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## **Optimization and Upgrading of Biogas from Brewery Waste for Boiler**

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## **Abstract**

*Rises in fuel prices and the continued pollution to the environment calls for a search to find cost effective and environmentally cautious methods of finding alternative fuels especially for industrial purposes while Ethiopia is spending around 2,000,000,000 birr/year for HFO. The treatment can be costly for the owners but a method such as anaerobic digestion can be used to treat the waste, minimize environmental pollution due to the use of fossil fuel at the same time minimize the financial cost. This study focuses on optimization and upgrading of biogas from brewery waste and for boiler. This research emphasizes on production of biogas from brewery waste and cow dung focusing on the optimization of process parameters such as temperature, HRT and TS for the maximal biogas production.*

*Optimization of those variables was carried out by General factorial Design Expert software. Firstly, the characteristics of each of the two items were investigated in detail comparatively. The results obtained can be summarized as follows: Biogas volume and composition from brewery waste was 0.5L, 35% using 10 day, 35 °C, 8%Ts and compared to Cow dung that yielded 3.9L, 70% using 10 day, 35 °C, 8%Ts. Therefore, to increase the amount of methane composition and yield brewery waste and cow dung were mixed based on the recommendation from literature Total solid of 4%, 8% and 12%, Temperature at 25 °C, 35 °C, 50°C and hydraulic retention time at 10, 15, and 20 days. From the experiment, all three parameters had significant effects on biogas volume and composition. The optimum conditions for maximizing the biogas yield and composition were 10 day, 35 °C, 8%Ts in which maximum biogas yield of 0.3 lit /gm. Out of which 60% is methane that is upgraded. The methane was upgraded to 81.4% methane using 25% caustic water absorption process.*

*During upgrading the carbon dioxide content reduced below 22% and hydrogen sulphide was negligible during the production step. The upgraded methane gave calorific value of 6967.84Kcal/m<sup>3</sup> which has energy generating potential of 8.1kwh/m<sup>3</sup>. While this waste has a potential to generate 15,240.636 kwh/day of energy which could cover 16.6% of HFO consumption it can generate energy equal to 12, 954.54 kwh/day and save 6,591,764.508 birr/year of its budget. In addition, there is a benefit for the environment and human health.*

*Key words-Anaerobic digestion, Biogas, Methane, Brewery waste, cow dung, and Heavy fuel oil*

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## Abbreviations

AD	Anaerobic digestion
APHA	American Public Health
ANOVA	Association Analysis of Variance
BGI	Name of Saint George Beer factory
BOD	Biological oxygen demand
CD	Cow Dung
COD	Chemical oxygen demand
C/N or C: N	Carbon to Nitrogen Ratio
DM	Dry Matter
HFO	Heavy fuel oil
HRT	Hydraulic Retention Time
KI	Potassium iodide
KWh	Kilowatt hour
PAHS	Polycyclic hydrocarbon compounds
PAC	Polycyclic aromatic compounds
pH	Power of Hydrogen
TS	Total solid
UASB	Up flow anaerobic sludge blanket
VS	Volatile solid

## **Chapter One**

### **1. Introduction**

#### **1.1 Background**

The beer production process is energy intensive and uses large volume of water. The production of beer involves the blending of the extracts of malt, hops, and sugar with water, followed by its subsequent fermentation with yeast (Wainwright, 1998). The brewing industry employs a number of batch-type operations in processing raw materials to the final beer product. The amount of water used to brew beer is several times the volume actually brewed. For instance, an average water consumption of 6.0 hectoliters is required to produce one hectoliter of bright beer. Large volume of water is being used by the industry for production of beer for two distinct purposes; as the main ingredient of the beer itself and as part of the brewing process for steam raising, cooling, and washing of floors, packaging, cleaning of the brew house during and after the end of each batch operation.

The brewing process is energy intensive, especially in the brew house, where mashing and wort boiling are the main heat consuming processes with high fuel consumption. Wastewater is one of the most significant waste products of brewery operations. Even though substantial technological improvements have been made in the past, it has been estimated that approximately 3-10 L of waste effluent is generated per liter of beer produced in breweries (Kanagachandran, 2006). The quantity of brewery wastewater will depend on the production and the specific water usage. Brewery wastewater has high organic matter content; it is not toxic, does not usually contain appreciable quantities of heavy metals. The cost of fossil fuels has increased significantly over the last 10 years worldwide and continues to spiral upward today. Limited fossil fuel resources, the increasing demand for energy worldwide, speculation in the fossil energy commodities market connected globally rising prices, and the ambition of the countries that signed the Kyoto Protocol to achieve the requested reduction in CO<sub>2</sub> emissions has led to the target to partially substitute fossil fuels with renewable energy sources or combustion of energy-rich waste for heat generation (Olajire, 2012). The conservation of fossil fuel resources will help reduce CO<sub>2</sub> emissions from fossil fuel combustion, greenhouse gas emissions, and possible climate changes due to these emissions (Buchhauser, 2006).

The demand for heat energy in beer production can be reduced through the use of waste heat as process heat or waste material for thermal energy. Another possible substitute for fossil fuel is anaerobic fermentation of brewery waste water (Ahrens, 2007). Anaerobic digestion (AD) can be used to treat the waste at the same time minimize the financial cost that is exploited to buy fuels for boiler like Heavy fuel oil. Ethiopia spends around \$ 71,093,319.29 (Petroleum, 2016) for HFO which is around 2,000,000,000 birr. Hence, the conversion of biodegradable waste into energy has great potential of reducing waste issues and financial costs while delivering energy, and economic benefits.

