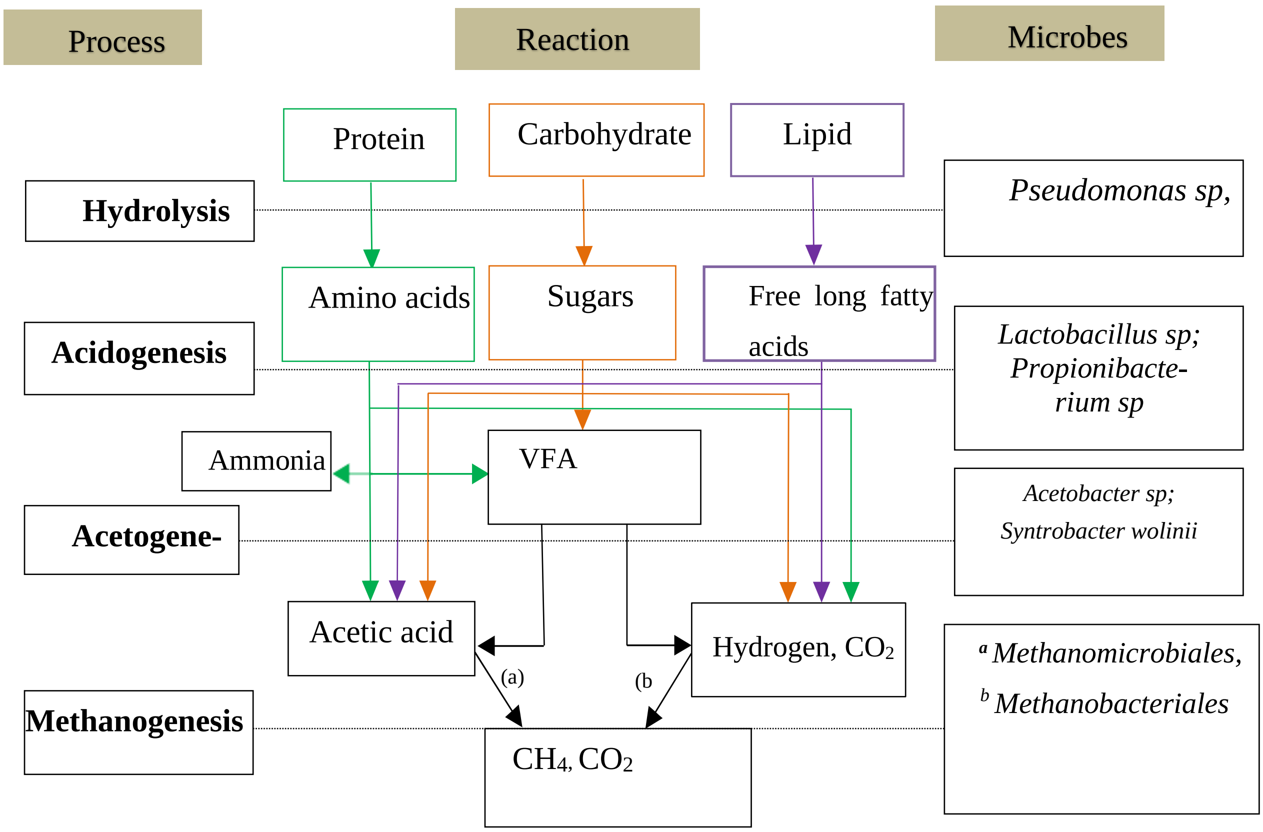

Figure 2.2: The fundamental process of AD (Sunyoto, 2019)

In the next stage, i.e. the acidogenesis stage, the resulting materials are transformed into volatile fatty acids, hydrogen, and carbon dioxide. The volatile fatty acids continue to be converted to hydrogen, carbon dioxide, and acetic acids in the acetogenesis stage, and finally, the methanogenesis stage decomposes the hydrogen, carbon dioxide, and acetic acid, and produces methane (Abatzoglou and Boivin, 2009; Demirbas and Balat, 2009).

2.3.2 The biochemistry of the anaerobic digestion process

The formation of methane, ammonia, hydrogen sulfide and carbon dioxide follow the general equation when biomass is chemically broken down to produce biogas biogas (Deublein, D., and Steinhauser, 2011). This equation depicted that; water content is one of the very important parameters affecting AD of solid wastes. Because water makes possible the movement and growth of bacteria facilitating the dissolution and transport of nutrients; and water reduces the limitation of mass transfer of nonhomogenous or particulate substrate.

$$C_cH_hO_oN_nS_s + y.H_2O \rightarrow CH_4 + n.NH_3 + s.H_2S + (c-x).CO_2$$

$$\text{Where, } x = \frac{1}{8}(4c + h - 2o - 3n - 2s) \tag{2.1}$$

$$y = \frac{1}{4}(4c - h - 2o + 3n + 2s)$$

The building blocks from which biogas is produced include carbohydrates, fats, and proteins as given by the following equation:

$$\text{Carbohydrates: } C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4 \tag{2.2}$$

$$\text{Fats: } C_{12}H_{24}O_6 + 3H_2O \rightarrow 4.5CO_2 + 7.5CH_4 \tag{2.3}$$

$$\text{Proteins: } 3H_{25}O_7N_3S + 6H_2O \rightarrow 6CO_2 + 6.5CH_4 + 3NH_3 + H_2S \tag{2.4}$$

Some of the sulfur binds with hydrogen to form H_2S while some remain in the residue of the effluent. A part of the carbon dioxide molecules binds to the ammonia molecules. The theoretical CH_4: CO_2 ratio of biogas is 71%:29%, but the actual ratio of methane to carbon dioxide is highly dependent on the composition of the biomass used in the AD process. The following steps indicate the Gibbs free energy balance when biogas is produced. The energy is originally captured during photosynthesis and stored in the organic biomass as described in the following steps (Deublein and Steinhauser, 2011):

$$CO_2 + H_2O + solar\,energy \rightarrow CH_2O + O_2 \tag{2.5}$$

$$carbondioxide + water + solar\ energy \rightarrow carbohydrate + oxygen$$

The following Gibbs free energy balance equation illustrates the release of energy and the degradation of organic biomass into biogas (Deublein and Steinhauser, 2011):

$$\text{Carbohydrate: } \mathrm{CH_2O} \rightarrow 0.5\ \mathrm{CH_4} + 0.5\ \mathrm{CO_2} \tag{2.6}$$

The solar energy stored through photosynthesis is released through the combustion of methane and oxygen that produces carbon dioxide and water as products (Deublein and Steinhauser, 2011):

$$0.5\ \mathrm{CH_4} + \mathrm{O_2} \rightarrow 0.5\ \mathrm{CO_2} + \mathrm{H_2O} \tag{2.7}$$

This closes the energy loop of the AD process. AD bio-reactions release very little heat during the fermentation process; thus, the digester must be heated and thermally well-insulated. Theoretically, the energy that is released during the combustion of biomass corresponds to the sum of the energy set free in the production of biogas plus the burning of methane. This energy is equal to the energy that was needed for photosynthesis.

2.4 Impact of process parameters on biogas production

Biogas production systems are multifaceted and complex, due to several factors such as pH, temperature, retention time, seeding, and total solid content.

2.4.1 Effect of pH value

pH value is the main factor in AD and the development of microbes and the survival of methanogenic bacteria during AD depends on the acidity of the environment that they require a near-neutral pH. pH levels that are too high or too low inhibit the growth of methanogenic microorganisms, which then reduces the production of biogas. The optimum pH level for methanogens to form methane is between 6.7 and 7.5 (Deublein and Steinhauser 2011).

Cattle manure is suitable for AD to produce biogas as it has a pH level of 7.5 that is within the optimal range of pH (Derikx et al., 1994). The AD process is severely inhibited when the pH level decreases to below 6.5 (acidic) and rises above 8.5 (alkaline). The higher volatile fatty acids are converted into acetate and hydrogen by obligate hydrogen-producing acetogenic bacteria. The accumulation of hydrogen can inhibit the metabolism of acetogenic bacteria (Raja and Wazir, 2017).

Bah *et al.* (2014) investigated the effect of pH in the range of 6.9-8.9 on the anaerobic co-digestion of palm pressed fiber and cattle manure to obtain the best condition for the activity of methanogenic microorganisms. They found that the optimum pH range was 6.9-7 at which, the highest methane production yield was achieved.

T. Zhang *et al*. (2015) examined the effect of initial pH value on methane production and under the thermophilic condition of anaerobic co-digestion of swine manure and maize stalk. Different initial pH at five levels (6.0, 6.5, 7.0, 7.5, and 8.0) with NaOH, HCl acid and three different manure ratios were tested. The result showed that at different initial pH a diverse methane production after 35 days was achieved. Also, the result revealed that the optimum pH was 6.81 with a 70% swine manure ratio.

Neshat *et al*. (2017) investigated the optimum pH for anaerobic digestion of cotton stalk, and cattle manure, either as sole substrate or co-substrate, was determined as 6.5. They expected lower pH levels in co-digestion wherein the concentration of VFAs was much higher than mono-digestion; however, because of the buffering capacity of manure, pH level did not change significantly.

Zhai *et al*. (2018) studied the effects of different initial pH (6.0, 6.5, 7.0, 7.5, and 8.0) and uncontrolled initial pH on co-digestion of kitchen waste with cow manure. They found that initial pH can affect pH variation during AD, VFA concentration, alkalinity, and ammonia concentration. They emphasized the significance of initial pH on AD and reported pH the optimum pH for their system was 7.5. Generally, acidification of the medium is one of the reasons for the failure of anaerobic digestion which can take place as a result of the presence and accumulation of VFAs at very initial stages of digestion (startup period).

2.4.2 Effect of temperature

Temperature is one of the most influential parameters which affect the performance and stability of AD. Anaerobic digestion can take place in all temperature regimes (Mattocks, 1984): psychrophilic bacteria range (less than 288K), mesophilic bacteria range (between 302K and 313K), and thermophilic bacteria range (323K–328K). Temperature variations can affect hydrolytic bacteria, acidogenic bacteria, and methanogenic bacteria. Deviation from optimum temperature can cause acidification due to the accumulation of VFAs. Methanogenic bacteria cannot also tolerate temperature fluctuations over 274 K/d.

Working at thermophilic conditions above 318 K can enhance the performance of AD because of the higher solubility of organic compounds, higher biochemical reaction rates, lower liquid viscosity, higher pathogen deactivation, and less odor emission (Buhr and Andrews, 1977). Suitable operating performance, stability, and less sensitivity to inhibitors are considered as the advantages of mesophilic operations (298–313) K.

Angelidaki and Ahring, (1994) investigated the effect of temperature in the range of 313-337 K, on thermophilic anaerobic digestion of cattle manure with two different ammonia concentrations (2.5 and 6.0 g/L) in continuously fed lab-scale digesters. When the ammonia load was high, the reduction of the temperature below 328K increased the biogas yield and better process stability, indicated by a lowering of the concentration of volatile fatty acids in the effluent.

Adelekan and Bamgboye, (2009) suggested that anaerobic bacteria communities can endure temperatures ranging from below freezing to above 330.2K, but they thrive best at temperatures of about 309.7K (mesophilic) and 327.4K (thermophilic). Bacterial activity, and biogas production, falls off significantly between about 312.4K and 324.7K and gradually from 308K to 273K. To optimize the digestion process, the digester must be kept at a consistent temperature as rapid changes will upset bacterial activity.

Sánchez *et al*. (2005) found biogas production to be greatest when the digester temperature was in the range of 305K to 313K. During the process of AD to reach optimum operating temperatures (303–310) K, some measures must be taken to insulate the digester, especially in high altitudes or cold climates. Straw or shredded tree bark can be used around the outside of the digester to provide insulation.

2.4.3 Effect of total Solid

Total solids concentration is a measurement that includes the combination of total dissolved solids and total suspended solids. TS test determines how much of the cow manure is composed of water and how much of the cow manure is solid. It also helps to identify whether the AD process is wet or dry. In wet digestion, the total solids content in the bio-digester is usually less than 15%, while in dry digestion the total solids in the digester feed are (15–40) %. Wet digestion is easier to regulate in terms of different process parameters, for example by pH and dry matter content (Deublein and Steinhauser, 2011). Due to the greater water content, wet digestion offers better mixing possibilities.

Mattocks, (1984) pointed that the percentage of TS should be between 5% and 12% while other source reported that the best biogas production occurs when TS is ranged from 7% to 10% because of avoiding solids settling down or impeding the flow of gas formed at the lower part of the digester. Therefore; dilution of organic substrate or wastes with water to achieve the desirable total solids percentage is required. The most favorable TS value is 8 % for better biogas production (Mukumba et al., 2017).

2.4.4 Hydraulic retention time

Hydraulic retention time is the average duration of time holding slurry in the digester. The retention time must be long enough to ensure that the number of microorganisms produced in the digester exceeds the microorganisms removed in the effluent. If the process could not be maintained at its optimum HRT, the unfavorable metabolic activity of microorganisms and undesirable products will have resulted. Long HRTs can lead to the death of microorganisms due to the shortage of nutrients; in contrast, short HRTs can result in cell intoxication or low methane yield. At high temperatures, a reaction occurs fast and so the degradation will also be faster and HRT will be less. A 25-day HRT is recommended for effective AD of organic matter under mesophilic conditions (Salminen and Rintala, 2002). The shorter HRT provides good substrate flow but delivers low biogas yields due to the microorganisms escaping in the effluent.

2.4.5 Seeding

To start and accelerate fermentation processes, a small amount of digested slurry, containing methane forming bacteria is added to the freshly charged plant. Seeding the digester speeds up the time required for digester start-up by inputting a population of anaerobic bacteria. Seeding the digester may be done in a few different ways. The most preferable method of seeding the digester is to obtain biosolids from a nearby operating digester. There may not be any digesters nearby, so this may not be possible. Another method of seeding the digester is to obtain microorganisms from the stomachs of cattle.

2.4.6 Summary of factors affecting the anaerobic digestion process

Several factors affecting biogas production discussed in various studies should be optimized for good biogas yield. According to all the factors that are mentioned above the suitable condition for the production of biogas with stability can be achieved when the temperature for the biogas production ranges from (310–330)K, pH for the suitable anaerobic digestion of the biogas is 6–8, TS concentration required ranges from 5%–9% and HRT should be higher for more micro-organisms to develop in biomass.

2.5 Challenges in Anaerobic Digestion

The AD process, despite being a matured approach for organic waste management, is still affected by three major limitations. Process stability, efficiencies, and product quality (impacted by instabilities induced by highly degradable organic substrates), management of effluents and emissions (volume of effluent and the degradation of input substrate that determines emission levels of CH_4 from the effluent) and the flexibility of an acceptable substrate (related to the inability to digest highly lignocellulose biomass without pretreatment).

2.6 A Conventional Approach for Alleviating the Challenges with AD

Predictable approaches mostly implemented to reduce the challenges in the AD process are alkaline chemical addition, two-stage digestion, and co-digestion. The application of alkaline chemicals reduces acid levels in the AD, thereby neutralizing the acidification process (Gao et al., 2015).

Two-stage digestion is another viable approach that promotes different types of oxidation and reduction reactions, pH optimal, and growth rate of acidogenic and methanogens. The two-stage approach has the advantage of hydrolyzing the substrate and buffering OLR in the first stage. In the second stage, the hydrolyzed and the homogenized substrate can be easily digested by the methanogens (Sunyoto, 2019).

Co-digestion is the simultaneous digestion of a homogenous mixture of two or more substrates. Substrates as food wastes, sewage waste, cattle manure, certain energy crops, and algae are good bases to obtain processes with good nutrient and trace element balances. These kinds of substrates can often be implemented for "mono-substrate" digestion, while substrates dominated by carbohydrates or fats need to be co-digested or digested in processes modified by e.g. nutrient and trace element additions, sludge recirculation (Alemu Gizaw Wakene, 2016). The microbial population in the digester and biogas yield is partly dependent on the ratio of the different types of waste within the substrate mix (Lin *et al*., 2012).

2.7 Biogas Upgrading

The utilization of biogas produced from organic materials such as agricultural wastes or manure is increasing. The deficiency with using biogas is also due to the presence of CO_2 (a non-combustible gas) in biogas lowers the calorific value and the specific energy density of biogas. Furthermore, it reduces its flame speed and the extent of flammability in comparison to natural gas (Budzianowski, 2016). These challenges affect the sustainability of biogas, and therefore, biogas upgrading which results in biogas with comparative properties to natural gas is an alternative pathway.

Seadi *et al*. (2008) state that after upgrading, biogas can be utilized as vehicle fuel or injected into the natural gas network used as natural gas. The upgrading will reduce all contaminants with certain concentrations such as carbon dioxide and hydrogen sulfide, through which the content of methane will be increased from the average 50-75% to more than 95%.

2.7.1 Challenges in small-scale biogas upgrading

(Andersson and Nordberg, 2017) reported that the value of the biogas produced at small scale facilities can be increased by upgrading it to vehicle fuel quality. However, commercial upgrading technologies available today are very costly for small scale applications. To upgrade biogas on a small scale (less than 200 Nm^3/h) has been too expensive to be interesting, due to the high specific investment costs of the upgrading equipment. For a plant with low capacity, more or less the same number of sensors, analysis equipment, control systems, and valves are needed as for a plant with a much larger capacity. The dimensions of the pipes and valves will be smaller, but the specific investment cost will be high.

2.7.2 Upgrading biogas within AD (An approach used in this study)

The existing literature suggests the need to improve the performance and biogas yields of AD through conventional approaches and commercial upgrading technologies. But conventional approaches do not comprehensively address the challenges in AD. Therefore, one possible solution to address the challenges is by utilizing biochar in AD operation.

The combination of pyrolysis and AD, as shown in Fig. 2.3, is increasingly seen as a relatively unconditional but promising approach to address these challenges. Pyrolysis can be used to valorize high lignocellulose biomass and effluent from AD. The present focus of this study is on the effect of biochar in AD to improve process stability through the reduction of substrate-induced inhibition and its effect in increasing the concentration of CH_4 (upgrading) in biogas.

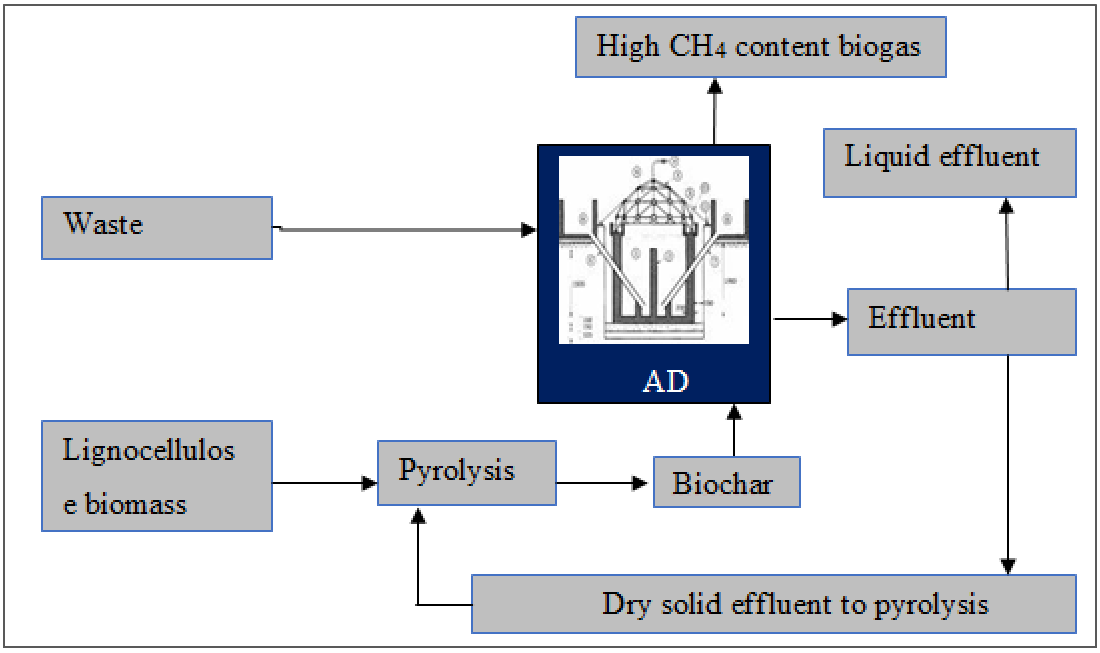

Figure 2.3: Process schematic for an AD process integrated with pyrolysis

2.7.3 Biochar

Biochar, the solid product of biomass pyrolysis, has been produced and utilized for several thousand years. According to the International Biochar Initiative (IBI), biochar is a stable and solid carbon-rich material obtained from the thermochemical conversion of biomass in an oxygen-limited environment without any form of activation (IBI 2012).