AD is one of the promising technologies for recovering energy from brewery waste. It is already a common alternative method for sewage and manure treatments. Since food waste has the advantage of high organic content compared with sewage or manure, AD is now increasingly considered as a viable alternative for recovering energy from the organic fraction of industrial waste. Anaerobic digestion is a biological process performed by many classes of bacteria and generally consists of four steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. The main product of this process, methane, can be used as a boiler fuel or co-generation of electricity and heat, and thus, can lead to reductions in greenhouse gas emissions.

## **1.2 Statement of the problem**

Today, about 90% of the total energy production all over the world is provided by combustion of fossil fuels (Barroso, 2003). This type of fossil fuels such as Heavy fuel oil is currently being used in process industries to generate heat energy. Unfortunately, Heavy fuel oil (hydrocarbon) combustion has a major impact on the global environment through the emission of CO<sub>2</sub>, which is a greenhouse gas. Furthermore, emission of NO<sub>x</sub>, SO<sub>x</sub>, polycyclic aromatic hydrocarbons (PAHs), CO, and particles leads to air pollution, acid rain, and health hazards (Barroso, 2003).

The number of industries that use Heavy fuel oil for boiler as a fuel are increasing from time to time. Investments in alcoholic, nonalcoholic beverages and soft drinks as well as stimulants industry have shown a tremendous progress. Currently, Heineken, BGI, Dashen, Meta, Raya Habesha, and Zebidar are beer companies operating in Ethiopia which collectively run 11 factories. Four giant liquor and two wine factories also make part of Ethiopian beverage industry. The typical cost of energy and utilities amount to between 3% and 8% of a brewery's general budget, depending on brewery size and other variables. A well-run brewery would use from 8 to

12 kWh electricity, 5 hL water, and 150 MJ fuel energy per hectoliter of beer produced. To illustrate, one MJ equals the energy content of about one cubic foot of natural gas, or the energy consumed by one 100 W bulb burning for almost three hours, or one horsepower electric motor running for about 20 min (NRC, 2010). This breweries and industries with their massive expansion result in increased waste production, fossil fuel consumption, and pollutant emission. This indicate there is much to be done to treat waste, minimize fossil fuel consumption, reduce pollutant emission, and environmental pollution. Waste produced should be treated before it is released to the environment. At the same time, waste treating mechanism can be a way to produce energy yielding gas like biogas which can be used to generate energy for boiler.

Presently, waste generated at Heineken brewery, Kilinto is treated using UASB but the biogas produced is flared, shows the company is inefficiently utilizing biogas, contributing to environmental pollution. Biogas is a fuel that can be used to run the Boiler which can reduce or mostly replace amount of fossil fuel (HFO, fuel at the present used to run the boiler). On the Contrary, the company is spending on average 39,728,905.93birr per year for HFO. By optimizing and upgrading biogas production from brewery waste with cow dung for Boiler the impact on the environment form usage of Heavy fuel oil can be minimized. Heineken should shoot for efficiently using biogas by utilizing biogas to produce energy for boiler. Using the upgraded Biogas to run the Boiler assists to reduce or mostly replace amount of fossil fuel (HFO) used to run the boiler as a result decrease pollutant emission and treat waste.

## **1.3 Objective**

### **1.3.1 General Objective**

The general objective of the research is to optimize and upgrade biogas production from brewery waste with Cow dung for boiler.

### **1.3.2 Specific Objective**

- To characterize brewery waste and Cow dung.
- To optimize biogas production.
- To upgrade biogas and investigate the CO<sub>2</sub> removal efficiency.
- To asses energy difference between the raw and upgraded biogas.

- To evaluate biogas equivalent energy demand.

#### **1.4 Scope**

This study is limited to optimization and upgrading of biogas from brewery waste and cow dung aiming to supply methane for boiler. Additionally, all of experimentation is done on a laboratory scale.

#### **1.5 Significance**

The laboratory-scale findings can be applied for further studies. This research can serve as a foundation for future research on scaling up similar researches. The outcome of the study will help to save energy and for environmental protection policy makers as a reference during preparation of a guideline for increasing number of alternative renewable energy technology means by using different resources, for substitution of fossil fuel throughout the country and for managing brewery waste. In general, it contributes to the economic advancement of the country through production of energy from wastes which reduce the amount of fuel import from abroad and it has great impact on reduction of greenhouse emission from industry sector.

## Chapter Two

### 2. Literature Review

#### 2.1 Energy from waste

The industry sector, as one of the major contributors towards energy deficiencies and greenhouse gas emissions at the same time to environmental pollution, is identified as an area that requires urgent intervention. More efforts are required to address the imagined fuel shortage and mitigate the environmental challenges. This can be achieved through research and systematic programmers aimed at greening the economy through a low carbon and resource-productive economy (African, 2010). As a renewable and sustainable source of energy, several countries have used biogas as a preferred option (Amigun, 2011). The primary objective of this study was to review and workout an efficient co-digestion strategy that would maximize methane yield from the complete digestion of selected industrial wastes.

Currently, Heineken, BGI, Dashen, Meta, Raya, Habesha, and Zebidar seven beer companies are operating in Ethiopia which collectively run 11 factories. Four giant liquor and two wine factories also make part of Ethiopian beverage industry. This breweries and industries with their massive expansion result in increased waste production, fossil fuel consumption, and pollutant emission.

One of the mechanisms to reduce the waste production, the fossil fuel consumption and pollutant emission and efficiently treat waste is through conversion of waste to biogas, a mixture accomplished through conversion to biogas, a mixture of mostly methane ( $\text{CH}_4$ ) and carbon dioxide ( $\text{CO}_2$ ), via anaerobic digestion. In practice, microbial anaerobic conversion to methane is a process for effective waste treatment, biological fertilizer and sustainable energy production. It has the potential for reducing the use of traditional biomass, the demand for fossil fuels like coal, oil, and natural gas which continued exploitation will significantly impact our environment and affect the global climate (Wilkie AC, 2008).

In Ethiopia, enough consideration is not given to producing biogas especially from biogas brewery waste upgrading and using it for Boiler. As a result, the country is losing reusable waste, as the same time polluting the environment and spending millions of dollars for importing (Fossil Fuel, heavy fuel oil) to run boilers which is polluting the environment. This research focuses

how to utilize waste from brewery waste with cow dung to optimize and upgrade it for Boiler to make possible the above explained activities. Optimization and upgrading of Biogas involve waste treatment and methane production. For further utilization of biogas, because raw biogas contains carbon dioxide which decreases the heating value and the efficiency of biogas upgrading the raw biogas removes the carbon dioxide and provides more efficient biogas for boiler use.

## **2.2 Anaerobic digestion**

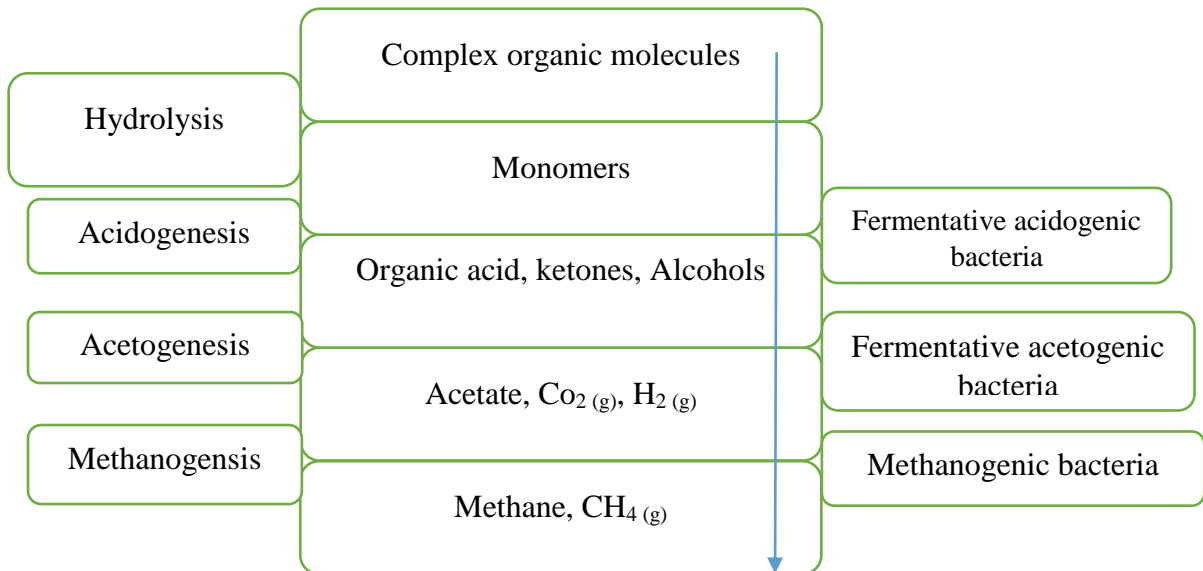
Anaerobic conversion of organic materials and pollutants is an established technology for environmental protection through the treatment of wastes and wastewater. The end product is biogas—a mixture of methane and carbon dioxide—, which is a useful, renewable energy source. Anaerobic digestion is a technologically simple process, with a low energy requirement, used to convert organic material from a wide range of wastewater types, solid wastes and biomass into methane. A much wider application of the technology is desirable in the current endeavors towards sustainable development and renewable energy production (de Mes, 2010).

In addition to creating clean-burning energy, anaerobic digestion also eliminates harmful pathogens and odors, and most importantly, the biogas process produces high-quality, nitrogen-rich fertilizer that can be used to replace chemical fertilizers made with fossil fuels. Unlike compost, biogas slurry is a liquid and can be applied on a commercial scale with existing farm equipment. The fertilizer replacement value of biogas slurry far exceeds any potential revenue from the gas itself (Wilkie AC, 2008).

### **2.2.1 Biological process**

Anaerobic digestion of solid substrates is typically divided to four main steps (Fig. 1). In hydrolysis, organic polymers are degraded by enzymes to soluble compounds, which are further degraded to e.g. volatile fatty acids (VFA),  $H_2$  and  $CO_2$  during acidogenesis. VFAs are oxidized in acetogenesis step to acetate,  $H_2$  and  $CO_2$  which are further converted to methane in methanogenesis (Anderson, 2002). Different microorganisms play a significant role in each stage of the processes. Therefore, intervention and follow up in all the stages is essential for enhanced and optimum methane production.

**Figure 1** : CH<sub>4</sub> and H<sub>2</sub> production from polymeric substrates partially adapted from (Anderson, 2002).



### 2.2.1.1 Hydrolysis

Enzymatic hydrolysis is the process where the fats, starches and proteins contained in cellulosic biomass are broken down into simple compounds (Rajeshwari, 1999). The microbial cell is impermeable to the cellulose molecule so the organism must excrete extracellular enzymes in order to make the carbon source available. At this stage polymers are converted into carbohydrate, fat and protein to simple sugar, fatty acid, and amino acid. The extra cellular catalysts act hydrolytically, converting the insoluble materials to soluble sugars that penetrate the cell membrane. The large molecular complex substances are soluble into simpler ones (especially volatile acids, which are low molecular weight organic acids) with the help of extracellular enzyme excreted by the acid forming bacteria. The phase is also known as polymer breakdown stage (Digest, 1980).