2.7.3.1 Biochar production, properties, and application

The thermochemical conversions of biomass usually used to produce biochar are pyrolysis and hydrothermal carbonization (HTC). Pyrolysis is the most well-known method in biochar production within the temperature of 200–1000℃ with little or no oxygen. Depending on temperature and residence time pyrolysis can be fast pyrolysis, where residence time is only seconds, and slow and intermediate pyrolysis, where residence time is from a few minutes to several hours or even days (Mohan et al., 2006).

Figure 2.4: Biochar (https://www.google.com/lewisbamboo.com)

Two special cases of pyrolysis are Torrefaction, which is mild pyrolysis in the temperature of 230–300℃, and gasification that happens in the temperatures above 800℃ in a controlled oxygen/steam environment and results mainly in gaseous end-products (Mohan et al., 2006). Biochar made from different materials with different methods have unique properties, and one type of biochar may not be suitable for all purposes. The most important properties governing the use of biochar are surface area, pore size distribution, and ion exchange capacity.

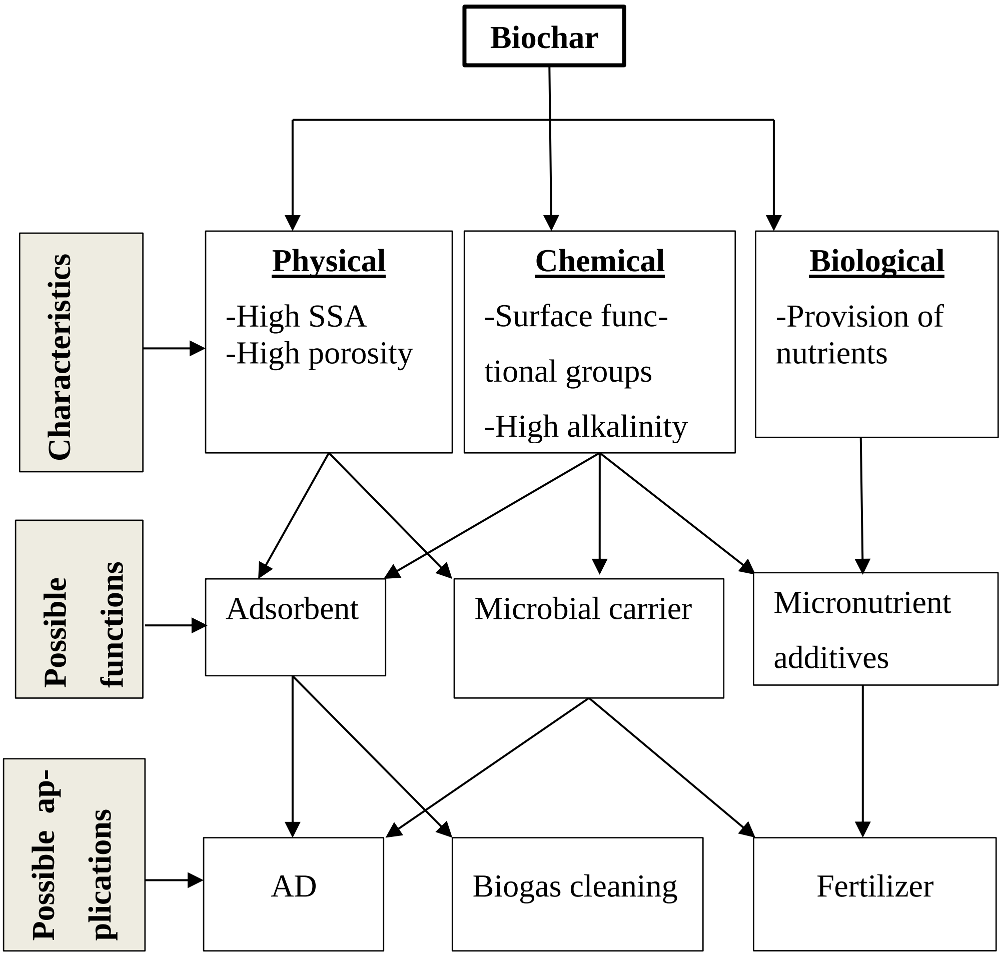

Figure 2.5: The characteristics, functions, and applications of biochar (Sunyoto, 2019)

Generally, the high pyrolysis temperatures favor biochar that is effective in adsorbing organic contaminants by increasing surface area, micro porosity, and hydrophobicity. On the other hand, biochar produced in low temperatures is better in removing inorganics and polar organic compounds by ion exchange capacity, electrostatic attraction, and precipitation (Ahmad et al., 2014).

Biochar production methods and estimated differences in biochar yields obtained from different methods are shown below in fig. 2.6 (Igalavithana et al., 2018). The figure shows that slow pyrolysis favors the production of biochar; and this is derived from solid biomass. Hydrothermal carbonization produces hydro char from sludge materials; while gasification favors the formation of the gaseous-phase products.

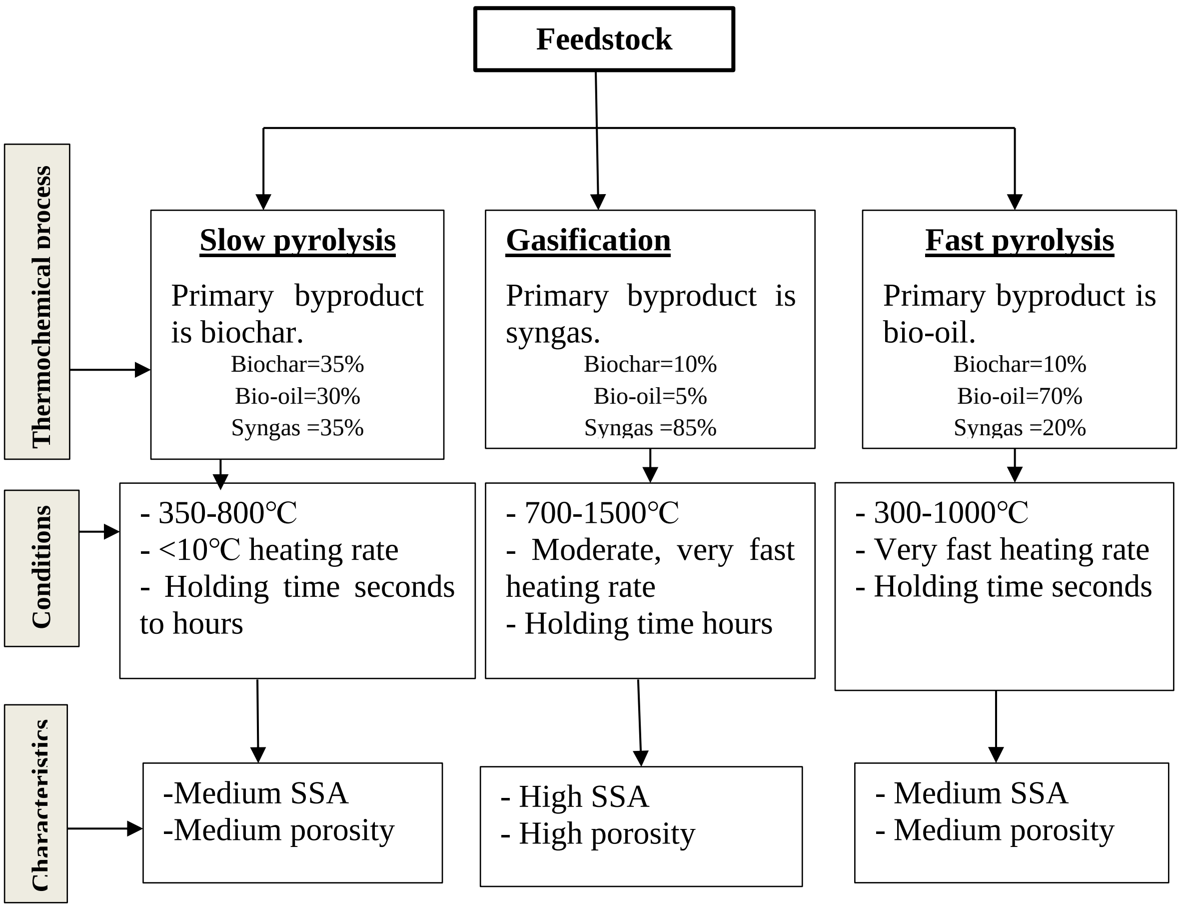

Figure 2.6: Biochar production methods and biochar yields (Igalavithana et al., 2018).

2.8 Effect of Biochar on the Anaerobic Digestion System

Biochar with its above-mentioned valuable characteristics for a wide range of applications therefore becomes an innovative aspect of this study. From carbon-based conductive materials, carbon-based activated carbon (AC) and biochar can be produced from agricultural waste. Their porous and bio-stable structure supports the formation of slow-growing methanogens, ensuring methanogenesis (Mumme et al., 2014).

Compared with AC, biochar is more easily produced at a lower pyrolysis temperature without activation (Luo et al., 2015). Biochar addition can also increase alkalinity, which was important to allow the AD system to buffer against acid shock and maintain a suitable pH range, and mitigate ammonia inhibition and facilitate CO_2 sequestration during AD (Li et al., 2017; D. Wang et al., 2017).

According to recent studies (Mumme et al., 2014b; G. Wang et al., 2018), the alkaline nature of biochar can enhance methane production by an increase in pH resulting from the conversion of CO_2 to carbonate. Improved buffering capacity can improve digester stability through alleviation of pH drop caused by the accumulation of VFAs.

Carbon materials such as activated carbon (AC), graphite, and biochar have been used for stimulating microbial activity in AD. The adsorption of inhibitory compounds by AC also enhanced the performances of the AD process (Xu et al., 2015). Despite these advantages, the application of AC to AD has been limited since direct disposal of AC would cause additional concerns for environmental pollution and safety (Luo et al., 2015).

Biochar could be a cost-effective material to stimulate microbial activities in AD due to its physical and chemical properties (i.e., biostability, porous and carbonaceous surface with various functional groups). These properties of biochar are similar to those of AC except the lower surface area of biochar than AC. Biochar provides favorable conditions for the microbial community in various ways. Physical characteristics, especially porous structure, and surface area facilitates biofilm formation which can improve resistance ability to various inhibitory compounds and can enhance microbial activity (Lü et al., 2016); (Luo et al., 2015).

2.8.1 Biochar as ammonium adsorbents

The ability of biochar to remove ammonium ions from matrices with high concentration has been addressed in a few studies. This would be beneficial in anaerobic digestion since adsorbing ammonium ions on to biochar could reduce the effects of ammonia inhibition.

Kizito *et al*. (2015) studied the adsorption of ammonium nitrogen from piggery manure anaerobic effluent slurry with slow pyrolyzed wood and rice husks. The adsorption was studied in leachate water separated from piggery slurry and in pure NH_4Cl - solution. They found out that the maximum adsorbed amount and removal percentages by wood biochar were 54.84 mg/g (73%) from pure solution and 44.64 mg/g (60%) from piggery slurry and with rice husk biochar 44.64 mg/g (60%) and 39.8 mg/g (53%) respectively. The initial ammonium concentrations were 1400 mg/L and added biochar concentrations 1–20 g/L.

Sarkhot *et al*. (2013) studied the effectiveness of biochar to adsorb ammonium from dairy effluent (ammonium concentration 0–1000 mg/L, biochar concentrations 5 g/L) and they found out that up to 5.3 mg/g (18%) of ammonium was adsorbed by the biochar.
Zhu *et al*. (2012) studied the removal of ammonium from aqueous solution by using activated carbons made from rice husks with initial ammonium concentrations of 40 mg/L and showed that the adsorption varied between 2.04 and 0.97 mg/g depending on the biochar concentrations (1–20 g/L).

The difference between the biochar's ability to adsorb ammonium ions can depend on various factors.

According to (Kizito et al., 2015) increase in initial ammonium concentration, temperature, smaller particle size, and contact time increase the adsorption. The adsorption decreased in low and alkaline pH and the best adsorption was found in the range of 6.5–7. The decrease in alkaline conditions can result from the conversion of ammonium to ammonia, which cannot be adsorbed very well onto biochars. The manufacturing and feedstock also have a significant role in biochar characteristics (Ahmad et al., 2014), and especially biochar made in lower temperatures (250–400)℃ has been found suitable for removing inorganic and polar contaminants.

2.8.2 Biochar concentration in AD

The amounts of biochar applied to anaerobic digesters in previous studies have some variations and the experiments have been done in wet conditions.

Luo *et al*. (2015) studied the effect of the addition of 0.5–1 mm biostable biochar (10 g/L) to mesophilic anaerobic digesters inoculated with crushed granules (1 g-VS/L) and fed with 4, 6, and 8 g/L glucose shortened the methanogenic lag phase by 11.4%, 30.3%, and 21.6% and raised the maximum methane production rate by 86.6%, 21.4%, and 5.2%, respectively, compared with the controls without biochar.

Mumme *et al*. (2014) investigated the behavior of biochars from pyrolysis in AD regarding their degradability and their effects on biogas production and ammonia inhibition. A batch fermentation experiment (42℃, 63 days) was conducted in 100 mL syringes filled with 30 g inoculum, 2 g biochar, and four levels of total ammonium nitrogen (TAN). The effect on biogas production was observed, which increased the methane yield by 32%.

Lü *et al*. (2016) evaluated the effectiveness of biochar of different particle sizes in alleviating ammonium (NH_4^+) inhibition (up to 7 g/L) during anaerobic digestion of 6 g/L glucose. Compared to the control treatment without biochar addition, treatments that included biochar particles 2–5 mm, 0.5–1 mm, and 75–150 mm in size reduced the methanogens lag phase by 23.9%, 23.8%, and 5.9%, respectively, and increased the maximum methane production rate by 47.1%, 23.5%, and 44.1%, respectively. These results confirmed that biochar accelerated the initiation of methanogens during anaerobic digestion under double inhibition risk from both ammonium and acids.

Shen *et al*. (2015) studied the effect of corn stover biochar on methane yield and quality in anaerobic digestion (AD) of sludge. The biochar amended digesters produced high-quality biogas (biomethane) with (> 90% CH_4 and < 5 ppb H_2S), facilitated CO_2 removal by up to

86.3%, boosted average CH_4 content in biogas by up to 42.4% compared to the control digester. The biochar addition enhanced the methane yield, and maximum methane production rate by up to 7.0%, and 27.6%, respectively.

Yang *et al.* (2017) studied the effect of granular activated carbon (GAC) added into a batch-mode anaerobic sludge digestion digester with an attempt to improve the sludge digestion. The results showed that with adding GAC from 0 to 5.0 g, the methane production increased by 17.4%, and the sludge reduction rate increased by 6.1 percent points (from 39.1% to 45.2%).

Fagbohungbe *et al*. (2016) studied the impact of different types of biochar and a biochar ratio on the anaerobic digestion of citrus peel waste was investigated. Citrus peel has an inhibitory effect on anaerobic digestion. The presence of biochar had two effects: a reduction in the length of the lag phase and greater production of methane relative to citrus peel waste only incubations. The microbial lag phases decreased with an increase in the citrus peel to biochar ratios, with 2:1 having the longest lag phase of 9.4 days and 1:3, the shortest, with a value of 7.5 days. The cumulative methane production in incubations containing biochar and citrus peel ranged from 163.9–185.0 ml CH4 g/VS, while citrus peel only produced 165.9 ml CH_4 g/VS.

L. Zhang *et al*. (2018) studied the effects of 15 g of activated carbon (AC) supplementation on anaerobic digestion (AD) of food waste in lab-scale performed in 1 L and 8 L digesters, while pilot-scale AD was conducted in a 1000 L digester. Pilot-scale digester without AC gave an average methane yield of 0.466 L/ (g VS)/day at a composition of 53–61% v/v methane. With AC augmentation, an increase of 41 % in methane yield was achieved in the 1000 L digester under the optimal organic loading rate (1.6 g VS_{FW}/L/day).

Meyer-kohlstock *et al*. (2016) investigated biochar in anaerobic digestion effects in solid-state fermentation of bio-waste. The influence of biochar was tested with a setup that simulates an industrial-scale biogas plant. The result showed that both the biogas and the methane yield increased around 5% with a biochar addition of 5% based on organic dry matter biochar to bio-waste. An addition of 10% increased the yield by around 3%.

Yun *et al*. (2018) investigated the effect of seven carbon materials having a specific surface area of 580–824 m^2/g as additives on the biogas yield. Dairy manure as substrate and activated sludge as inoculum was used for the biogas yield. The result indicates that the addition of carbon significantly improves the biogas yield (380–502 mL/g TS).

Md Rashedul Islam *et al*. (2016) performed research work using a 1-liter capacity conical flask and 8 % TS to find out the production of biogas from cow dung using charcoal and gelatin as additives. Five laboratory-scale experimental set-ups were constructed using 0, 0.2, 0.4, 0.6, and 0.8% gelatin and 0.5% charcoal with cow dung as an additive at the ambient temperature of 26°C–32°C. The total gas yield without using gelatin additive was found to be 12 L/kg cow dung. The maximum gas yield was found from 0.2% gelatin additive and 23% more as compared to without gelatin gas production.

Zhang *et al*. (2018) conducted a batch of anaerobic digestion experiments using diary manure, anaerobic sewage sludge as inoculum, and low-cost composited accelerants consisting of urea (0.2–0.5) %, bentonite (0.5–0.8) %, active carbon (0.6–0.9) %, and plant ash (0.01-0.3) % to improve the methane yield and effluent utilization. Total biogas yield (485.7–681.9 mL/gVS) and methane content (63.0–66.6) % were found by adding accelerants compared to those of the control group (361.9 mL/gVS, 59.4%).

Jang *et al*. (2018) studied the effects of dairy manure-derived biochar (M-BC) on methane production in anaerobic digestion (AD) of dry dairy manure were investigated with three different concentrations of biochar (0, 1, and 10 g/L) and temperatures (psychrophilic, 20°C; mesophilic, 35°C; thermophilic, 55°C). Compared with the AD without any biochar, the cumulative methane and yield in the AD with 10 g/L biochar were increased to 27.65% and 26.47% in psychrophilic, 32.21%, and 24.90% in mesophilic, and 35.71% and 24.69% in thermophilic digestions.

Gómez *et al*., (2018) studied the assessment on biogas production carried out using samples of swine manure (SM) supplemented with char in one case and pre-treated by microwave irradiation in the other. This experimental setup was allowed for the comparison of the biological degradation observed under these two different configurations and therefore aids in understanding the effect of char particles on the process. The result showed similar performance for both systems, with an average improvement of 39% being obtained in methane production when compared to the single digestion of SM.

Cai *et al*. (2016) investigated the addition of various amounts of biochar to A of food wastes at different ratios of inoculum to a substrate (ISR) to evaluate the effect of biochar as a functional additive and to optimize the additive concentrations of biochar. The biochar treatments at ISR 2, 1, and 0.8 shortened the lag phase of digestion by (2.0–10.9) %, (43.3–54.4) %, and (36.3–54.0) %, and raised the maximum methane production rate by (100-

275) %, (100–133.3) %, and (33.3–100) % respectively, compared to control biochar. Therefore, the effectiveness of biochar depended on the additive amount of biochar.

2.9 Summary of literature and gaps

This chapter demonstrated the challenges of AD technology and previously taken measures through a comprehensive literature review. The existing literature implements conventional process-related routes for managing AD instability but still have their disadvantages.

The use of two-stage digestion does not guarantee process stability. Depletion of the neutralizing alkali chemical results in the increase of process acidification. The application of additives beyond the acceptable limits inhibits the AD process. The addition of alkali chemicals such as NaOH and $CaCO_3$ solutions can obviate the problem until the system becomes stable; nevertheless, some of these chemicals can cause other problems (Aboudi *et al*., 2015). The practical implementation of co-digestion requires that all the necessary substrates are available at all times. In general, these techniques may mitigate AD instability could not improve the biogas quality (methane content in the biogas).

Biogas upgrading is gaining global interest due to its potential to increased energy efficiency and improved sustainability. Conventional technologies for biogas upgrading include physical and chemical absorption, pressure swing adsorption, membrane separation, and cryogenic cooling. However, commercial upgrading technologies available today are very costly for small scale applications (Andersson and Nordberg, 2017).

To upgrade biogas on a small scale (less than 200 Nm^3/h) has been too expensive to be interesting, due to the high specific investment costs of the upgrading equipment. For a plant with low capacity, more or less the same number of sensors, analysis equipment, control systems, and valves are needed as for a plant with a much larger capacity. The dimensions of the pipes and valves will be smaller, but the specific investment cost will be high. In addition to this activated carbon was used in AD for adsorption of contaminants in biogas. Despite these advantages, the application of AC to AD has been limited since direct disposal of AC would cause additional concerns for environmental pollution and safety (Luo et al., 2015) and since it needs activation so that farmers in a rural area may not afford cost related to activation. Therefore, it is suggested to investigate the impurities removal using biochar derived from sources of waste/feedstock.

Biochar could be a cost-effective material to stimulate microbial activities in AD due to its physical and chemical properties (i.e., biostability, porous and carbonaceous surface with various functional groups). These properties of biochar are similar to those of AC except the lower surface area of biochar than AC (Luo et al., 2015). Compared with AC, biochar is more easily produced at a lower pyrolysis temperature without activation. Biochar with its aforementioned beneficial characteristics for a wide range of application, therefore, become the innovative aspect of this study.

In the aforementioned literature, different types of biochar have been used in the study of the reduction of biogas impurities such as H_2S and ammonia. However, up to now, there are limited studies on the reduction of biogas impurities such as carbon dioxide which affects energy quality.

Most of the previous works on AD focus on the addition of biochar by mixing completely with the substrate. However, this technique may not much effective because the sludge may fill pores of biochar which affects the adsorption capacity. In this study through various considerations, increasing methane yield from anaerobic digestion of cow dung by mixing 50% of the total corn cob derived biochar with a substrate and 50% without mixing instead of keeping it at the top of the media is proposed and has to be tested. It is expected that this study will fill the gaps in the literature about AD stability, the biochar application in the AD system for impurity reduction. The thesis investigates the preparation, utilization of biochar in the AD, and gas upgrading.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Introduction

This chapter presents a detailed methodology, and techniques to achieve the study objectives. The present investigation will focus on the effect of corn cob derived biochar on methane and biogas yield from fresh cow dung. Figure 3.1 shows the schematic diagram of the overall strategies for the experimental study.

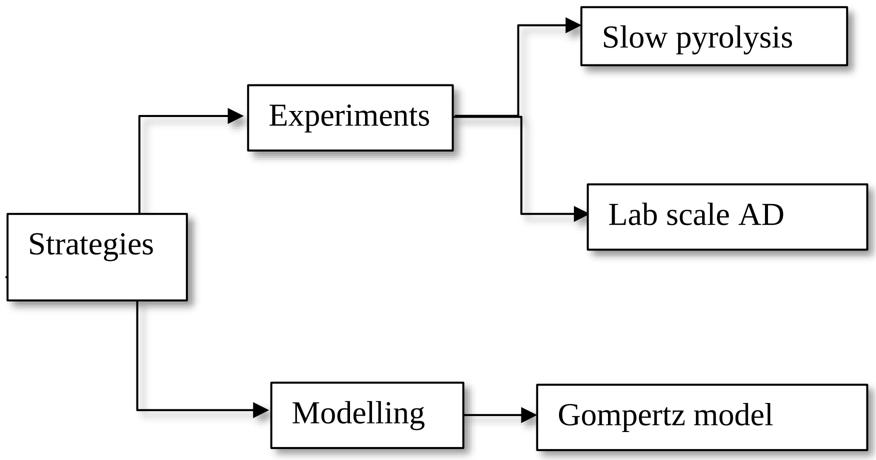

Figure 3.1: Study strategies

3.2 Materials

The following materials were used for experimental evaluation for this study.

Substrate: feedstock materials for biogas production (cow dung). Cow dung is a favorable feedstock for AD due to its high nutrient content and because the cow dung already contains the biogas-forming bacteria when the manure is still fresh (Deublein and Steinhauser, 2011).

Inoculum: rumen fluid (intestine residue) for seeding purposes.

Corn cob for biochar production and biochar for facilitating digestion, increasing biogas quality, and reduce process inhibitions. The samples were collected and transported to Debre Berhan University, Chemical Engineering Department laboratory, and the experiment was conducted.

Table 3-1: List of materials used in the study

Materials name	**Area collected**	**Purpose**
Corn cob	East Gojjam	Production of biochar
Cow dung	Debre berhan	Generation of biogas
Intestinal residue	Debre berhan city abattoir	For seeding
Chemicals used	**Bought from**	**Purpose**
Starch, HCl	Kirkos	To prepare a 5% HCl solution
Potassium iodide	Kirkos	Preparing the iodine solution
Potassium iodate	Kirkos	Preparing a sodium thiosulphate solution
Iodine	Kirkos	Preparing the iodine solution
NaOH	Kirkos	Preparing an alkaline solution

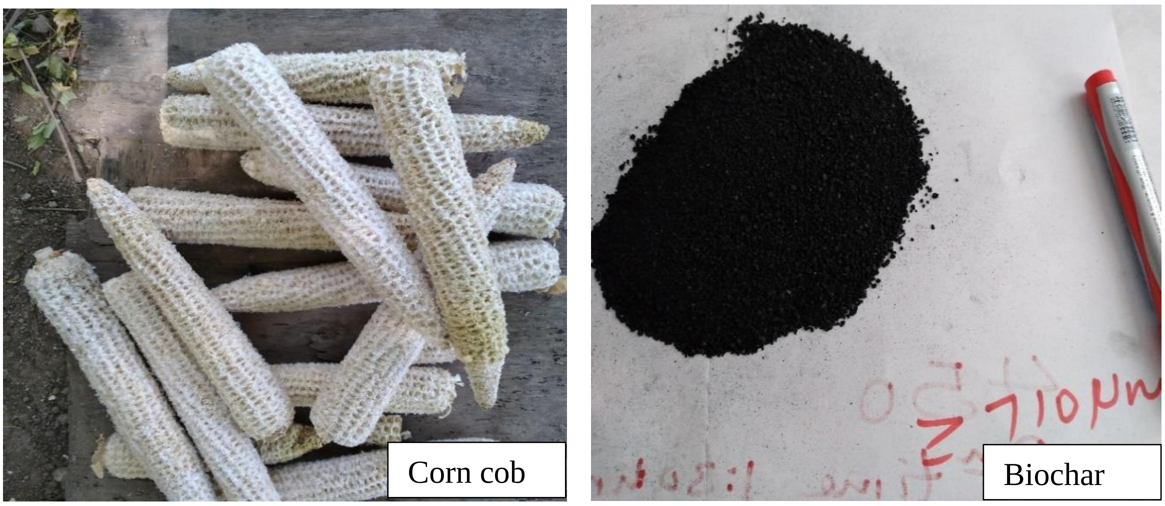

Figure 3.2: Corn cob and Biochar

3.3 Equipment and measuring instruments

The necessary equipment's and measuring instruments were used in this study summarized as follows:

Table 3-2: Equipment's and measuring instruments used in this study

Equipment	Manufacturer (Model)	Application or purpose
Mixing tank (Baldi)	NA	For preparing a homogenous mixture of feed
Universal hot air oven	NA	TS
Muffle Furnace	NA	VS and biochar production
pH meter	PHS-1701	pH
Thermometer	NA	Measure water bath temperature
Digital Weight Balance	NA	Measure the mass of CD and corn cob samples.
Plastic bottles	NA	Used as Digester
Water bath	NA	For sustaining temperature level at 37°C
Tubes	NA	For the flow of gas from the digester to the airbag
Rollers	NA	To control gas flow lines
Airbag	NA	To collect biogas
Additives	Superglue	To form an anaerobic system inside the digester
Crucibles	NA	Sample holder during the experiment
Desiccator	NA	For cooling samples to room temperature
Graduated cylinders	NA	For gas measurement

3.4 Preparation of Raw materials

3.4.1 Preparation of CC-BC

The raw material (corn cob) used in this study was collected from rural areas particularly East Gojjam where a large quantity of Maize has been produced. Due to the high volatile content in corn cob, it is suggested that corn cob is a suitable feedstock for the thermo-chemical conversion process such as pyrolysis.

Figure 3.3: Corn cob before and after sizing

3.4.2 Pyrolysis of corn cob

The corn cob BC was prepared via the pyrolysis of the corn cob. Corn cob was placed in a crucible and introduced in an electric furnace where the temperature was set up at 350℃, 450℃, and 550℃ for 30min, 1, and 1.5 hours each.

3.4.3 Characterization of CC-BC

After the pyrolysis, all biochar was crushed and sieved with between 850 and 150 µm according to ASTM D1762-84.

A. Proximate analysis

The proximate analysis was conducted with the ASTM technique. The values of moisture content, ash content, and volatile matter of corn cob were determined according to the standard test method ASTM D1762- 84, which was published by the American Society for Testing and Materials, is commonly used for this purpose. The moisture, volatile matter, and ash content calculations are as follows(ASTMD1762-84, 2011):

$$\text{Moisture}\left(\%\right) = \frac{w_1 - w_2}{w_1} \text{ x } 100 \tag{3.1}$$

$$\text{Volatile matter}\left(\%\right) = \frac{w_2 - w_3}{w_2} \text{x}100 \tag{3.2}$$

$$\text{Ash}\left(\%\right) = \frac{w_4}{w_2} \text{x}100 \tag{3.3}$$

Where, w_1 is the weight of the air-dried sample, w_2 is the weight of the sample after being heated at 105℃, w_3 is the weight of the sample after being heated at 950℃, and w_4 is the weight of the residue after being heated at 750℃.

B. Surface area and pore size

Brunauer-Emmett-Teller (BET) is a method commonly used to calculate the biochar surface area. The iodine adsorption method has very rarely been used to determine the biochar surface area (Igalavithana et al., 2018). Iodine adsorption indicates the internal surface a rea where in many cases the result is close to Brunauer-Emmett-Teller (BET) surface area (M.R.M Adib, 2016).

The method was originally developed for surface area determination in organic matter-rich soils and activated C (ASTM D4607-94, 2007). The test method of ASTM D4607-94 (ASTM D4607-94, 2007) explains the detailed methodology of iodine absorption. Iodine number I_n of the carbon using the equation (ASTM D4607-94, 2007):

$$I_n = \frac{X}{M} A \tag{3.4}$$

$$X = (12.693N_1) - (279.246N_2V) \tag{3.5}$$

Where, X = mg of iodine adsorbed by the biochar

V = volume of sodium thiosulphate solution in ml

M = mass of activated carbon in g

N_1 = normality of iodine solution

N_2 = normality of sodium thiosulphate solution

A = correction factor, depending on residual normality N_r of the filtrate

$$N_r = N_2 \frac{V}{50} \tag{3.6}$$

3.4.4 Preparation and characterization of cow dung and inoculum

The substrate used in this study was collected from rural areas particularly around Debre Berhan. The collected samples were characterized using the standard methods.

Determination of total solid (TS)

The total solid content of the cow dung (CD) can be determined by the procedure given by APHA 1995. The percent of total solids is computed using the formula (APHA., 1995).

$$\%\ TS = \frac{C-A}{B-A} \times 100 \tag{3.7}$$

Where, A = Weight of crucible, g

B = Weight of wet sample + crucible, g

C = Weight of dried crucible + dried residue, g

Determination of volatile solids (VS)

The volatile solids content of the sample can be determined by adopting the procedure furnished by APHA 1995. The loss in weight is now the volatile matter present in the samples were also calculated using (APHA 1995):

$$\% \text{ VS} = \frac{\text{B - C}}{\text{B - A}} \times 100 \quad (3.8)$$

Where, A = Mass of empty clean and oven-dried silica crucible, g

B = Mass of silica crucible + sample, g

C = Mass of silica crucible + sample after ignition, g

3.4.5 Inoculum preparation

Due to the presence of higher content of anaerobic bacteria in the rumen of the animals and the abundance of rumen waste disposal from the nearby slaughterhouse (Debre Berhan city slaughterhouse), the source of inoculum was intestine residue from slaughterhouse mix with water on TS basis and large inorganic particles were removed from the sludge by passing it through a 5-mesh sieve.

Figure 3.4: Inoculum preparation

3.4.6 Media preparation

Total solids concentration for the cow dung was observed greater than 16% that is the upper threshold limit for wet digestion (Mattock, 1984). Thus, its total solid was first determined by drying at 105°C until a constant mass was observed on drying (24 h).

Figure 3.5: (A) Inoculum, biochar, and cow dung slurry, and (B) Preparing mixture

Figure 3.6: (C) Pouring the mixture, and (D) Adding biochar with various concentrations

The amount of water to be added to fresh cow dung to adjust its total solids concentration to 8%, which is optimum for wet anaerobic digestion, was computed from the following simple mass balance. Cow dung was mixed with inoculum with a 1:1 ratio in a mixing tank used in all the experiments.

Finally, the prepared media was also mixed with 50% BC by weight and feed into the laboratory scale digester for biogas production.

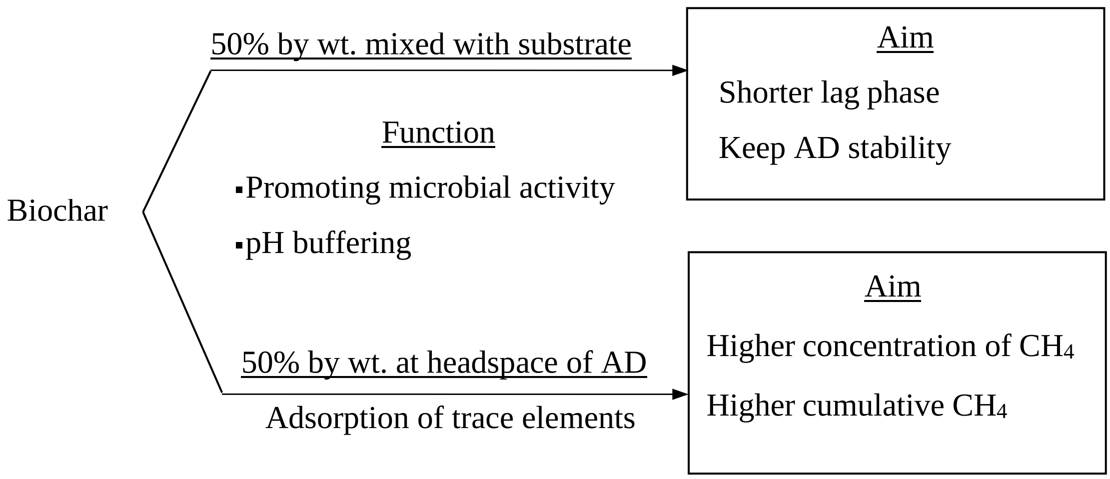

Figure 3.7: The mechanisms of using BC for promoting biogas quality in AD

3.5 Lab-scale Biogas Production Experiment

The AD experiments were conducted in liter digesters at mesophilic temperature (37℃ ± 1℃) with a working volume of 0.8L. The control (ADM_0) and digesters amended with biochar at four different concentrations.

3.6 The Modified Gompertz Model

A modified Gompertz equation was used to correlate experimental data to quantify the cumulative methane production and the correlation fitting was done using SPSS statistics. To obtain lag phase, maximum production potential, and production rate under the mesophilic condition and different concentrations of biochar, modified Gompertz model using the following equation (Luo et al., 2015):

$$M\left(t\right) = Px\exp\left\{-\exp\left[\frac{R_{max}xe}{P}\left(\lambda - t\right) + 1\right]\right\} \tag{3.9}$$

Where M(t) (mL) is the cumulative methane production; P is the maximum methane potential (mL); R_{max} (mL/day) is the maximum methane production rate; λ (days) is the lag phase (minimum time to produce biogas (days), e is Euler number which is 2.7183, and t is time.

CHAPTER FOUR

SIZING DIGESTER

4.1 Introduction

Biogas digesters are used to produce methane gas and the size of the digesters is commonly bigger. People who live in poor conditions and are familiar with the uses and the advantages of using methane gas wants to have a biogas digester at home for replacing the cooking gas as the ever-increasing price of cooking gas is adding to their woes.

4.2 Customers Energy Demand for Cooking

According to (DHS, 2016), rural family have the average of 4.9 members per household, so if this value is taken for determining the energy demand, there might happen energy deficiency for large family size with more than 4.9 persons per household (10 considering new visitors is taken for this study), need biomass energy to produce their daily food. To perform biogas production for cooking, the energy requirement has to be determined. Households in rural areas mainly need energy for cooking, lighting, and empowering of low voltage appliances. Lighting and empowering of elementary appliances require a relatively low amount of energy which can be satisfied with electricity from photovoltaic cells.

4.2.1 Amount of biogas required

To perform a heat requirement analysis, the biogas production rates have to be determined. The amount of biogas required to fulfill the energy demand for cooking can be estimated using two ways. The first method is to obtain the input heat energy, the amount of heat energy contained in the biogas fuel must be equal to the required heat energy for cooking per person. The amount of heat energy available in the fuel per person (Q_{biogas}) (Yunus and Boles, 2008).

$$Q_{bio} = m_{bio} \times LHV \tag{4.1}$$

Where, Q_{bio} = Heat energy available in the biogas, KJ /person,
m_{bio} = Weight of biogas used in the stove, kg and
LHV = Lower heating value of fuel (biogas), KJ/kg.

Alternatively, taking the average value of biogas required per day per person which is a simple method and used in this study. The digester is designed to produce biogas that can fulfill the energy demand of 10 people for their cooking application. The average amount of biogas required to fulfill the energy demand of a person per day for cooking applications is 0.225 m^3 of biogas (Leulseged Tarekegn, 2018). Also (Khan, 2009) described that biogas required for cooking is about 0.225 m^3/person per day. The designed biogas digester is responsible to produce 2.25 m^3 of biogas per day for 10 people.

The total quantity of biogas required for cooking for 10 persons will be

$$V_{biogas} = N \times 0.225 m^3 \, of \, biogas / person / day \tag{4.2}$$

Where, N = number of persons = 10

$$N = 10 \times 0.225 \text{ m}^3 = 2.25 \text{ m}^3\text{/day}$$

Hence, biogas may drip while flowing to the stove through piping, and energy is lost during cooking and for compensation, it is assumed that 10% of biogas generated should be added.

Table 4-1: Biogas requirement on a daily and monthly basis

Time	**Gas requirement**	**No of the members in a single family**	**Total gas needed**	**Considering a 10% loss**
Daily basis	0.225 m^3/person	10	2.25 m^3	2.475 m^3
Monthly basis	6.75 m^3/person	10	67.5 m^3	74.25m^3

4.2.2 Cow dung and number of cow requirement

(Kuria and Maringa, 2008) explained the standard relationships used to size the biogas units based on a zero grazed cow as follows:

- 1 cow produces 10 kg of cow dung per day.
- The solid matter content in cow dung is 18%.
- The density of cow dung slurry is 1090 kg/m^3

Let z be the number of cows, total cow dung produced =10z kg/day.

But, according to (Khan, 2009) only 70 % of dung can be collected. This means 30% is lost during grazing and (Khan, 2009) also reported that gas yield per day from cow dung is 0.34 m^3/kg of dry matter.

$$\text{Collectable cow dung } (70\%) = 7\text{z kg/day}$$

$$\text{Weight of dry solid mass in cow dung} = 18\% \times 7\text{z kg/day}$$

$$\text{Gas production per day for 10 people} = \text{gas yield } \left(\text{m}^3\text{/kg of dry matter}\right) \times \text{TS} \times 7\text{z kg/day}$$

$$2.475 \text{ m}^3\text{/day} = 0.34 \times 0.18 \times 7\text{z}$$

$z = 5.77 \cong 6$. Thus, six cows are required to feed the plant.

The amount of cow dung required to produce 2.475 m^3 is calculated as

$$\text{Daily feeding of cow dung} = 7 \times 6 = 42\text{kg}$$

Table 4-2: Feedstock requirement on a daily and monthly basis

Time	CD (kg)/person	single family member	Total CD (kg)
Daily basis	4.2	10	42
Monthly basis	126	10	1260

4.3 Sizing of Anaerobic Digester

Biogas digester design plays a crucial role in digester performance and some considerations are taken into account. The following aspects were considered during the design process: durability, airtightness, availability of local materials, and easy operation. The main design parameters are total solid content and hydraulic retention time.

TS contained in a substrate is usually used as the material unit to indicate the biogas production rate of the materials. The most favorable TS value is 8% for better biogas production (Mukumba et al., 2017), and HRT. For mesophilic digestion where temperature varies from 25-35℃, the HRT was greater than 20 days. In the thermophilic environment, HRT is usually less than 10 days. Shortening retention time can lead to an increase in the volatile fatty acids (Mukumba et al., 2017), and this is why mesophilic digestion was considered.