These monomers become substrates for the microorganisms in the second stage where they are converted into organic acids by a group of bacteria. This process is natural, but could be enhanced by external application of enzymes for better methane production. For example, the

hydrolysis of cellulose and hemi-cellulose is considerably enhanced by the application of hydrolytic enzymes of fungal origin on selected substrates, and increases methane yield.

#### **2.2.1.2 Acid formation (Acidogenesis)**

In this stage the products of hydrolysis are metabolized by obligatory anaerobic bacteria collectively called Acidogenic bacteria. The soluble compounds formed in the hydrolysis (e.g. glucose, xylose) are further oxidized to e.g. volatile fatty acids (acetic, propionic, butyric etc.),  $H_2$  and  $CO_2$  in the acid genesis step (Fig. 1) (also referred to as fermentation) by fermentative bacteria. In fermentation, some of the molecules of the substrate are reduced, whereas others are oxidized, usually to  $CO_2$ . The interesting products as initial intermediate product for the formation of methane gas are volatile fatty acids (VFA), hydrogen, and carbon dioxide. The overall performance of the anaerobic digestion is affected by the concentration of individual fatty acids (short chain fatty acids) formed in the acidogenic stage because acetic acid and butyric acid are the preferred precursor for methane production (Hwang, 2001). As pH drop occurs owing to acetate accumulation, microbes would limit acidification from metabolism by producing lactate or butyrate of acetate or by re-up taking acetate to acetyl-coenzymes (Anderson, 2002).

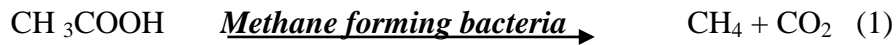
#### **2.2.1.3 Acetogenesis**

The term 'Acetogen' refers to the collection of bacteria that generates acetate ( $CH_3COOH$ ) as a product. Simple molecules created through the acidogenesis phase are further digested by acetogens to produce largely acetic acid as well as carbon dioxide and hydrogen (Buswell and Sollo, 1948). Acetogen are the vital link between hydrolysis, acidogenesis and the methanogenesis in anaerobic digestion. Acetogenesis provides the two main substrates for the last step in the methanogenic conversion of organic material, namely hydrogen and acetate. Both the acidogenesis and acetogenesis produce the methanogenic substrates, acetate,  $H_2$  and  $CO_2$ . Homoacetogens consume  $CO_2$  and  $H_2$  producing acetate.

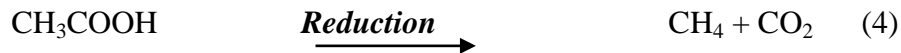
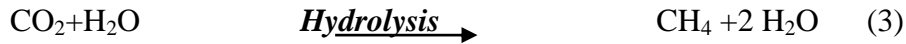
#### **2.2.1.4 Methane formation (Methanogenesis)**

Organic acids as formed above are converted into methane ( $CH_4$ ) and  $CO_2$  by the bacteria which are strictly anaerobes, called methane fermenters (Rai, 2004). Three classes of methanogenic substrates are known, i.e.  $CO_2$  type substrates ( $CO_2$ , CO, formate), methyl substrates (methanol,

methylamine, dimethylamine, trimethylamine) and acetotrophic substrates (acetate) (Anderson, 2002). In anaerobic digesters treating wastewater biosolids, 70 % of the methane derives from acetate and 30% from hydrogen. Acetotrophic methanogens degrade acetic acid. Hydrogenotrophic methanogens produce methane autotrophically from carbon dioxide (carbon source and electron acceptor) and hydrogen (electron donor). Anaerobic reactions will ultimately lead to production of CH<sub>4</sub> and CO<sub>2</sub>, thus, in traditional AD process the biogas is mainly composed of methane (50-70 %) and carbon dioxide. Methanogenic bacteria generate methane by fermenting acetic acid to methane (CH<sub>4</sub>) and CO<sub>2</sub> and by reducing CO via hydrogen gas or by other bacterial species.



Similarly, CO<sub>2</sub> can be hydrolyzed to carbonic acid and to methane as in equations 3 and 4.



## 2.2.2 Factors affecting biogas production

### 2.2.2.1 Temperature

Both fixed temperature at which bio-digestion take place and temperature fluctuation affect the quantity and quality of biogas production. For the former case, methane bacteria (methanogenes) work best at a temperature of 35-38 °C and fall in gas production starts at 20 °C and stops at a temperature of 10 to 13 °C. In this connection, there are two significant temperature zones in anaerobic digestion and two types of microorganisms that should be considered, mesophilic and thermophilic. The optimum mesophilic temperature lies at about 35 °C, while the thermophilic temperature is around 55 °C. Most of the sewage digestion tanks are heated at 35 °C so as to reduce the time required for digestion and minimize the capacity of the tanks. Others reported that more biogas is produced at mesophilic temperature zones than at room temperature.

#### **2.2.2.2 pH or hydrogen ion concentration**

PH of slurry changes at various stages of digestion. In the initial acid formation stage, in the fermentation process, the pH is around 6 and much of CO<sub>2</sub> is given off. In the latter 2-3 weeks' time, the PH increases as the volatile acid and N<sub>2</sub> compounds are digested and CH<sub>4</sub> is produced. To maintain a constant supply of gas, it is necessary to maintain a suitable pH range in the digester. The digester is usually buffered to maintain the pH at 6.5 to 7.5. In this pH range, the micro-organisms will be very active and bio-digestion will be very efficient (Rozzi, 2000). The introduction of too much raw material can cause excess acidity and the gas-producing bacteria will not be able to digest the acids quickly enough. The addition of a little ammonia can raise the pH value very fast. If the pH grows too high (not enough acid), fermentation will slow until the digestive process forms enough acidic carbon dioxide to restore balance.