A surface cylindrical biogas digester was chosen because it was easy to feed, insulate, clean, and easy to construct, relatively small amounts of slurry (a mixture of manure and water) are added daily and remove slurry after every hydraulic retention period. This enables gas and fertilizers are produced continuously and predictably. The anaerobic digester has its parts which include mainly digester chamber, hydraulic chamber, gas holder, and piping.

4.3.1 Volume calculation of digester chamber

The size or volume (VD) of the digester is determined by the length of the retention time (HRT) and by the amount of fermentation slurry supplied daily. The size of the digester largely depends on the amount of waste to be added. The dimensional parameters to be considered during sizing are:

V_{gs} =Volume of the gas storage chamber
V_f =Volume of the fermentation chamber
V_H =Volume of the fermentation chamber
V_S =Volume of the sludge layer
V_c =Volume of gas collecting chamber

Figures 4.1, 4.2, and 4.3 are adapted from (Chendu and Sichuan, 2009)

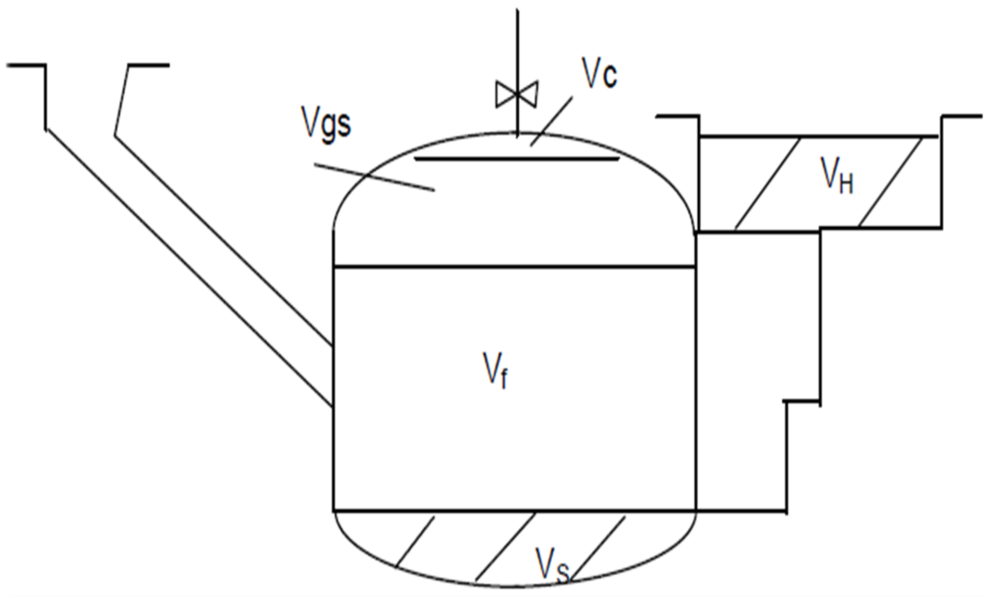

Figure 4.1: Cross-section of a digester

The V_c is the volume of the biogas chamber which is the upper part of the digester needed to collect and store the biogas. The fermentation chamber is the place below the V_c where the liquid mixture of effluent is stored until complete decomposition.

The total volume of cylindrical-shaped biogas digester with a hemispherical head will be: -

$$V = V_c + V_{gs} + V_f + V_s \tag{4.3}$$

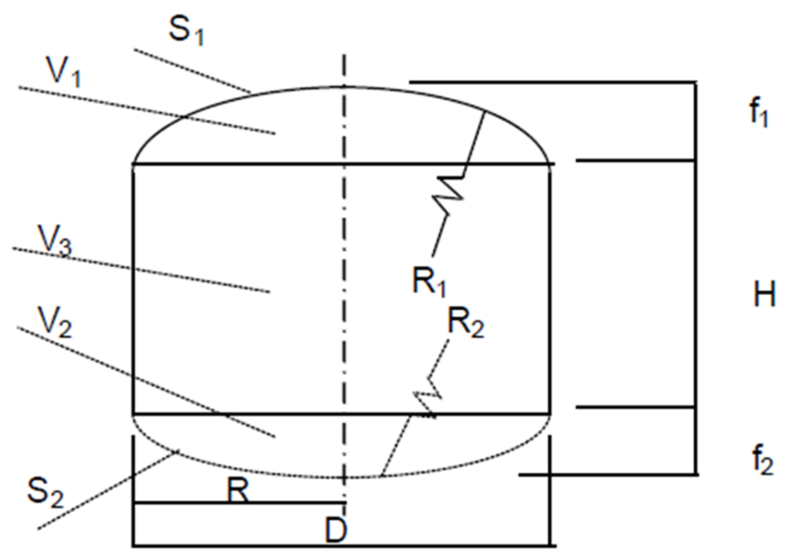

Figure 4.2: The geometry of the cylindrical-shaped biogas digester

The parameters in fig 4.2 stand for:

- The volume of fermentation chamber=V_f =V_3
- Volume of sludge layer = V_2 = V_s
- R_1 and R_2 are the crown radius of the upper and bottom layer of the digester
- S_1 and S_2 art the surface area of the upper and the lower dome (m^2) respectively
- f_1 and f_2 are the maximum distance of the upper and lower dome (m)
- H is the height of the fermentation chamber (m)

Previously the number of cows required to produce 2.475 m^3 of biogas per day was determined as 6. The retention time is dependent on the prevailing temperature in a digester and on the type of substrate used. Most biogas digesters in operating in the mesophilic temperature range (20°C < t < 40°C). For liquid manure undergoing fermentation in this temperature range, the following approximate retention times apply (Kuria & Maringa, 2008).

- Liquid cow manure 20-30 days (for mesophilic condition).

Let HRT = 30 days (for temp. 37°C) taking maximum HRT.

Calculating the total discharge

$$T_d = D_{dp} \times N \tag{4.4}$$

Where, T_d = Total discharge (kg/day)

D_{pd} = Discharge per day (kg/day)

N = Number of Cows

T_d = 7 kg x 6 = 42 kg/day which is total manure available.

Calculating the total solids of fresh discharge (T_{sfd})

$$T_{sfd} = T_d \times CT_{swt} \tag{4.5}$$

Where, T_{sfd} = Ts of fresh discharge (kg/day)

CT_{swt} = Concentration of TS in fresh discharge by weight (kg TS/kg discharge)

TS of fresh discharge = 42 kg$\times$0.18 = 7.56 kg where 0.18 is the TS of fresh cow dung (Khan, 2009).

Calculating the total influent

$$T_{ir} = \frac{T_{sfd}}{T_{sfc}} \tag{4.6}$$

Where, T_{ir} = Total influent required (kg)

T_{sfc} = Ts of favorable concentration (%)

According to (Mattocks, 1984) best biogas production occurs when the total solid is ranged from 7% to 10%. The most favorable TS concentration value is 8% for better biogas production (Mukumba et al., 2017).

To make a favorable condition, an 8% concentration of TS

$$T_{ir} = \frac{7.56 \text{ kg}}{8\%} = 94.5 \text{ kg}$$

Calculating water in the input influent

$$W_a = T_{ir} - T_d \tag{4.7}$$

Where W_a = Daily water addition (kg/day)

Water to be added to make the discharge 8% concentration of TS

$$W_a = 94.5 \text{ kg} - 42 \text{ kg} = 52.5 \text{ kg}$$

Thus, the daily feed of slurry = 94.5 kg by weight = 94.5 kg / 1090 kg/m^3 = 0.086697 m^3 by volume.

Calculating the working volume of the digester

$$\begin{cases} W_{vd} = V_{gs} + V_f \\ W_{vd} = \left[\dfrac{T_{ir} \times HRT}{\rho_{slurry}} \right] \\ W_{vd} = 0.80V \end{cases} \tag{4.8}$$

Working volume of the digester, $w_{vd} = V_{gs} + V_f$

$$V_{gs} + V_f = \frac{T_{ir} \times HRT}{\rho_{slurry}}$$

$$V_{gs} + V_f = \frac{94.5 \text{ kg/day} \times 30 \text{ days}}{1090 \text{ kg/m}^3} = \frac{2835 \text{ kg}}{1090 \text{ kg/m}^3}$$

$$W_{vd} = 2.752 \text{ m}^3$$

The geometry of the bio-digester of the fixed dome type is simple as shown in Fig. 4.3. It consists of two semi-spherical domes and a cylindrical shape connecting them. Even the semi-spherical shapes are not identical; all the dimensions can be related to the main diameter by the relations in Table 4.3. below.

When attempting to estimate the value of each of the geometrical dimensions to build the Bio-Digester, there are a group of assumptions to adopt. The main diameter and the total volume play a vital role in designing the digester. The following table shows the geometry relations of both main diameter and total volume.

Table 4-3: Assumptions for volume and geometrical dimensions (Mukumba et al., 2017)

For volume	For geometrical dimensions
➢ $V_c \leq 5\%$ V ➢ $V_s \leq 15\%$ V ➢ $V_{gs} + V_f = 80\%$ V ➢ $V_{gs} = V_H$ ➢ $V_{gs} = 0.5\,(V_{gs} + V_f + V_s)$ K Where K = Gas production rate per m^3 digester volume per day. For this study K = 0.4 m^3/day	➢ D=1.3078 X $V^{1/3}$ ➢ $V_1 = 0.0827D^3$ ➢ $V_2 = 0.05011D^3$ ➢ $V_3 = 0.3142D^3$ ➢ $R_1 = 0.725D$ ➢ $R_2 = 1.0625D$ ➢ $f_1 = D/5$ ➢ $f_2 = D/8$ ➢ $S_1 = 0.911\ D^2$ ➢ $S_2 = 0.8345\ D^2$ where D is the diameter of digester.

From geometrical assumptions:

$$V_{gs} + V_f = 0.80V$$

$$V = 2.752/0.8 = 3.44m^3$$

Using empirical geometrical relations-following

$$D = 1.3078 \times V^{1/3} \tag{4.9}$$

(Putting value $V_{gs} + V_f = 2.752\ m^3$) and D = 1.3078 V $^{1/3}$ = 1.974 m ≅ 2 m

$$\begin{aligned} V_3 &= 0.3142D^3 \\ V_3 &= 0.3142(2)^3 = 2.514\ m^3 \end{aligned} \tag{4.10}$$

Combining Eq. 4.9 and 4.10, digester height;

$$H = \frac{4 \times 0.3142 \times D^3}{3.14 \times D^2} \tag{4.11}$$

$$H = \frac{4 \times 0.3142 \times (2\ m)^3}{3.14 \times (2\ m)^2} = 0.8\ m$$

Calculating the Digester geometrical parameters

By knowing the value of ‘D’ and ’H’ we can find all other geometrical parameters. Therefore, the value of each parameter is calculated by substituting the value of diameter in the above geometrical relation presented in table 4.3.

Now we find from the assumption as we know the value of 'D' and 'H'.

- $V_1 = 0.0827D^3 = 0.662\, m^3$
- $V_2 = 0.05011D^3 = 0.4\, m^3$
- $R_1 = 0.725D = 1.45\, m$
- $R_2 = 1.0625D = 2.13m$
- $f_1 = D/5 = 0.4$ m
- $f_2 = D/8 = 0.25$ m
- $S_1 = 0.911\, D^2 = 3.644\, m^2$
- $S_2 = 0.8345\, D^2 = 3.34\, m^2$

4.3.2 Volume calculation of hydraulic chamber

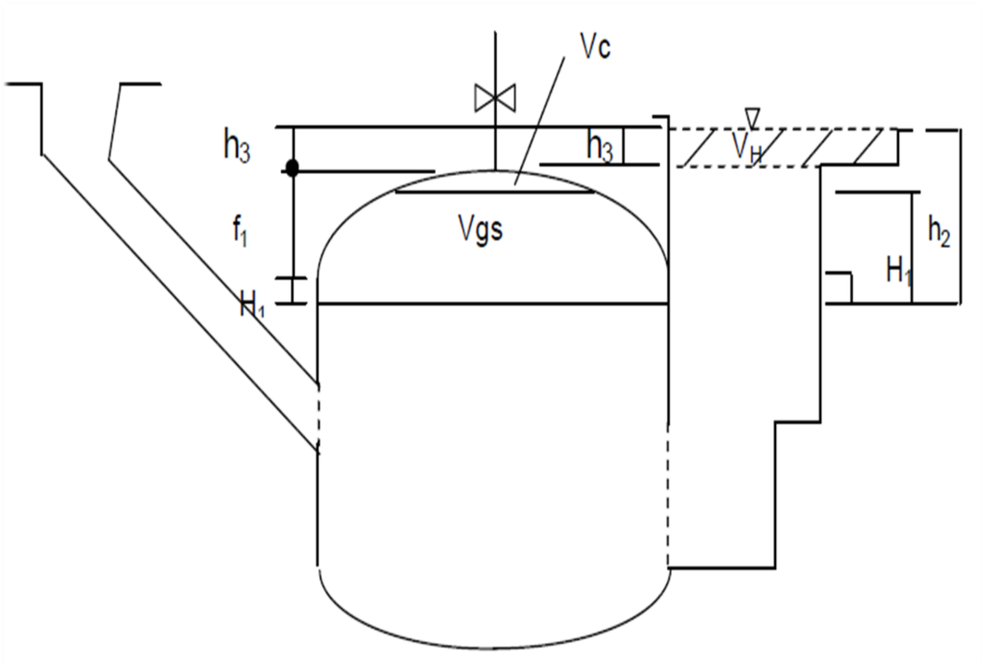

Figure 4.3: Geometrical dimensions of the hydraulic chamber

Where, h = Distance between ground surface level and dome top (m)

h_3 = Hydraulic chamber height (m)

H_1 = Height of gas layer inside V_3 (m)

$$V_H = \frac{3.14 \times D_H^2 \times h_3}{4} \tag{4.12}$$

From volumetric assumptions

$$V_{gs} = V_H \tag{4.13}$$

From assumptions, V_{gs} = 50% of total daily gas yield

$$Y_{dg,total} = T_{sfd} \times Y_{dg} \tag{4.14}$$

Where, Y_{dg} = Volumetric gas yield by TS mass $\left(m^3/Kg\ T_{sfd}\right)$ and

$Y_{dg,total}$ = Total volumetric gas yield $\left(m^3/Kg\ T_{sfd}\right)$

$$V_{gs,vol} = 0.5\left(W_{vd} + V_s\right)K \qquad (4.15)$$

$$= 0.5 \times (2.752 + (0.15 \times 3.44)) \times 0.4 = 1.07\ m^3$$

Again, V_{gs} = 50% of daily gas yield

$$V_{gs,TS} = 0.5\ \left(Y_{dg,total} \times t_{inc}\right) \qquad (4.16)$$

$$= 0.5 \times TS \times \text{gas-producing rate per Kg of TS}$$

The gas yield of cow dung = 0.34 m^3/kg TS (Khan, 2009).

$$= 0.5 \times \left(42\ kg \times 0.18\right) \times 0.34\ m^3/kg\ TS = 1.285\ m^3$$

From A and B let V_{gs} = 1.285 m^3 because 1.285 > 1.07

$$V_c + V_{gs} = (0.05 \times 3.44m^3) + 1.285m^3 = 1.457m^3$$

As V_1 is known from geometry and diameter D

$$V_1 = [\left\{V_c + V_{gs}\right\} - \left\{\frac{\pi \times D^2 \times H_1}{4}\right\} \qquad (4.17)$$

$$0.662m^3 = [(1.457m^3) - (\frac{\pi \times (2m)^2 \times H_1}{4})]$$

$$H_1 = 0.0253\ m$$

From the geometry of the hydraulic chamber in the drawing above

$$h = h_3 + f_1 + H_1 \qquad (4.18)$$

Where h is the height representing gauge pressure of the biogas (mm) of effluent volume. Assume pressure inside dome h = 800 mm to 2000 mm H_2O above atmospheric.

1 mm H_2O = 10 N/m^2 or 10 Pascal or 0.1 m Bar of pressure units.

Let h, is fixed @ 800 mm water volume (1 mm = 10 N/ m^2)

$$h = 0.8H = h_3 + f_1 + H_1 \qquad (4.19)$$

$$h_3 = \left(0.8 \text{ x } 0.8\ m\right) - (0.4\ m + 0.0253\ m)$$
$$h_3 = 0.2147\ m$$

Again, from equation 4.12 and 4.13 D_H can be derived as:

$$D_H = \sqrt{\frac{4 \times V_H}{3.14 \times h_3}} = \sqrt{\frac{4 \times 1.285}{3.14 \times 0.2147}} = 2.76m \qquad (4.20)$$

4.3.3 Analytical prediction of biogas upgrading for Large scale applications

The experimental data can be correlated with the size of digester required to attain the energy demand of ten people for cooking.

From small scale upgrading, a maximum of 755.5 ml of biogas with high methane concentration compared to other options was produced from a 1L digester with 8g/800ml of CC-BC450. However, the total amount of biogas required to fulfill the energy demand of 10 people per day for food cooking is 2.475 m^3 of biogas.

The calculated working volume of the pilot-scale digester is = 2.752 m^3. ADM_2 is selected to predict the case of large-scale applications because it generates biogas with a high concentration of methane.

Thus, 755.5mL of biogas was generated from 800mL of substrate mixed with 4g (50% by weight) of CC-BC450. So, the quantity of biogas generated from 2.752 m^3 volume substrate can be calculated as

$$\text{PSBG} = \frac{\text{Working volume of pilot scale AD}}{\text{Working volume of lab scale AD}} \times \text{biogas generated in lab scale} \quad (4.21)$$

Where PSBG is pilot-scale biogas generation

$$= (2.752\ m^3) / 800\ ml \times 755.5\ ml = 2.59\ m^3$$

Which is higher than 2.475 m^3 and can provide energy for producing daily food.

The amount of biochar required to generate 2.59 m^3 of biogas has to be determined as

$$\text{CC-BC450 PS} = \frac{\text{Working volume of pilot scale AD}}{\text{Working volume of lab scale AD}} \times \text{CC-BC450 added in lab scale} \quad (4.22)$$

Where, CC-BC450 PS is the biochar required for pilot scale AD

$$= (2.752cm^3) / 800\ ml \times 8g = 27.52kg$$

To transform lab-scale experiments of this work to pilot scale biogas generation for food-producing application for a family of 10 members 27.52 kg of corn cob derived biochar would be utilized.

CHAPTER FIVE

EXPERIMENTAL SETUP AND TEST PROCEDURES

5.1 Introduction

This chapter presents the description of the experimental setup and procedures for each experiment mainly pyrolysis and anaerobic digestion.

5.2 Details of Experiment

The general experimental procedure followed in this work is illustrated as follows using the flow chart of fig 5.1.

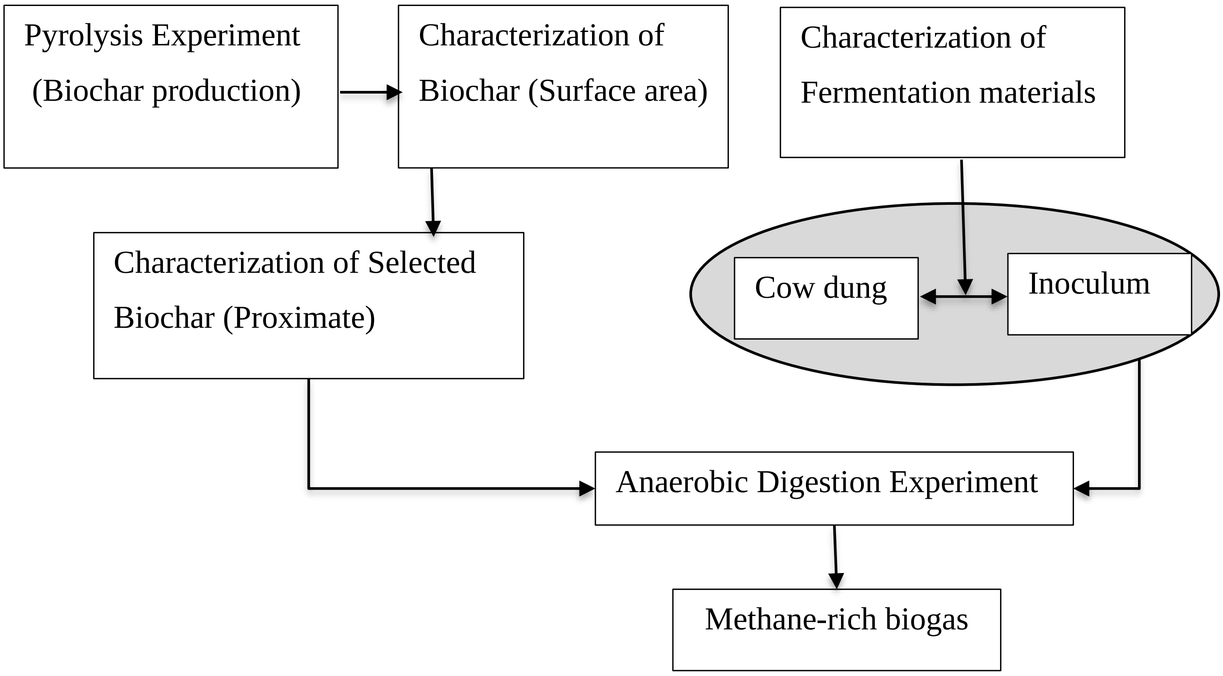

Figure 5.1: General experimental procedures of the present work

As shown in figure 5.1. First, biochar has to be produced with a slow pyrolysis method at different temperatures and characterized. Also, substrate and inoculum have to be characterized and finally go into anaerobic digestion experiment for biogas production.