#### **2.2.2.3 Carbon to Nitrogen ratio**

Besides carbon the quantity of nitrogen present in the input material is a crucial factor in the production of biogas. The elements of carbon (in the form of carbohydrates) and nitrogen (as protein, ammonium nitrates) are the main food of anaerobic bacteria. Carbon is used for energy and nitrogen for building the cell structure. The bacteria use up carbon about 30 times faster than they use up nitrogen. So, carbon and nitrogen should be present in the proper proportion i.e.: N is 30:1 (R. Scott Frazier, 2015). If the ratio is higher, the nitrogen will be exhausted while there is still a supply of carbon left. This causes some bacteria to die, releasing the nitrogen in their cells and eventually restoring the equilibrium. Digestion proceeds slowly as this occurs. On the other hand, if there is too much nitrogen, fermentation (which will stop when the carbon is exhausted) will be incomplete and the "leftover" nitrogen will not be digested. This lowers the fertilizing value of the slurry. Halim (2011) reported that the greatest methane production per unit occurred when the C: N ratio of the feed was 25:1. Such 25:1 to 35:1 ratio could be maintained only when cow dung is supplemented and mixed with plant materials depending on the substrate used.

#### **2.2.2.4 Total Solid (TS) and Volatile solid (VS) Content**

The cow dung is mixed usually in proportion of 1:1 (by weight) in order to bring the total solid content to 8-10 %. The raw cow dung contains 80-82% of moisture. The balance 18-20 % is termed as total solids. The adjustment of total solid content helps in bio-digesting the material at the faster rate, and also in deciding the mixing of the various crop residues, weeds, and plants

etc. as feed stocks in biogas digester .Elias (2010) studied that the TS and moisture contents of fresh cow dung and VS (as percentage of TS) and ash content were 16 %, 84 %, 79.11 % and 20.89 %, respectively.

#### **2.2.2.5 Hydraulic Retention Time (HRT)**

The period of retention of the material for biogas generation depends on the type of feed stocks and the temperature .Normal retention period is between 30 and 45 days and in some cases 60 days (Rajeshwari, 1999). Depending on the waste material and operating temperature, a batch digester starts producing biogas after two to four weeks, slowly increasing in production then dropping off after three or four months (HilkiahIgoni, 2010). Here it should be noticed that gas may be produced before these periods test (Yitayal, 2012). Too short retention time means an inefficient extraction of methane, so full revenue is not realized. Too long retention time means too much is spent on surplus capacity or not enough substrate is being added to maximize revenue.

#### **2.2.2.6 Feed stocks and Co-digestion**

According to (Wilkie AC, 2008), the feed stocks for Feed stocks and Co-digestion biogas generation can be composed of carbohydrates, lignocelluloses, proteins, fats or mixtures of these components. All plant and animal wastes or leaf of plants prepared for this purpose could be used as the feed materials for a digester. When feedstock is woody or contains more of lignin, then bio-digestion becomes difficult. Cow and buffalo dung, human excreta, poultry droppings, pig dung, waste materials of plants, cobs, etc can all be used as feed stocks. To obtain an efficient bio-digestion, these feed stocks are combined in proportions (Rajeshwari, 1999). The feed stocks for anaerobic digestion vary considerably in composition, homogeneity, fluid dynamics and biodegradability. In intensive animal farming, pig and cow slurries are reported to contain dry matter contents in the range of 3 to 12 %. Chicken manure contains 10 to 30 % TS. Some agro-industrial wastes may contain less than 1 % TS, while others contain high TS contents of more than 20 %. This results in some substrates being able to be fermented only when mixed with other substrate or diluted. Consequently, the need for different substrates such as manure, organic wastes and green plant materials for biogas production is increasing from time to time. For example, the substrates used in Germany are composed of 48 % animal excrement, 26 % organic waste and 26 % renewable green raw materials. It has been reported

that the performance of digesters could be considerably improved by means of co-substrate addition and hence increase degradation efficiency and biogas production.

#### **2.2.2.7 Uniform Feeding and Dilution**

One of the prerequisites of good digestion is uniform feeding of the digesters so that the microorganisms are kept in a relatively constant organic solid concentration at all times. Therefore, the digester must be fed at the same time every day with a balanced feed of the quality and quantity. All waste materials fed to a biogas plant consist of solid substance, volatile organic matter and nonvolatile matter (fixed solids) and water. During anaerobic fermentation process, volatile solids undergo digestion and non-volatile solids remain unaffected. For optimum gas yield through anaerobic fermentation, normally, 8-10 % TS in feed is required (Rajeshwari, 1999) This is achieved by making slurry of fresh cattle dung in water in the ratio of 1:1. However, if the dung is in dry form, the quantity of water has to be increased accordingly to keep the desired amount and consistency of the input (i.e., ratio could vary from 1:1.25 to even 1:2) If the dung is too diluted, the solid particles will settle down into the digester and if it is too thick, the particles impede the flow of the gas formed at the lower part of the digester.

#### **2.2.2.8 Mixing of the contents of the digester**

According to (Budiyono, I. Syaichurrozi, S. Sumardiono, 2014), since bacteria in the digester have very limited reach to their food, it is necessary that the slurry is properly mixed and bacteria get their food supply. He reported that slight mixing improves the fermentation; however a violent slurry agitation retards the digestion.

Some method of stirring the slurry in a digester is always advantageous. If not stirred, the slurry will tend to settle out and form a hard scum on the surface, which will prevent release of the biogas. This problem is much greater with vegetable waste than with manure, which will tend to remain in suspension and have better contact with the bacteria as a result (Sasse., Kellner, & Kimaro, 1991).