5.3 Experimental setup and procedures for corn cob pyrolysis

The slow pyrolysis of corn cob was conducted using a muffle furnace. Initially, the crucible was weighed, and then the corn cob sample was added into the crucible and covered with the lid for performing each run. During this process, the desired temperature was maintained for the desired period to undergo the pyrolysis process.

Figure 5.2: Loading of sample to the crucible and then to a furnace for CC-BC production

After attaining the required values of the temperature, the particular pyrolysis process was initiated for the desired time. After achieving the required process time with a stabilized temperature pyrolysis process was completed and biochar is produced in the crucible. The experimental process variables used in this study were temperature between 300℃ and 600℃, reaction time from 30 to 90 min.

Figure 5.3: Unloading of a sample from furnace and weight of CC-BC

After completion of the process, the furnace was turned off and the cooling unit was started using a desiccator to drop the temperature of produced biochar up to 25℃. After cooling down, the solid biochar was collected manually from the crucible. However, the gases produced during pyrolysis were in small quantity and therefore vented out. Finally, it goes to characterization and is used for the desired application which was an anaerobic digestion test. A similar procedure was followed for the pyrolysis of all nine samples at different reaction times and temperatures.

5.4 Experimental setup and procedures for CC-BC characterization

5.4.1 Iodine number test

The surface area in (mg/g) was determined by following the test method of ASTM D4607-94 (ASTM D4607-94, 2007) which explains the detailed methodology of iodine adsorption.

Figure 5.4: Iodine number determination for CC-BC

The physicochemical properties of a selected sample of corn cob derived biochar was determined by following the procedure furnished by ASTMD 1762-84 which was described in the methodology section.

5.4.2 Moisture content and Total solid

Heat the muffle furnace to 750℃ and place previously ignited porcelain crucibles and covers in the furnace for 10 min. cool the crucibles in a desiccator for 1 h.

Figure 5.5: Adjusting muffle furnace and loading sample for TS of CC-BC450

Weigh the crucibles and add to each approximately 1 g, weighed to the nearest 0.1 mg, of the ground sample.

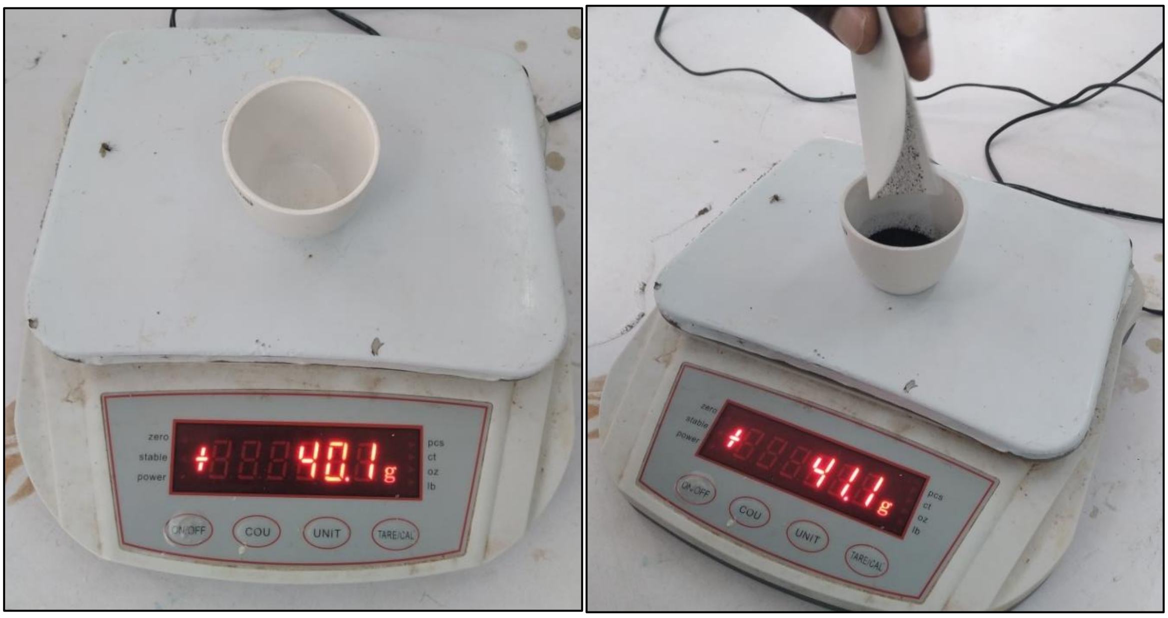

Figure 5.6: Weigh of crucible and sample for TS of CC-BC450

Place the samples in the oven at 105°C for 2 h. Place the dried samples in a desiccator for 1 h and weigh.

Figure 5.7: Weight of crucible and sample after drying for TS of CC-BC450

5.4.3 Volatile matter

Heat the muffle furnace to 950℃. Preheat the crucibles used for the moisture determination, with lids in place and containing the sample, as follows: with the furnace door open, for 2 min on the outer ledge of the furnace (300℃) and then for 3 min on the edge of the furnace (500℃). Then move the samples to the rear of the furnace for 6 min with the muffle door closed. Watch the samples through a small peep-hole in the muffle door. If sparking occurs, results will be in error. Cool the samples in a desiccator for 1 h and weigh.

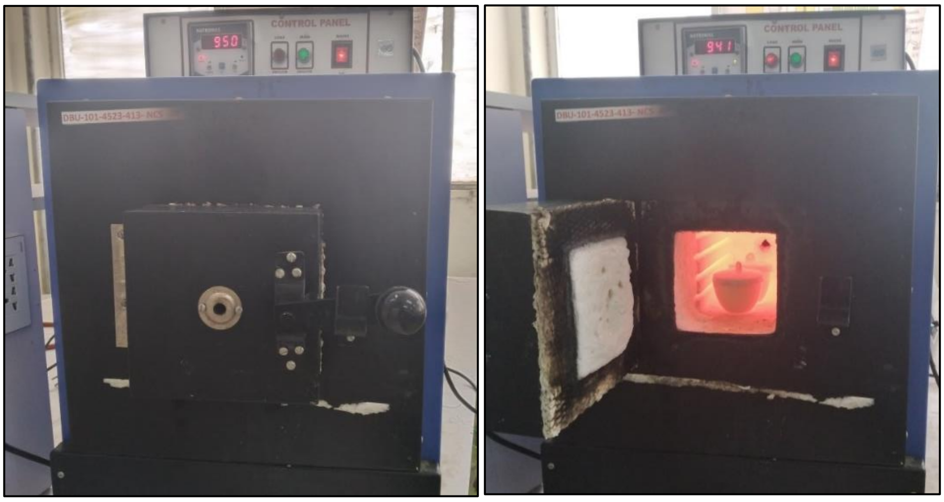

Figure 5.8: Adjusting furnace and loading of sample for VS of CC-BC450

Figure 5.9: Weight of crucible and sample after ignition for VS of CC-BC450

5.4.4 Ash content

Place the lids and the uncovered crucible used for the volatile matter determination, and containing the sample in the muffle furnace at 750°C for 6 h. Cool the crucibles with lids in place in a desiccator for 1 h and weigh.

Figure 5.10: Ash content of CC-BC450

5.5 Experimental setup and procedures for substrate characterization

The physicochemical properties of the sample were determined by the following procedure furnished by APHA 1995.

5.5.1 Total solid (TS)

These were the procedures followed for TS determination; A crucible was properly washed and dried in the laboratory oven at a temperature of 105℃ for one hour. The crucible was stored and cooled in a desiccator until needed. The crucible was re-weighed before use (g). The laboratory oven was switch on and allowed to reach a temperature of 105℃. This temperature was maintained throughout the experiment.

Figure 5.11: Weight of crucible after cleaning, heating, and adjusting oven for TS of CD

10g of freshly collected samples were weighed using an electrical balance (digital weight measuring device) and placed inside an electric hot air-oven maintained at 105℃ using a crucible. The crucible was allowed to stay in the oven for 24 hours, then taken out, cooled to room temperature in a desiccator, and weighed.

Figure 5.12: Weight and Loading of the crucible with the substrate for TS of CD

5.5.2 Volatile matter

The following procedures were followed in the determination of the volatile solid of the substrates used. A known mass of residue obtained from the determined of the total solids is placed in a silica crucible and ignited in a muffle furnace at 550 $\pm$ 50°C for 30 minutes. Then the crucible is taken out of the muffle furnace, partially cooled in air, kept in desiccators for few minutes, and then weighed.

5.6 Experimental setup and procedures for Anaerobic digestion

The AD experiments were conducted in plastic bottles of 1 L capacity used as a digester at mesophilic temperature (37°C±1°C) with a working volume of 0.8L. The control and digesters amended with corn cob derived biochar at four different concentrations (4, 6, 8, and 10 g/800mL of media) were investigated. Each experimental condition was conducted in duplicate, with all digesters placed in a water bath. Five samples, one without biochar and four with the addition of biochar were prepared with inoculum by mixing the cow manure and biochar. To set the TS value to 8%, water was added to the prepared samples. The experimental sets were labeled as ADM_0, ADM_1, $ADM_{1.5}$, ADM_2, and $ADM_{2.5}$.

Table 5-1: Experimental conditions used for anaerobic batch experiments

Labels	Ingredients
ADM_0	Inoculum + substrate
ADM_1	ISB (4g CC-BC450/800mL of media)
$ADM_{1.5}$	ISB (6g CC-BC450/800mL of media)
ADM_2	ISB (8g CC-BC450/800mL of media)
$ADM_{2.5}$	ISB (10g CC-BC450/800mL of media)

The experiment was done using a total of 10 aforementioned capacity plastic bottles placed in a water bath at 37°C. The plastic digester's effective volume was fully immersed in the bath and equipped with a stretchable tube having a roller as a valve which is directly connected to the urine bag and then to the reversed graduated cylinder for biogas measurement. Biogas formed was measured by the liquid displacement method. The valve was used to control the flow of gas for composition analysis. The un immersed portion of the digester was insulated to prevent heat loss.

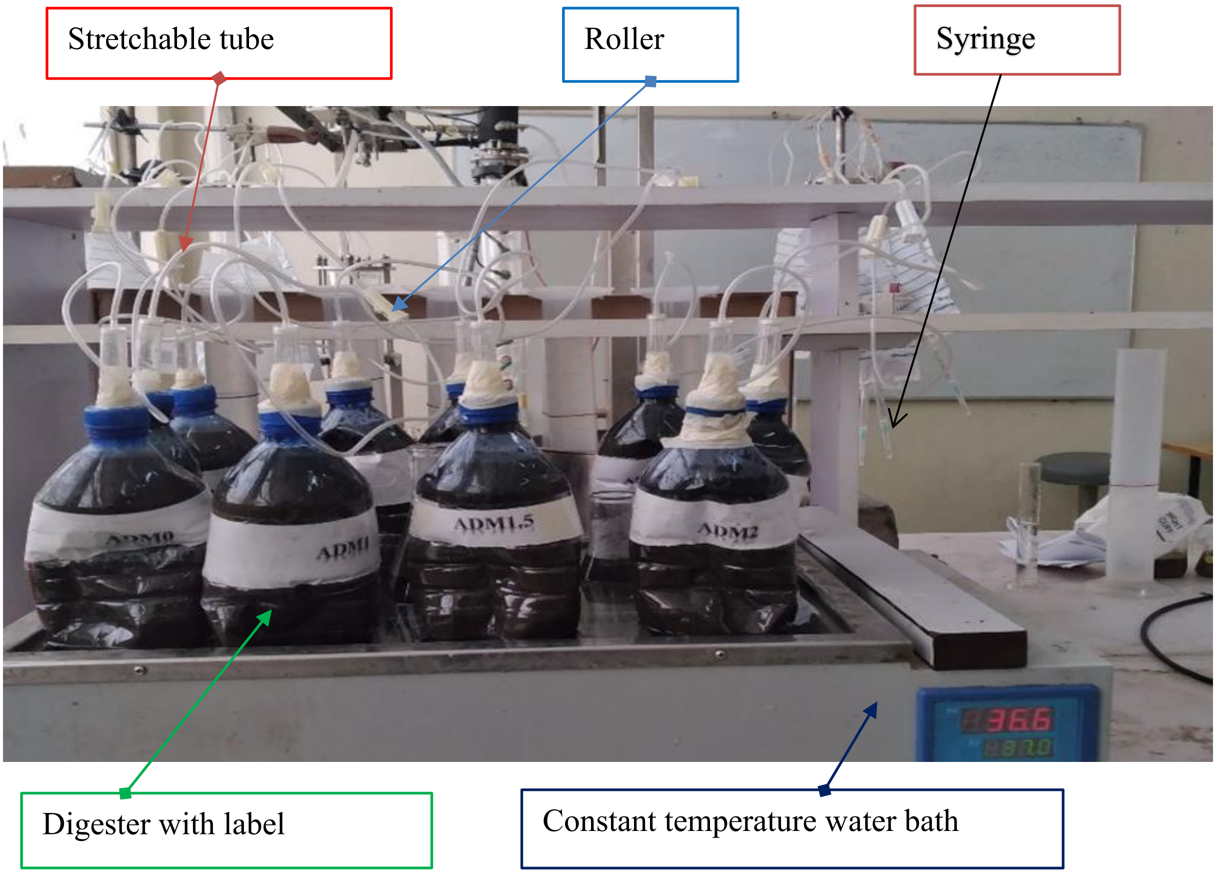

Figure 5.13: The experimental set up of batch anaerobic digestion before insulation

5.7 Measuring yield and quality of biogas

The gas production was measured by water displacement method whereas the quality, which is the content of methane from the biogas, is estimated by the displacement of sodium hydroxide solution. The gas produced in the plastic bottle was captured in the airbag and allowed to pass to a graduated cylinder filled with water. When a gas bubble entered the graduated cylinder with water, the gas replaced the water, which was then forced out of the graduated cylinder. The displaced water indicates the total volume of biogas produced.

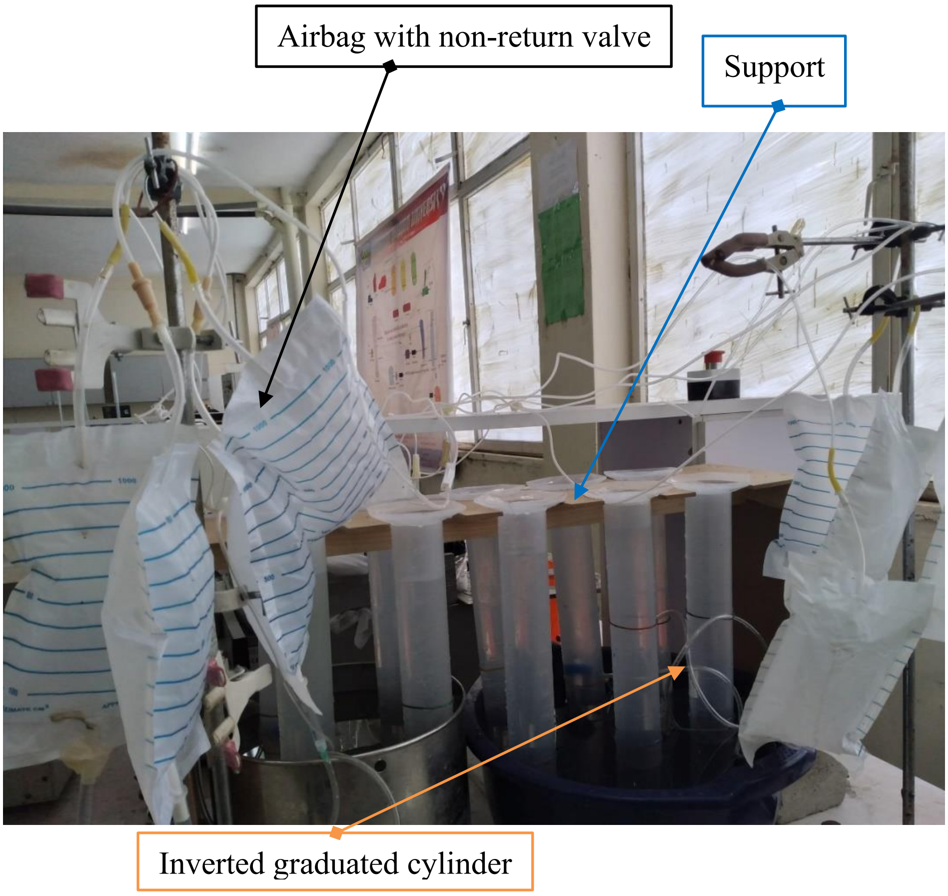

Figure 5.14: Measurement of biogas using the water displacement method

Note that a small amount of gas coming out of the digester which is stored in the airbag also allowed passing through a 5% NaOH solution in another inverted graduated cylinder. The CO_2 and H_2S from the biogas would be retained in the solution whereas the methane would displace its equivalent volume of NaOH. Collecting the displaced solution and measuring its volume using a measuring cylinder would give the volume of methane from the produced biogas.

CHAPTER SIX

RESULT AND DISCUSSION

6.1 Introduction

This section describes the results obtained during the laboratory scale experiment of anaerobic digestion of cow dung. The characteristics of biochar and substrates used in the study, biogas production, CH_4 production without and with biochar addition are presented. The experiments were conducted in a Liter digester with different concentrations of biochar to achieve the objectives of the thesis.

6.2 Characteristics of CC-BC at Different Operating conditions

The important physical characteristic of biochar is the specific surface area (SSA). These characteristics are affected by different feedstock and operating conditions of pyrolysis (Masebinu et al., 2019). The surface area of CC-BC produced at different pyrolysis temperatures and reaction time was determined using the iodine number test method (ASTM D4607-94, 2007) as shown in fig. 6.1.

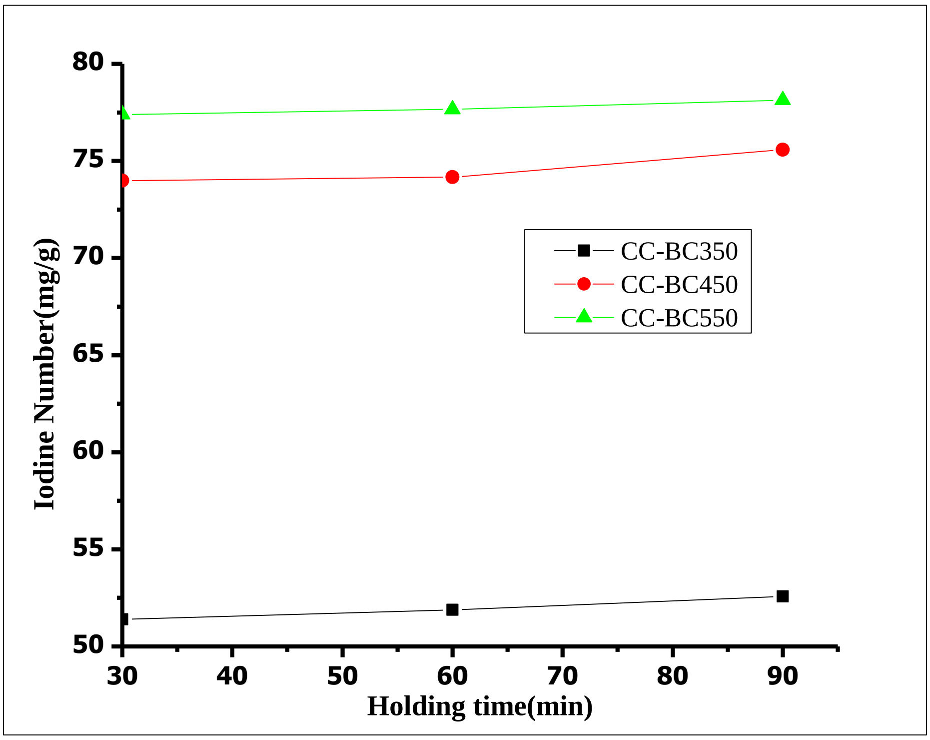

Figure 6.1: Effect of temperature and time on SSA of CC-BC

The iodine number of prepared biochar was CC-BC550 (78.14 mg/g), CC-BC450 (75.58 mg/g), and CC-BC350 (52.58 mg/g). It has been observed that the iodine number could be a parameter that could approximately determine the surface area per gram of CC-BC.

This iodine number indicates that the development of microporous structure and adsorption site on its surface.

The result also indicates that the surface area of the biochar was directly correlated with pyrolysis temperature. But according to (Masebinu et al., 2019) the higher the pyrolytic temperature, >450℃, the more suitable the biochar is for the adsorption of organic contaminants, because of the improved surface area, the increased distribution of micropores, and the higher level of hydrophobicity.

However, due to the loss of oxygen-containing and hydrogen-containing functional groups at temperatures above 450℃, the capacity to adsorb organic contaminants will be impacted negatively. Conversely, biochar produced at lower temperatures, less than 450℃, is suitable for the adsorption of inorganic and nonpolar organic contaminants. CO_2 being a nonpolar compound can be adsorbed into the sorption sites of biochar and retained in the appropriately sized pores (Masebinu et al., 2019). Considering the aforementioned reasons CC-BC450 was selected for the study and sent to further characterization.

Moisture content, yield, ash, volatile matter, and resident matter contents of selected CC-BC at pyrolysis temperatures of 450℃ for 60min. The result of proximate analysis (MC, AC, and VM) of the corn cob derived biochar according to ASTM D1762-84 has shown in Table 6.1.

Table 6-1: CC-BC characterizations produced at 450℃ and 60 minutes

Parameter	**Mass of crucible, g**	**Mass of sample, g**	**Temperature, ℃**	**Residence time, min**	**Result in (%)**
TS	40.1	$w_1 = 1$	105	1440	96.5
Moisture	40.1	$w_1 = 1$	105	1440	3.5
VM	40.1	$w_2 = 0.965$	950	11	32.22
Ash	40.1	$w_3 = 0.654$	750	3600	5.07

6.3 Characteristics of the substrates used

The fresh cow dung was analyzed concerning total solids and volatile solids content, moisture content, and pH. The characteristics of CD a single substrate and inoculum were determined and the results are shown in Table 6.3 below. When the CD and inoculum were characterized, the mean value of the total solid and volatile solid for CD were 16% and 84.5 % and for inoculum were 17.3 % and 83% respectively.

Table 6-2: Initial characteristics of the substrate

Materials	Types of analysis			
	TS (%)	VS (%)	MC (%)	pH
Cow dung	16	84.5	84	7.12
Inoculum	17.3	83	83.7	6.89

Total solids concentration is one of the most important waste characteristics. As indicated in Table 8, fresh cow dung has a TS of 16 in percentage. But according to (Mukumba et al., 2017) and (Mattocks, 1984), 8% of TS is favorable for AD. As a result, some amounts of water have to be added to prepare a wet organic feed mixture with 8% total organic solids for biogas production in the anaerobic fermentation process.

The pH is regarded as the key indicator of operational stability. The initial pH of the input substrate and inoculum before seed into digester was 7.12 and 6.89 respectively. So, this result was in agreement with the pH range of the input mixture in the digester between 6.80 and 7.60, which is suitable for anaerobic microorganisms. The VS is an important factor in determining the BMP of a particular type of biomass, as the VS is broken down to produce biogas. According to (Deublein and A. Steinhauser, 2011), the amount of VS in the manure determines the biogas yield from the AD process to produce methane gas.

The value of VS indicates that fresh cow manure contains high organic matter which explains energy content for biogas production. The results of the proximate analysis of feed material showed that the moisture content of the cow dung was 84%. This result is comparable with the study done by (Zhang et al., 2007) who carried out the study on cattle manure and found that the optimum moisture content was 74 to 90%. Therefore, the result is more likely similar to this researcher.

6.4 Lab-scale biogas production

Ten lab-scale anaerobic digesters were developed and utilized for the digestion of cow dung as a single substrate in this study. The AD experiments were conducted for approximately 33 days to examine biogas production from cow dung with various concentration of biochar using digesters labeled as ADM_0, ADM_1, $ADM_{1.5}$, ADM_2, and $ADM_{2.5}$, where M represents the temperature and the number after M represents the concentration of CC-BC450 (g/800L of digester) divided by four which was shown in the experimental setup. The production of biogas started on the 14th day for all digesters.

6.4.1 Measurement of Biogas production

The production of biogas was observed and volumes of the biogas collected were recorded during the experiment period of 33 days. Biogas production was measured until biogas production is reduced.

The daily biogas production rates from the digestions of the CD without the addition of biochar in ADM_0 and with the addition of biochar in ADM_1, $ADM_{1.5}$, ADM_2, and $ADM_{2.5}$ are shown in Fig. 6.1. It was observed that biogas production started on the 14th day in all the digesters, and increased for consecutive days. After that, it reached its peak point. The peak values of daily biogas production rates were found to be 93, 83, 72, 68, and 57 mL/day after 29, 23, 27, 25, and 29 days of digestion from ADM_1, $ADM_{1.5}$, ADM_2, and $ADM_{2.5}$ respectively.

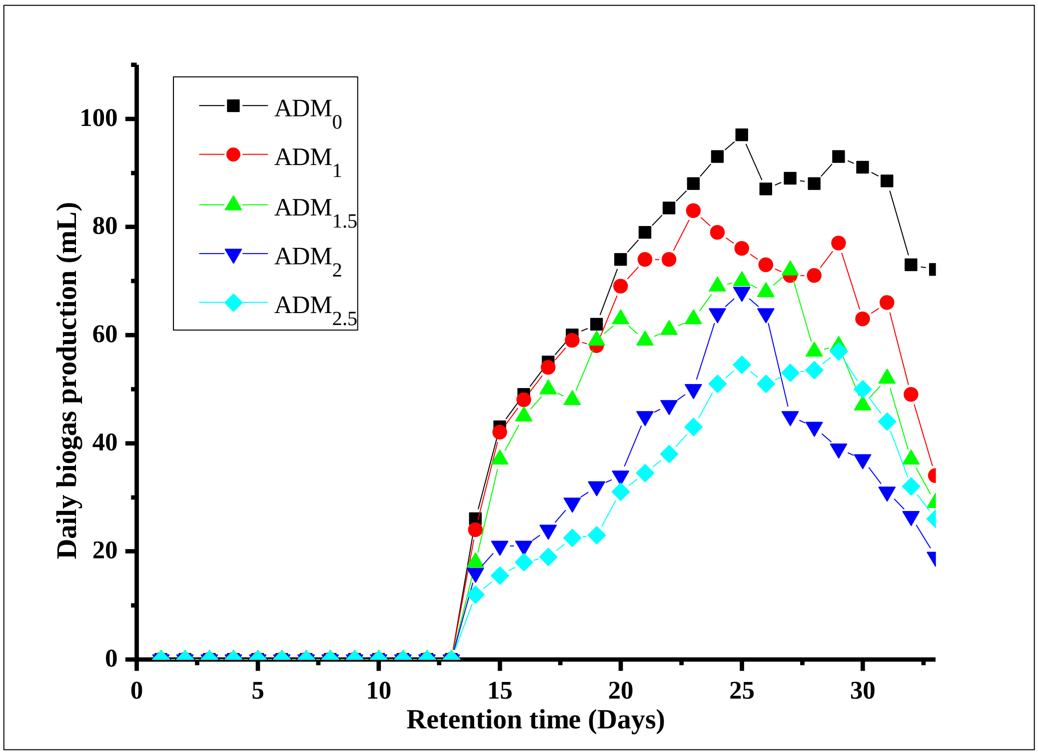

Figure 6.2: Daily biogas production of cow dung

The digester ADM_0 followed by ADM_1 produced biogas at a higher rate per digester volume than the other three digestion tests during periods of the experiment, this maximum rate indicates that CD can be used as a single substrate for the production of energy but still needs additives to enhance energy quality.

As shown in fig 6.2, on the first 14^{th} day of the experiment, biogas production was not formed yet and tend to decrease at the end period of the experiment. During the period between set-up and initial gas production the microorganism responsible for the process were completely inactive. The aerobic bacteria present were using up all the oxygen present in the digester during this period. After all oxygen has been used up, the acid forming bacteria became active and gas production began. This is predicted due to the biogas production rate in the batch condition is directly corresponds to the specific growth rate of methanogenic bacteria in the digester. In the range of 14 to 30 days of observation, gas production is significantly increasing due to the exponential growth of microorganisms.

6.5 Effect of CC-BC450 on Biogas and Methane Production

The current study was conducted to examine the beneficial effect of biochar on methane production. The results show that biochar significantly increased methane production.

6.5.1 Identification of biochar concentration for highest biogas production

The time course of cumulative biogas production for the digestion of CD for different experimental conditions is shown in Fig. 6.2.

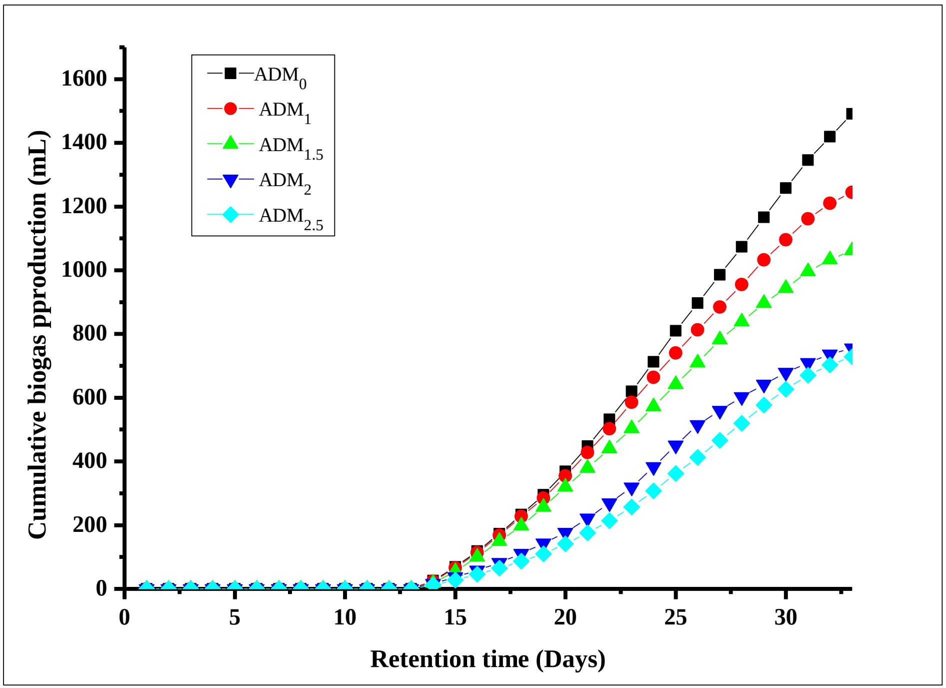

Figure 6.3: Cumulative biogas production

This experiment indicates that there was higher biogas production for ADM_0 (1491.1 mL), (1244 mL) for ADM_1, (1062 mL) for $ADM_{1.5}$, (755.5 mL) for ADM_2, and $ADM_{2.5}$ (728.5 mL) per volume of the digester respectively. Cumulative biogas production decreased with the increase of biochar concentration. Biogas production of all biochar-amended digesters was significantly lower than that of ADM_0. This is due to trace elements of biogas such as carbon dioxide and hydrogen sulfide were adsorbed into the adsorption site of CC-BC450, and this result is consistent with (Shen et al., 2015).

6.5.2 Identification of biochar concentration for highest CH_4 production

Fig. 6.4 shows the daily methane production of each group of experiments. All digester showed a gradual increase in daily methane production and eventually decrease afterward. This can be explained as at the beginning of gas production, the anaerobes present in the organic material became active. When gas production began to rise, they were fully established and were acting on more substrate. At the peak of production, they were acting on the maximum amount of organic matter possible. After this point, gas production began to drop because the excess substrates were being converted to methane. At this point also, there is a steady decline in the amount of substrate available to the bacteria to act on. This decline continues until gas production gradually comes to an end. While the process progresses, the condition becomes more appropriate for the methane forming bacteria.

The digesters with the addition of CC-BC450 (ADM_1, $ADM_{1.5}$, ADM_2, and $ADM_{2.5}$) showed high daily methane production than those of the ADM_0.

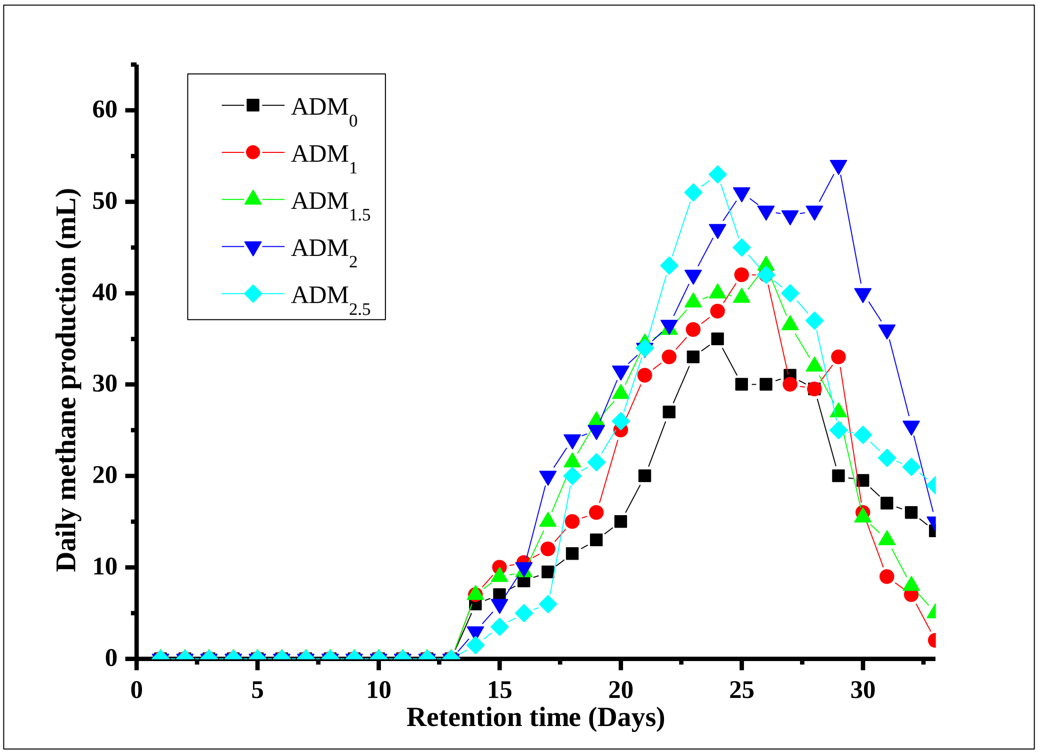

Figure 6.4: The time course of methane production rate for the tested conditions

There was methane production from the ADM_1 with the second-lowest peak methane production and there were small peaks of methane production in the late stage of AD. This performance may be explained by the presence of toxic organic compounds in CD, causing a decrease in the microbes' activity and the inhibition of cow dung anaerobic digestion. The increased methane yields in the late stage were the result of recovered microbial activity and decomposition and utilization of organic compounds in CD due to the presence of CC-BC450.

The digesters with CC-BC450 addition attained high peaks of daily methane production than ADM0 and declined slowly afterward, indicating that the addition of CC-BC450 mitigates the inhibitory effect of CD on the AD system. The addition of CC-BC450 can reduce the microbial adaptation period and lead to a more rapid onset of the growth phase (Mumme et al., 2014).

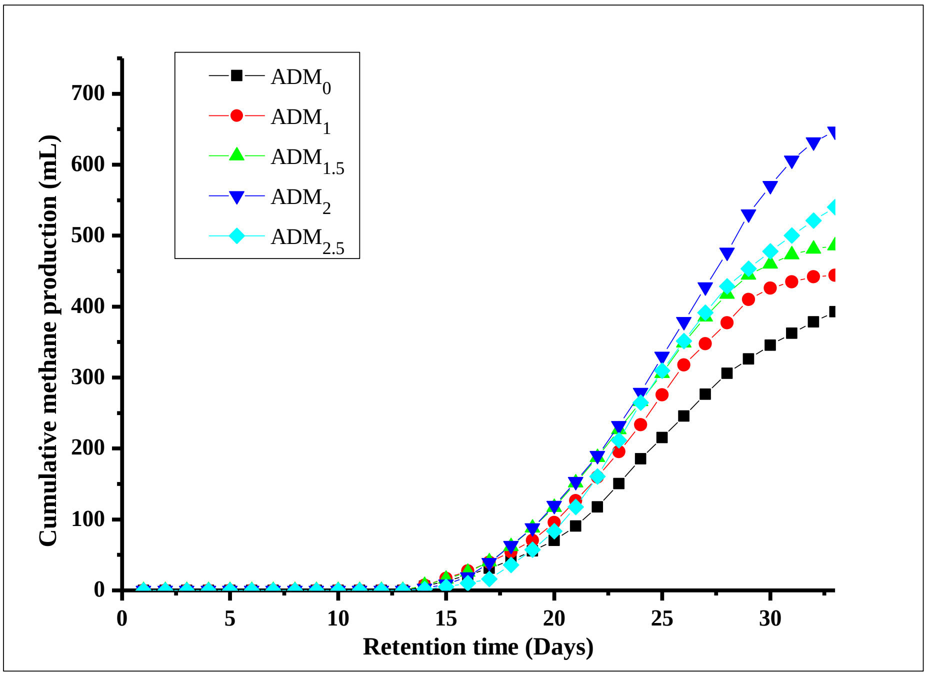

Figure 6.5: Cumulative methane production with various concentration of biochar

Fig.6.5 shows the cumulative methane production obtained in each group of experiments. In the first 13 days, there was no difference in methane production observed between all digesters. All digesters showed uniform and similar trends, exhibiting a slow increase during the first 20 days and then a rapid increase after the 20th day.

The cumulative methane production of the $ADM_{2.5}$ exceeded that of the ADM1.5 on the 23rd day and exceeded that of the ADM_1 on the 21st day. For ADM_1, $ADM_{1.5}$, ADM_2, and $ADM_{2.5}$, the cumulative methane production at the last stage was much higher than that of the control digester, indicating that these four biochar samples can rapidly alleviate the toxicity of CD and accelerate the degradation of organics so that AD can start quickly.

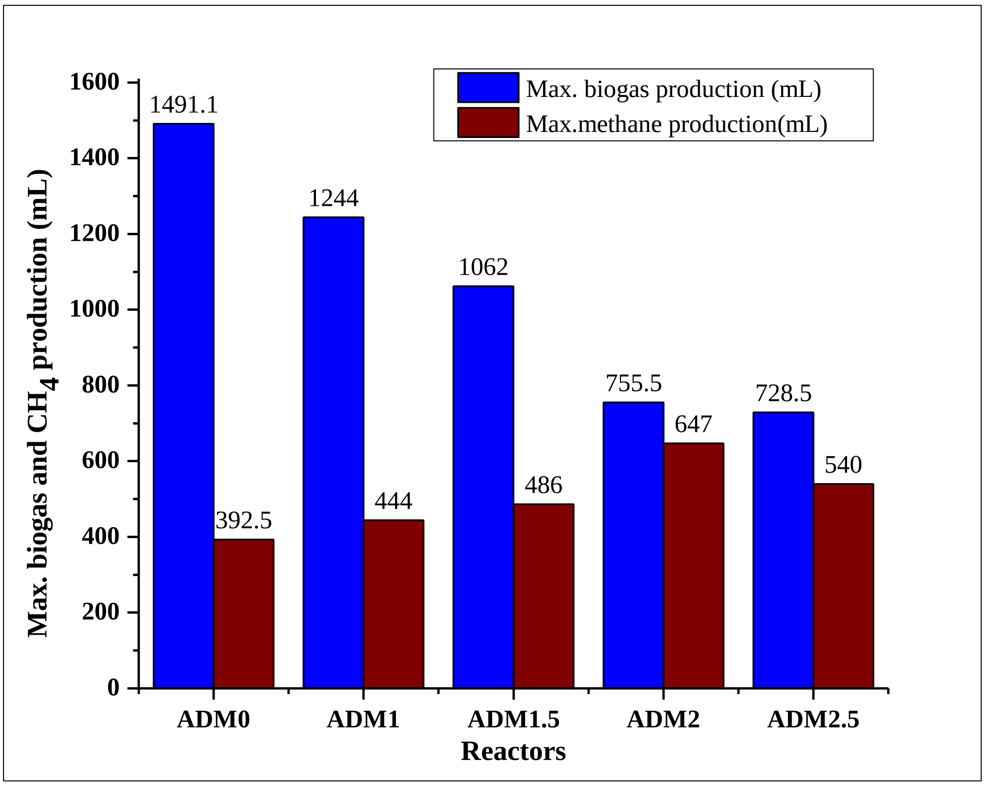

Figure 6.6: Maximum biogas and CH_4 vs CC-BC450 concentrations

Simultaneously, in the presence of CC-BC450, all digesters showed a slight improvement in accumulative methane production. This indicated that CC-BC450 addition could accelerate CD digestion by providing buffering in the whole anaerobic process and result in higher methane production.