#### **2.2.2.9 Inoculation**

The use of a source high in anaerobic microbes (digester effluent for example) to start up an anaerobic system is called inoculation. According to (Wilkie AC, 2008), the quality and quantity of inoculums are critical to the performance, time required, and stability of bio-methanogenesis during commissioning (startup) or restart of an anaerobic digester. In manures and some wastes

the microbes needed for digestion may be already present in the waste in small numbers, albeit sufficient to act as inoculums, and will develop into a fully functional bacterial population if the right conditions are provided (Wilkie AC, 2008).

## **2.3 Brewery waste**

General process of brewery waste is divided into two sections namely Brewing and packaging. Brewing includes the process that starts from malt milling to producing fermented and bright beer. Packaging make the beer marketable by packing in different size bottles.

### **2.3.1 Brewing**

The simplest preparation of beers involves incubating and extracting malted, ground up cereal grains (usually barley) with warm water. Sometimes the ground malt is mixed with other starchy materials and/or enzymes. The liquid is then separated from the solid by filtration. The spent grain is discharged and sold for cattle food. The solution obtained is called wort that is boiled with hops or hop preparations. The boiled wort solution is clarified and cooled. The cooled wort is fermented by yeast that is pitched after wort cooling stage. Spent grain is generated during the mashing process and is removed from the brewing process from the mash- or mash filter before the boiling step of brewing occurs. Spent brewers' grains are an abundant brewery by-product that is high in protein (more than 20%) and fiber, which can be used as animal feed or, in some instances, spent grain can be used in foods for human consumption.

With regards to animal feed, brewers' grains may be wet or dry in their final form for animal feed, with the wet grains typically being sold as cake for ruminant feeds, while dry spent grain is used for monogastric feeds. Brewers' spent grain provides the essential nitrogen-containing nutrients animals require in their feed (Mussatto, 2014). Large breweries typically have their spent grain removed by animal feed producers who process the spent grain as a base material for animal feed, rather than having it delivered directly to farms. Spent grain offers an economic advantage to the animal feed market because it is a low-cost alternative to costly materials, such as soy bean. The nutritional and functional properties of spent grains have very comparable uses in human food as they do in animal feed (Fărcaș, et al., 2014) reports that brewers' spent grain has desirable nutritional characteristics for the human diet.

Usually the beer is clarified, packaged and served while effervescent with escaping carbon dioxide. Beers are made in amounts ranging from a few hectoliters (hl) a week to thousands of hl. On average 6 bottles of water is consumed to produce 1 bottle beer (Dennis, 2000). Therefore, waste related to brewery can be huge quantity. Most of the waste consist spills of beer during brewing, from flashing steps in tanks different unit operations as well as from CIP (cleaning in place) and water from cleaning the floors.

During the fermentation process, yeast cells can multiply numerous times, which results in a markedly greater yeast mass than what is added at the commencement of a fermentation. The fermentation conditions of each brewery influence the yeast growth rate. Similarly to spent grain, some breweries sell their spent yeast as animal feed as a source of protein and water-soluble vitamins (Djuragic, Levic, & Serdanovic, 2010). Spent yeast also takes up a significant position in human nutrition due to its high nutritional benefits. Well-known brands of yeast spreads are produced with spent brewers' yeast in numerous countries, although these products use extracts of yeast as it is uncommon to use whole brewers' spent yeast in human food applications. Yeast extracts are also used in food manufacturing to provide flavour (Munch, Hofmann, & Schieberle, 1997).

### **2.3.2 Packaging**

The packaging process makes the beer produced from the brewing department marketable in different sized glasses. On the process waste is generated from bottle washer and crate washer because returned bottles from the market are being used over and over. The other as a transporting mechanism from one to the other chain conveyer is used and lubricants are used to minimize the friction. The others include spills of beer from the filling step in filler.

### **2.4 Cow Dung**

The generally accepted value for the BOD of manure is approximately 27,000 mg/kg of excreted manure although it contributes to the BOD of the wastewater stream (EPA, 2002). COD from the animal dung was put at 15, 000 – 30, 000 mg/L. The liquid paunch juice has a chemical oxygen demand (COD) of up to 80,000 mg/l. It is a homogeneous, green colored liquid that is highly suitable for digestion in an anaerobic plan. Ethiopia owns the largest number of cattle's in Africa so this waste is widely available.

## **2.5 Biogas**

One excellent source of energy is Biogas. This is produced when bacteria decompose organic material, especially in the absence of oxygen. Biogas is a mixture mostly methane and Carbon dioxide. Methane is the main component of natural gas. It is relatively clean burning, colorless, and odorless. This gas can be captured and burned for cooking and heating. This is already being done on a large scale in some countries of the world.

### **2.5.1 Composition of Biogas**

Biogas from sewage digesters usually contains from 55 to 65 % methane, 35 to 45 % carbon dioxide and <1 % nitrogen, biogas from organic waste digesters usually contains from 60 to 70% methane, 30 to 40 % carbon dioxide and < 1 % nitrogen, while in landfills methane content is usually from 45 to 55 %, carbon dioxide from 30 to 40 % and nitrogen from 5 to 15 %. Besides the main components, biogas also contains hydrogen sulphide and other sulphide compounds, siloxanes, aromatic and halogenated compounds. Although the amounts of trace compounds are low compared to methane, they can have environmental impacts such as stratospheric ozone depletion, the greenhouse effect and / or the reduction in local air quality.

#### **2.4.1.1 Methane**

Methane is the primary component of in raw biogas and a component of firedamp in coal mines. It is also a product of anaerobic bacteria decomposition of underwater vegetation, which is why methane is also referred to as marsh gas. Methane burns easily in air, which results in it forming carbon dioxide and water vapor. Methane is usually stable, but air with methane content between 5 and 14 percent is highly explosive.