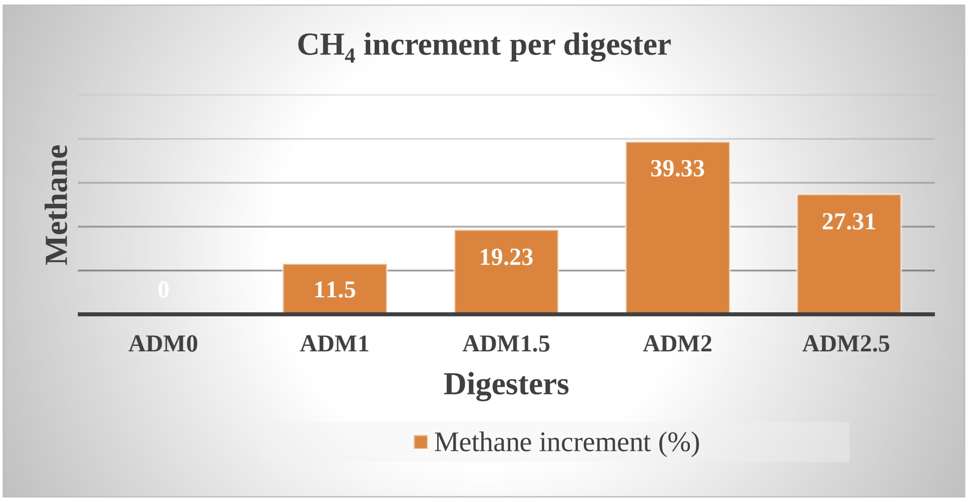

Figure 6.7: Percentage of methane increment by volume per digesters

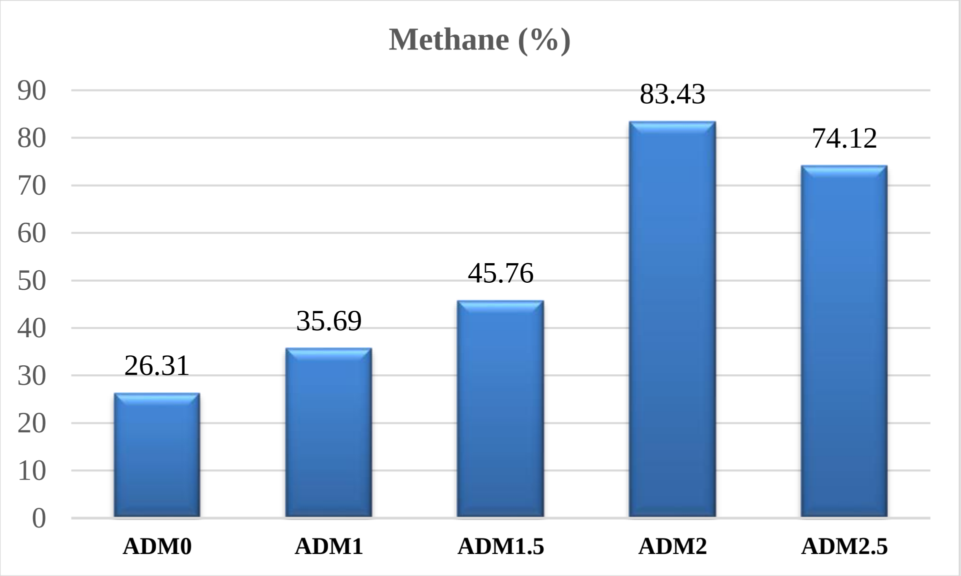

Figure 6.8. The percentage of methane from AD with various concentration of CC-BC450

As shown in figure 6.8, increasing biochar concentration increases methane production rate and cumulative methane production. This indicates that CC-BC450 adsorbed trace elements in the biogas. This led to an increase in the percentage composition of methane.

6.6 Analysis of the cumulative CH_4 with the Modified Gompertz Model

The results of methane gas produced in each run were plotted against time and were fitted using the modified Gompertz model to determine the highest methane production (mL) as shown from Fig.6.9. to Fig. 6.12.

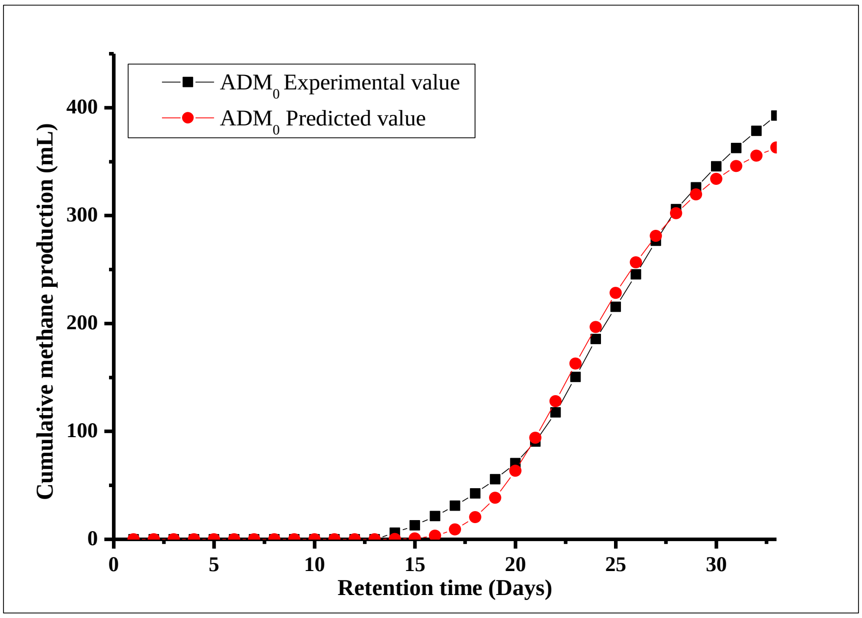

Figure 6.8: Methane production (mL) without CC-BC450 from Gompertz model

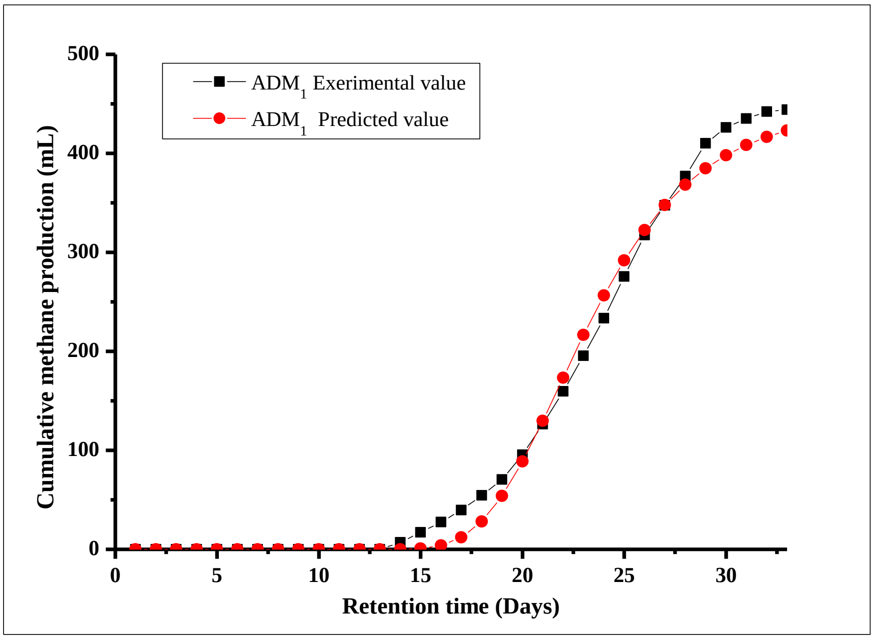

Figure 6.9: Methane production (mL) with 4g of CC-BC450 from Gompertz model

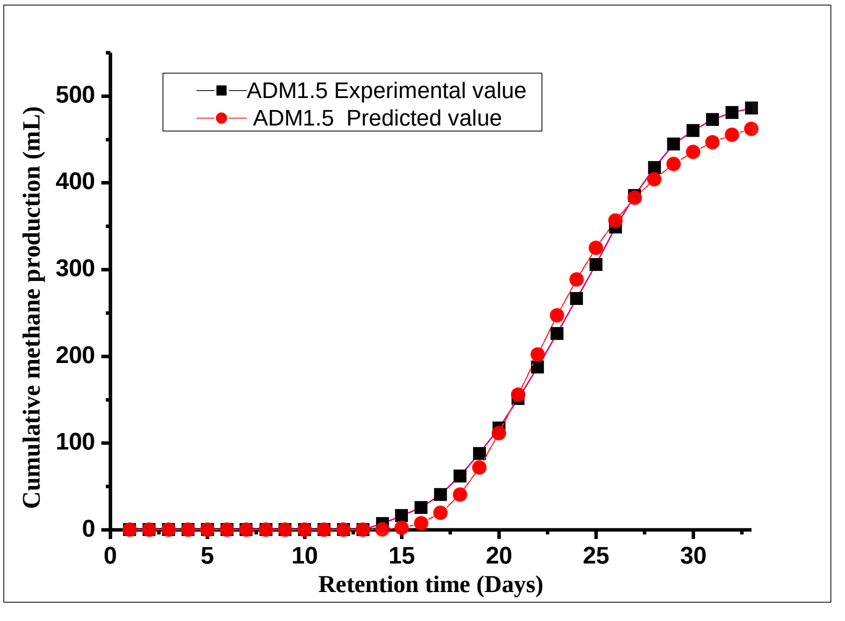

Figure 6.10. Methane production (mL) with 6g of CC-BC450 from Gompertz model

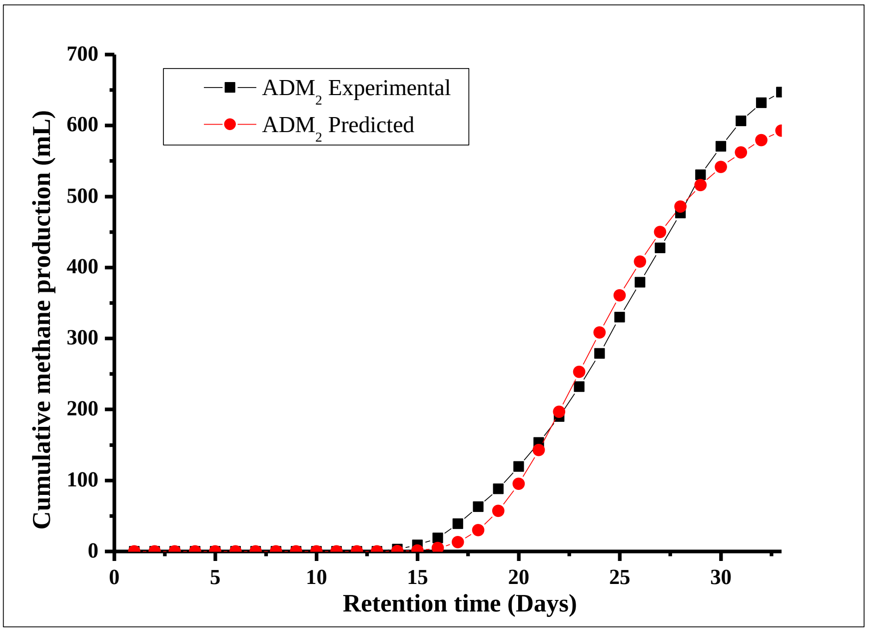

Figure 6.11: Methane production (mL) with 8g of CC-BC450 from Gompertz model

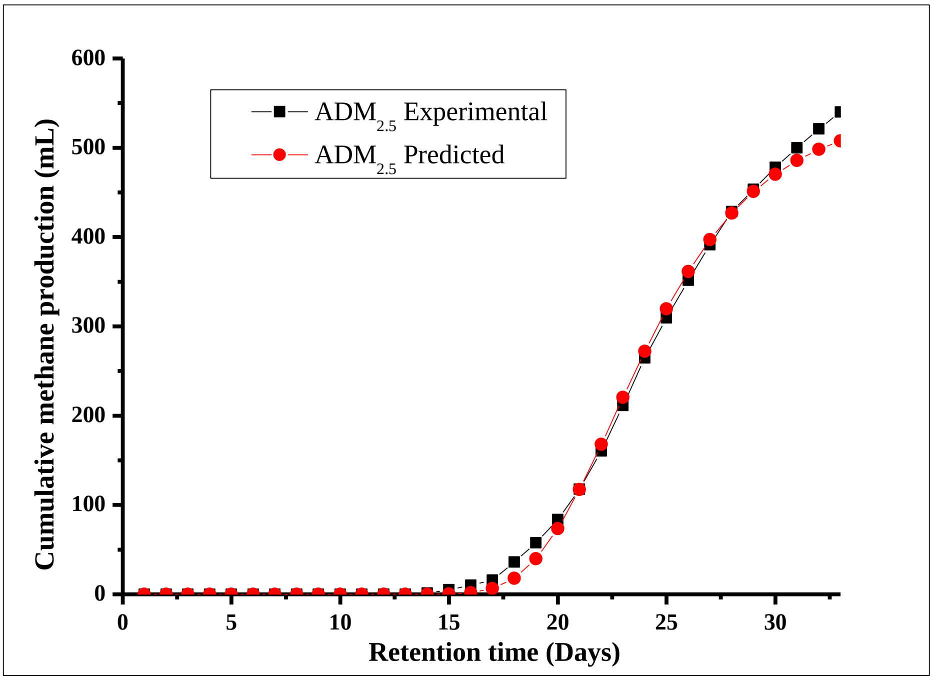

Figure 6.12. Methane production (mL) with 10g of CC-BC450 from Gompertz model

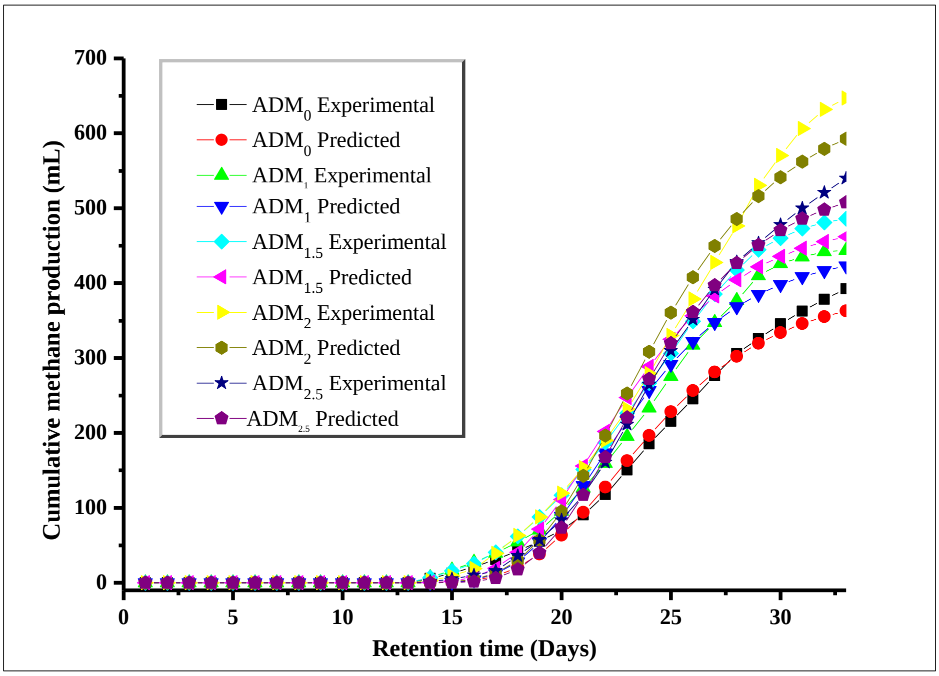

Figure 6.13: Comparison of CH_4 production at different concentrations of CC-BC450

The results obtained from the modified Gompertz equation is given in Table 6.3. The highest methane production was found in run ADM_2 that representing the concentrations of 8g/800mL, which corresponding to the Gompertz constants of P = 592.82 ml, R_{max} = 56.517 mL/day, and L = 17.53 days. Meanwhile, the trends of methane production obtained were comparable among other runs that contained CC-BC450 at d/t concentrations.

Table 6-3: Modified Gompertz equation parameter values for CH_4 production

AD	P (mL)	R_{max} (mL/day)	λ (day)	R^2
ADM_0	363.09	35.348	18. 42	0.993
ADM_1	422.94	43.050	18.348	0.994
$ADM_{1.5}$	462.22	46.501	17.65	0.994
ADM_2	592.82	56.517	17.53	0.990
$ADM_{2.5}$	507.57	53.062	17.527	0.997

The experimental data of cumulative methane production was also fitted using the Gompertz model and the fitted curves were presented. The R^2 of all of the fittings ranged from 0.993 to 0.997, suggesting a good fitting between experimental data and the modeling results. As shown in Table 6.3, the R_{max} of the digesters with biochar additions were higher than that of the control. However, the R_{max} increased as the biochar addition increased from

0 to 8 g/800mL biochar and then decreased as the biochar addition was further increased to 10 g/800mL. The *P* of all digesters amended with biochar was higher than that of the control, whereas, the digesters with higher biochar additions (10g/800mL) showed lower *P*. The highest *P* was achieved for the culture with an 8 g/800 mL biochar addition.

By adding CC-BC450, λ of ADM_1 decreased from 18.42 days to 18.348 days; λ of $ADM_{1.5}$ decreased from 18.42 days to 17.65 days; λ of ADM_2 decreased from 18.42 days to 17.53 days, and λ of $ADM_{2.5}$ decreased from 18.42 days to 18.527 days, respectively. Similarly, Luo et al. (2015) reported that the addition of fruitwood derived biochar (10 g/L) shortened the λ by 16.5%, 11.4%, 30.3%, and 21.6% during AD of 2 g/ L, 4 g/L, 6 g/L, and 8 g/L of glucose, respectively.

Additionally, the experimental data from (Jang et al., 2018) indicated that by adding M-BC, λ of P1 and P10 decreased from 10.81 days to 10.48 day and 9.26 day, λ of M1 and M10 decreased from 2.08 day to 1.87 days and 1.52 day; λ of T1 and T10 decreased from 3.94 days to 3.58 day and 2.98 days, respectively.

6.7 Evaluation against literature data

Apart from comparing with the control, the results from the present study are compared with the literature data on the batch lab-scale methane production with the addition of different types of biochar. Similar studies report the beneficial effects of biochar on CH_4 production (Table 6.4). The present work is in good agreement with other studies in the literature using various wastes as the feedstock and the results were within the range of the findings of other studies.

Table 6-4: A comparison of the current experimental results with the literature data

Feedstock of AD	Feedstock of biochar	Biochar addition (g/L)	Operating condition (Type, Temperature, and pH)	Methane yield compared to control (%)
AD Sludge	PS and WH	20	Batch, 42°C, and N.A	32
DM	Diary manure	1-10	Batch, 35°C and 7.7	5-24.5
Food waste	Fruit woods	2-10	Batch,35°C and 7	39-44
FW and AS	Sawdust	2-15	Batch, 35°C, and N.A	2-4
Glucose	Fruit woods	10	Batch, 35°C and 7	11.5
This study	Corn cob	4-10	Batch, 37°C and 7.12	39.33

As shown in table 6.4. at the appropriate concentrations of biochar, the CH_4 production increased by 2-44% compared to the control, depending on the types and addition ratio of biochar, the feedstock of AD, and operating conditions as reported by (Mumme et al., 2014), (Jang et al., 2018), (Cai et al., 2016), (G. Wang et al., 2018), and (Luo et al., 2016) respectively.

CHAPTER SEVEN

CONCLUSIONS AND RECOMMENDATIONS

7.1 Introduction

The outcomes of this study have contributed useful experimental data on the effect of utilizing biochar in AD to enhance CH_4 production in lab-scale AD. This chapter tells the key conclusion and recommendations as follows.

7.2 Conclusions

While much work has been done in modifying the biochar for adsorption of desired organic or inorganic compounds, very less is known on its application in anaerobic digestion and the overall quality of the biogas. In this study, the effect of biochar addition on the CH_4 production in the laboratory-scale AD of cow dung under the same initial pH and mesophilic conditions has been studied.

Physicochemical analysis of corn cob biochar showed positive results for using CCBC450 in AD to improve biogas quality when compared with the control sample. The results of this study show that the reprocessing of crop residues such as corn cob into biochar and its application to AD was beneficial in many ways. Due to its physicochemical properties, biochar derived from corn cob has been shown to improve biogas quality. The application of AC to AD also has a similar advantage but direct disposal of AC with effluent would cause additional concerns for environmental pollution and safety (Luo et al., 2015). Thus, the use of biochar instead of AC has the potential to reduce the extent of environmental issues.

The most important finding from this research was that the CC-BC450 added to the digester has a significant effect on cumulative methane production and methane production rate. The effect of biochar addition on CH_4 production in AD was observed and increased the maximum CH_4 production by 11.59-39.33%. This indicated that CC-BC450 can stable the digestion process and enhances the microbial activity of methanogens and adsorption of CO_2 and H_2S. The optimum biochar addition was found to be 8g/800mL. Under the optimum condition, the P and R_{max} were 592.82 mL and 56.517 mL/day. It is found that the quality of biogas produced mostly depends on the concentration of biochar added based on their surface area value and, the best performance of methane production was obtained at CC-BC concentration of 8g/800mL.

From the result obtained, cow dung which can be found in abundance everywhere in Ethiopia, are a very good feedstock for biogas production, and utilizing CC-BC can also increase the quality of gas production. In conclusion, based on the results derived from this study, as well as previous studies, biochar should be considered as an alternative solution for increasing energy quality from biogas and environmental problems, also it has been demonstrated as an eco-friendly system.

7.3 Recommendations

The present study demonstrated the possibility of increasing the quality of biogas using biochar amended digester as well as AD stability. However, various new gaps have also been identified during the evaluation of the findings of the current study. Based on this thesis work, the following recommendations are suggested for future research which is related to biogas production using biochar.

- The biochar used in the study, however, was only limited to one type of biochar, which was the CC-BC, prepared at 450°C. Considering the different characteristics which may be possessed by different types of biochar, their effects in AD may be different. There could be some biochars that may not show the same or similar beneficial effects as CC-BC450 studied in the present work does and it would be scientifically interesting and practically useful to clearly define the key characteristics of biochar and relate them to their effects in enhancing CH_4 production in AD operations. Therefore, further studies using different types of biochar in AD are recommended.
- This work was done on the study of the effect of CC-BC450 under a fixed set of operating conditions of AD, further studies have to be done to examine the effect of CC-BC addition under various operating conditions.
- Also, the characteristics of CC-BC are limited to surface area and proximate which was clearly understood that how pyrolysis temperature influences factors as surface area, and from this analysis, the potential uses of the biochar as an additive for AD processes. However, in future work further characterization has to be done including scanning electron microscopy, and elemental analysis should be performed to determine the exact composition and morphology of CC-BC biochar samples.
- The results of the present study show the potential benefit of using CC biochar in anaerobic digestion on a laboratory scale on a batch basis, but more research is required to fully understand how lab-scale results can be translated to commercial-scale systems.

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APPENDICES

Appendix A: Biochar Production Data Sheet

Sample	Mass of crucible, g	Mass of CB sample, g	Temperature, °C	Residence time (min.)	(Mass of crucible +sample), g	Biochar yield, g
1	114.2	43	350	30	129.4	15.2
2	118.3	42	350	60	133.3	15
2	115.5	45.5	350	90	130.2	14.7
4	114.2	42.1	450	30	125.9	11.7
5	115.5	44.8	450	60	126.9	11.4
6	58.6	20	450	90	64.1	5.5
7	58.6	20	550	30	63.7	5.1
8	56.1	20	550	60	61.3	5.2
9	57	20	550	90	62	5

Appendix B: Biochar Sample Characterization, Surface Area Data Sheet

Solution standardization										
$P(mL)$	$R(N)$	$S(mL)$ in triplicate			$N_1(N)$	$I(mL)$	$S(mL)$ *in triplicate*			$N_2(N)$
		1	2	3			1	2	3	
25	0.1	18.1	18.9	18.1	0.136173	25	15.6	15.4	15.4	0.084245

$N_1 = (P \times R)/S$ and $N_2 = (S * N_1)/I$

N_1 (N)	N_2 (N)	$Time$ (min)	T_{bp} (°C)	M (g)	V (mL)	N_r (N)	A	X (mg)	I_n (mg/g)
0.084245	0.136173	30	350	1	12.18	0.033172	0.9263	55.5904	51.4934
0.084245	0.136173	60	350	1	11.92	0.032464	0.928	55.9177	51.8917
0.084245	0.136173	90	350	1	11.67	0.031783	0.9313	56.4609	52.5821
0.084245	0.136173	30	450	1	10.71	0.029168	0.9425	77.1767	73.9971
0.084245	0.136173	60	450	1	9.63	0.026227	0.9588	77.3514	74.1646
0.084245	0.136173	90	450	1	9.45	0.025737	0.9613	78.6248	75.5821
0.084245	0.136173	30	550	1	8.94	0.024348	0.97	79.8869	77.4903
0.084245	0.136173	60	550	1	8.87	0.024157	0.9708	79.9937	77.6579
0.084245	0.136173	90	550	1	8.45	0.023013	0.9788	79.8389	78.1464

Appendix C: Biochar Sample Characterization, Proximate Data Sheet

Biochar characterization produced at 450 and 60 minutes					
METHOD:ASTM D1762-84					
The material used: locally available corn cob					
Parameter	Mass of crucible, g	Mass of sample, g	Temperature, ℃	Residence time, min	Result, (%)
Total solid	40.1	$w_1 = 1$	105	1440	96.5
Moisture	40.1	$w_1 = 1$	105	1440	3.5
volatile matter	40.1	$w_2 = 0.965$	950	11	32.22
Ash	40.1	$w_3 = 0.654$	750	3600	5.07
				$w_4 = 0.0149$	

Appendix D: Cow dung sample characterization before and after digestion

Substrate characterization experiment						
METHOD: APHA 1995						
The material used: Fresh cow dung						
Parameter	*A*	*B*	*C*	Temperature, ℃	Residence time,min	Result, %
Total solid	58.7	68.7	60.3	105	1440	16
Moisture	58.7	68.7	60.3	105	1440	84
volatile matter	58.7	60.3	58.95	600	30	84.5
pH						7.12

Appendix E: Anaerobic digestion experiment results

A. Biogas production rate (mL/day)

Daily biogas production (mL/day)					
Retention Time, days	ADM_0 (Control)	ADM_1 (4g/800mL)	$ADM_{1.5}$ (6g/800mL)	ADM_2 (8g/800mL)	$ADM_{2.5}$ (10g/800mL)
1	0	0	0	0	0
2	0	0	0	0	0
3	0	0	0	0	0
4	0	0	0	0	0
5	0	0	0	0	0
6	0	0	0	0	0
7	0	0	0	0	0
8	0	0	0	0	0
9	0	0	0	0	0
10	0	0	0	0	0
11	0	0	0	0	0
12	0	0	0	0	0
13	0	0	0	0	0
14	26	24	18	16	12
15	43	42	37	21	15.5
16	49	48	45	21	18
17	55	54	50	24	19
18	60	59	48	29	22.5
19	62	58	59	32	23
20	74	69	63	34	31
21	79	74	59	45	34.5
22	83.5	74	61	47	38
23	88	83	63	50	43
24	93	79	69	64	51
25	97	76	70	68	54.5
26	87	73	68	64	51
27	89	71	72	45	53
28	88	71	57	43	53.5
29	93	77	58	39	57
30	91	63	47	37	50
31	88.5	66	52	31	44
32	73	49	37	26.5	32
33	72.1	34	29	19	26

B. Cumulative biogas production (mL)

Cumulative biogas production (mL)					
Retention Time, days	ADM_0 (Control)	ADM_1 (4g/800mL)	$ADM_{1.5}$ (6g/800mL)	ADM_2 (8g/800mL)	$ADM_{2.5}$ (10g/800mL)
1	0	0	0	0	0
2	0	0	0	0	0
3	0	0	0	0	0
4	0	0	0	0	0
5	0	0	0	0	0
6	0	0	0	0	0
7	0	0	0	0	0
8	0	0	0	0	0
9	0	0	0	0	0
10	0	0	0	0	0
11	0	0	0	0	0
12	0	0	0	0	0
13	0	0	0	0	0
14	26	24	18	16	12
15	69	66	55	37	27.5
16	118	114	100	58	45.5
17	173	168	150	82	64.5
18	233	227	198	111	87
19	295	285	257	143	110
20	369	354	320	177	141
21	448	428	379	222	175.5
22	531.5	502	440	269	213.5
23	619.5	585	503	319	256.5
24	712.5	664	572	383	307.5
25	809.5	740	642	451	362
26	896.5	813	710	515	413
27	985.5	884	782	560	466
28	1073.5	955	839	603	519.5
29	1166.5	1032	897	642	576.5
30	1257.5	1095	944	679	626.5
31	1346	1161	996	710	670.5
32	1419	1210	1033	736.5	702.5
33	1491.1	1244	1062	755.5	728.5

E. CH_4 Production rate, mL/day

Daily CH_4 Production (mL/day)					
Retention Time	ADM_0 (Control)	ADM_1 (4g/800ml)	$ADM_{1.5}$ (6g/800ml)	ADM_2 (8g/800ml)	$ADM_{2.5}$ (10g/800ml)
1	0	0	0	0	0
2	0	0	0	0	0
3	0	0	0	0	0
4	0	0	0	0	0
5	0	0	0	0	0
6	0	0	0	0	0
7	0	0	0	0	0
8	0	0	0	0	0
9	0	0	0	0	0
10	0	0	0	0	0
11	0	0	0	0	0
12	0	0	0	0	0
13	0	0	0	0	0
14	6	7	7	3	1.5
15	7	10	9	6	3.5
16	8.5	10.5	9.5	10	5
17	9.5	12	15	20	6
18	11.5	15	21.5	24	20
19	13	16	26	25	21.5
20	15	25	29	31.5	26
21	20	31	34.5	34	34
22	27	33	36	36.5	43
23	33	36	39	42	51
24	35	38	40	47	53
25	30	42	39.5	51	45
26	30	42	43	49	42
27	31	30	36.5	48.5	40
28	29.5	29.5	32	49	37
29	20	33	27	54	25
30	19.5	16	15.5	40	24.5
31	17	9	13	36	22
32	16	7	8	25.5	21
33	14	2	5	15	19

F. Cumulative CH_4 Production (mL)

Cumulative CH_4 production (mL)					
Retention Time, days	ADM_0 (Control)	ADM_1 (4g/800mL)	$ADM_{1.5}$ (6g/800mL)	ADM_2 (8g/800mL)	$ADM_{2.5}$ (10g/800mL)
1	0	0	0	0	0
2	0	0	0	0	0
3	0	0	0	0	0
4	0	0	0	0	0
5	0	0	0	0	0
6	0	0	0	0	0
7	0	0	0	0	0
8	0	0	0	0	0
9	0	0	0	0	0
10	0	0	0	0	0
11	0	0	0	0	0
12	0	0	0	0	0
13	0	0	0	0	0
14	6	7	7	3	1.5
15	13	17	16	9	5
16	21.5	27.5	25.5	19	10
17	31	39.5	40.5	39	16
18	42.5	54.5	62	63	36
19	55.5	70.5	88	88	57.5
20	70.5	95.5	117	119.5	83.5
21	90.5	126.5	151.5	153.5	117.5
22	117.5	159.5	187.5	190	160.5
23	150.5	195.5	226.5	232	211.5
24	185.5	233.5	266.5	279	264.5
25	215.5	275.5	306	330	309.5
26	245.5	317.5	349	379	351.5
27	276.5	347.5	385.5	427.5	391.5
28	306	377	417.5	476.5	428.5
29	326	410	444.5	530.5	453.5
30	345.5	426	460	570.5	478
31	362.5	435	473	606.5	500
32	378.5	442	481	632	521
33	392.5	444	486	647	540

G. Predicted values of cumulative methane production

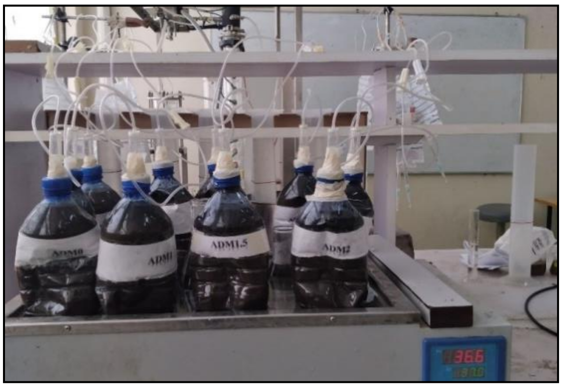
Predicted cumulative CH_4 production (mL)					
Retention Time, days	ADM_0 (Control)	ADM_1 (4g/800mL)	$ADM_{1.5}$ (6g/800mL)	ADM_2 (8g/800mL)	$ADM_{2.5}$ (10g/800mL)
1	0	0	0	0	0
2	0	0	0	0	0
3	0	0	0	0	0
4	0	0	0	0	0
5	0	0	0	0	0
6	0	0	0	0	0
7	0	0	0	0	0
8	0	0	0	0	0
9	0	0	0	0	0
10	0	0	0	0	0
11	0	0	0	0	0
12	0	0	0	0	0
13	0.02	0.01	0.05	0.03	0
14	0.16	0.13	0.43	0.22	0.03
15	0.86	0.91	2.16	1.21	0.27
16	3.22	3.91	7.47	4.57	1.62
17	9.06	11.96	19.44	13.01	6.33
18	20.39	28.07	40.63	29.72	17.95
19	38.54	53.87	71.72	56.99	39.87
20	63.52	88.65	111.17	95.24	73.44
21	94.02	129.68	155.84	142.78	117.23
22	127.89	173.41	202.22	196.51	167.7
23	162.82	216.51	247.19	252.79	220.59
24	196.78	256.52	288.58	308.34	272.1
25	228.32	291.99	325.17	360.63	319.52
26	256.57	322.36	356.52	408.05	361.35
27	281.16	347.68	382.73	449.81	397.03
28	302.1	368.34	404.25	485.73	426.71
29	319.62	384.95	421.67	516.08	450.92
30	334.07	398.14	435.61	541.34	470.39
31	345.87	408.52	446.67	562.13	485.85
32	355.42	416.64	455.38	579.09	498.04
33	363.09	422.94	462.22	592.82	507.57

H. Cumulative biogas production and CH_4 (%) and CH_4 increment

Digesters	ADM_0 (Control)	ADM_1 (4g/800mL)	$ADM_{1.5}$ (6g/800mL)	ADM_2 (8g/800mL)	$ADM_{2.5}$ (10g/800mL)
Biogas (mL)	1491.1	1244	1062	775.5	728.5
Methane (%)	26.31	35.69	45.76	83.43	74.12
Others	NA	NA	NA	NA	NA
Percentage of methane increment and trace element reduction					
Methane (mL)	392.5	444	486	647	540
Increment CH_4 (%)	0	11.5	19.23	39.33	27.31
Trace element reduction, %		9.38	19.45	57.12	47.81

Appendix F: Experimental setups, Materials, and Equipment

A. Experimental setups

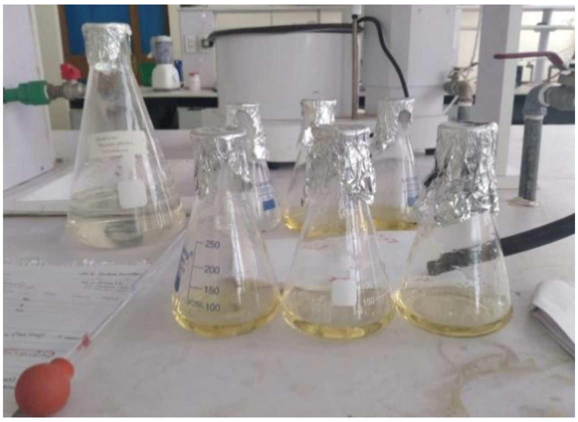


A.1: Digesters placed in water bath

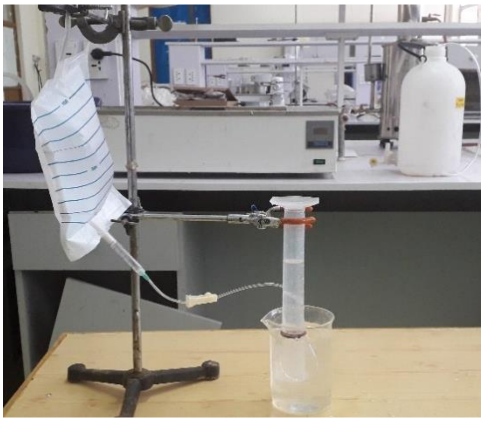
A.2: Biogas measurment with WDM

A.3: Filtration using sandpaper

A.4: Pouring 5% HCl into CC-BC sample

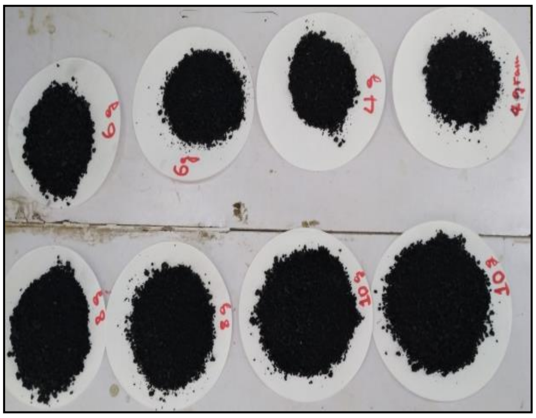


A.5: Yellow light observed during titration



A.6: Methane measurement

B. Materials



B.1: Corn cob

B.2: Corn cob derived biochar

B.3: Chemicals

B.4: Prepared solutions

B.4: Cow dung slurry

B.5: Intestinal residue

C. Equipment’s

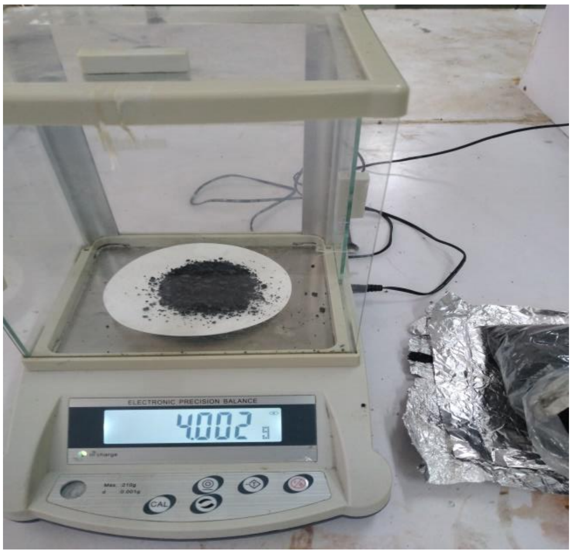
C.1: Muffle furnace

C.2: Universal hot air oven

C.3: Constant temperature water bath

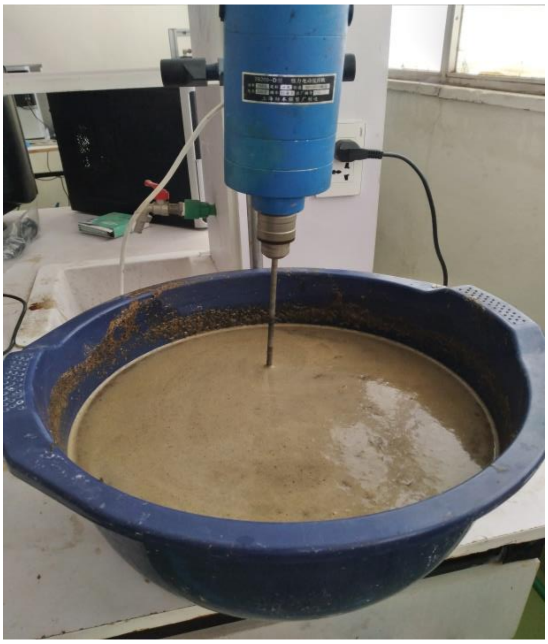
C.4: PHS-1701 pH meter

C.5: Desiccator



C.6: Digital weight balance

C.7: Weight balance



C.8: Electric agitator

C.9: Streachable tube

C.10: Syringe