#### **2.4.1.2 Carbon dioxide**

CO<sub>2</sub> is able to be converted from a gas to a solid to a liquid. It has almost twice the density of air, making it able to be poured from a container. Molecular mass: 44.01 g/mol, colorless because it is a gas, odorless, melting point -55.6 °C boiling point -78.5 °C is not flammable .In aqueous environment it becomes carbonic acid and it's not reactive with water

#### **2.4.1.3 Sulphur compounds**

The main sulphur compound in biogases is hydrogen sulphide (H<sub>2</sub>S). Other reduced sulphur compounds, as sulphides, disulphides and thiols, can also be found in biogases. In the presence

of water, sulphur compounds can cause corrosion to compressors, gas storage tanks and engines, and thus these compounds need to be removed before biogas can be utilized as energy. In biogas, in anaerobic conditions hydrogen sulphide and other sulphide compounds originate along several different pathways. For example, methanethiol and dimethyl sulphide are formed from the degradation of sulphur-containing amino acids (e.g., in manure) and from the anaerobic methylation of sulphide. When dimethyl sulphide is reduced, following to methanogenic conversion, methane and methanethiol are formed. Methanethiol later forms methane, carbon dioxide and hydrogen sulphide.

#### **2.4.1.4 Hydrogen Sulphide**

Hydrogen sulphide ( $H_2S$ ) is a colourless, very poisonous gas. It is inflammable and forms explosive mixtures with air (oxygen).  $H_2S$  has a characteristic smell of "rotten eggs". This odor is only apparent in a small concentration range (0.05-500 ppm).  $H_2S$  is soluble in water forming a weak acid. A combustion product of  $H_2S$  is  $SO_2$ . This makes the exhaust gases very corrosive (sulphuric acid) and contaminates the environment (acid rain).  $H_2S$  is very poisonous (comparable to hydrogen cyanide) lower toxic limit 10 ppm  $H_2S$  (Kapid S., 2004). Hydrogen sulphide is formed during microbiological reduction of sulphur containing compounds (sulphates, peptides, amino acids). Hydrogen sulphide is formed in the biogas plant by the transformation of sulphur-containing protein. This can be protein from plants and fodder residues. However, when animal and human feces are used, bacteria excreted in the intestines are the main source of protein. Inorganic sulphur, particularly sulphates, can also be biochemically converted to  $H_2S$ .

Dissolved  $H_2S$  is contained in the fermentation slurry. Equilibrium is set up between the dissolved  $H_2S$  and the  $H_2S$  in the gas phase. The dissolved  $H_2S$  in high concentrations can be toxic to the bacteria in the slurry. It can inhibit the production of biogas and cause its composition to alter. The presence of  $H_2S$  gas in biogas makes it corrosive to metal parts. Iron is subject to surface attack, although not major corrosion. Galvanized parts are similarly subject to surface corrosion. The effect on non-ferrous metals in components, such as pressure regulators, gas meters, valves and mountings, is much more serious. They are very quickly corroded. These materials also corrode in gas engines (seals and valves).

## **2.6 Biogas Utilization**

Biogas can be used for all applications designed for natural gas. Different methods of environmental rating gave natural gas a 75% over all advantage over diesel and a 50% advantage over petrol. Upgrading raw biogas to >95% methane, positions the gas as an alternative vehicle fuel, and reduces compression and storage requirements. The value added to biogas by upgrading and compression is as good as compressed natural gas; however upgraded biogas has the added advantage of lower emission profile associated with combustion (Euroserv-er, 2008). Raw biogas is mainly used for heating and lighting. Combined heat and power (CHP) is used to convert biogas from fermentation tanks into electricity. However, in most cases, the heat is not efficiently used as a result of which about 60% of the energy is lost.

### **2.6.1 Boiler fuel**

Boilers do not have a high gas quality requirement. Gas pressure usually has to be around 8 to 25 mbar. It is recommended to reduce the H<sub>2</sub>S concentrations to values lower than 1.000 ppm which allows to maintain the dew point around 150°C. The sulphurous acid formed in the condensate leads to heavy corrosion. It is therefore recommended to use stainless steel for the chimneys or condensation burners and high temperature resistant plastic chimneys. Most of the modern boilers have tin-laminated brass heat exchangers which corrode even faster than iron chimneys. Where possible, cast iron heat exchangers should be utilized. It is also advised to condense the water vapour in the raw gas. Water vapour can cause problems in the gas nozzles. Removal of water will also remove a large proportion of the H<sub>2</sub>S, reducing the corrosion and stack gas dew point problems.

### **2.6.2 Vehicle fuel**

The utilization of biogas as vehicle fuel uses the same engine and vehicle configuration as natural gas. In total there are more than 1 million natural gas vehicles all over the world, this demonstrates that the vehicle configuration is not a problem for use of biogas as vehicle fuel. However, the gas quality demands are strict.

With respect to these demands the raw biogas from a digester or a landfill has to be upgraded. Through upgrading we obtain a gas which has a higher calorific value in order to reach longer driving distances, has a regular/constant gas quality to obtain safe driving, does not enhance corrosion due to high levels of hydrogen sulphide, ammonia and water, does not contain

mechanically damaging particles, does not give ice clogging due to a high water content, has a declared and assured quality. In practice this means that carbon dioxide, hydrogen sulphide, ammonia, particles and water (and sometimes other trace components) have to be removed so that the product gas for vehicle fuel use has methane content above 95 vol% (Miller, 1996).

In different countries different quality specifications for vehicle fuel use of biogas and natural gas are applied. Upgraded biogas is actually the cleanest vehicle fuel possible with respect to environment, climate and human health (Amigun, 2011).

## **2.7 Biogas Upgrading Technologies**

In order to guarantee that a gas product can safely and efficiently be used in engines, motors kitchen stoves as bio-fuel or to be injected into the natural gas network the bio-methane must meet a gas quality specification. Upgraded biogas (bio-methane) has similar properties to natural gas, which has been used as a vehicle fuel for decades. To utilize bio-methane as a fuel for vehicles, the same engine and vehicle configuration that is used for natural gas can be used.

In 1999 Sweden developed a national standard for the use of biogas as a vehicle fuel upon request of the Swedish motor industry (Persson J. O., 2003). In order to use biogas as a vehicle fuel or for injection into the natural gas network the biogas must be cleaned (the CO<sub>2</sub> and H<sub>2</sub>S removed) and upgraded (>95% methane) to produce bio methane which has a higher calorific value, to provide longer driving distances, or an energy content corresponding with the gas distributed via the natural gas grid (Persson, 2006). The quality standards ensure that the bio-methane does not aggravate corrosion, does not contain mechanically damaging particles, and has a declared and assured quality (Euroserv-er, 2008). Biogas upgrading processes need to be designed to avoid or minimize emissions. For example, in absorption processes some of the methane can be absorbed to the absorption liquid and be released into the air with the exhaust gas, hydrogen sulphide, other reduced sulphur compounds and halogenated compounds in exhaust gas can have environmental and health risks if released into the air untreated. The absorption liquid used in the process should also be treated, for example with other wastewaters (SEP, 2004). A number of gas upgrading technologies have been developed for the treatment of natural gas, town gas, sewage gas, landfill gas etc. water scrubbing, chemical absorption, pressure swing adsorption, membrane purification, cryogenic separation, biological processes.

### **2.7.1 Absorption**

The separation principle of absorption is based on different solubility of various gas components in a liquid scrubbing solution. In an upgrading plant using this technique the raw biogas is intensively contacted with a liquid within a scrubbing column filled with packing in order to increase the contact area between the phases.

Carbon dioxide has a higher solubility in water than methane. Carbon dioxide will therefore be dissolved to a higher extent than methane, particularly at lower temperatures. As a result, the remaining gas stream is enriched with methane and the scrubbing liquid leaving the column is rich in carbon dioxide. In order to maintain the absorption performance, this scrubbing liquid has to be replaced by fresh liquid or regenerated in a separated step (desorption or regeneration step). Currently, three different upgrading technologies embodying this physical principle are available.

#### **2.7.1.1 Physical absorption: Water scrubbing**

Water scrubbing is used to remove carbon dioxide and also hydrogen sulphide from biogas, since these gases are more soluble in water than methane. The absorption process is purely physical. Usually the biogas is pressurized and fed to the bottom of a packed column where water is fed on the top and so the absorption process is operated counter-currently.

Water scrubbing can also be used for selective removal of hydrogen sulphide since hydrogen sulphide is more soluble than carbon dioxide in water. The water which exits the column with absorbed carbon dioxide and/or hydrogen sulphide can be regenerated and recirculated back to the absorption column. The regeneration is made by de-pressurizing or by stripping with air in a similar column. Stripping with air is not recommended when high levels of hydrogen sulphide are handled since the water will soon be contaminated with elementary sulphur which causes operational problems. The most cost efficient method is not to recirculate the water if cheap water can be used, for example, outlet water from a sewage treatment plant (Richardson, 2002). The effluent water leaving the column is saturated with carbon dioxide and is transferred to a flash tank where the pressure is abruptly reduced and the major share of the dissolved gas is released. As this gas mainly contains carbon dioxide, but also a certain amount of methane (methane is also soluble in water, but to a smaller extent) this gas is piped to the raw biogas inlet. The drawback of this method is that the air components oxygen and nitrogen are dissolved in the water during regeneration and thus, transported to the upgraded bio-methane gas stream.

Therefore, bio-methane produced with this technology always contains oxygen and nitrogen. As the produced bio-methane stream is saturated with water, the final step in upgrading typically is gas drying, for example by the application of glycol scrubbing. The rate of CO<sub>2</sub> and H<sub>2</sub>S absorption depends upon the factors such as, gas flow pressure, composition of biogas water flow rates, purity of water and dimension of scrubbing tower.

#### **2.7.1.2 Organic physical absorption**

Very similar to water scrubbing, this technology uses an organic solvent solution (e.g. polyethylene glycol) instead of water as a scrubbing liquid. Carbon dioxide shows higher solubility in these solvents than in water. As a result, less scrubbing liquid circulation and smaller apparatuses are needed for the same raw biogas capacity.

#### **2.7.1.3 Chemical absorption**

Chemical absorption is characterized by a physical absorption of the gaseous components in a scrubbing liquid followed by a chemical reaction between scrubbing liquid components and absorbed gas components within the liquid phase. As a result, the bonding of unwanted gas components to the scrubbing liquid is significantly stronger and the loading capacity of the scrubbing liquid is several times higher.

The chemical reaction is strongly selective and the amount of methane also absorbed in the liquid is very low resulting in very high methane recovery and very low methane slip. Due to the high affinity of especially carbon dioxide to the used solvents (mainly aqueous solutions of Monoethanol amine (MEA), Diethanol amine (DEA), and Methyldiethanol amine (MDEA)) the operating pressure of amine scrubbers can be kept significantly smaller compared to pressurized water scrubbing plants of similar capacity.

Chemical absorption involves the formation of reversible chemical bonds between the solute and the solvent. Regeneration of the solvent, therefore, involves breaking of these bonds and correspondingly, a relatively high energy input. Chemical solvents generally employ either aqueous solutions of amines, i.e. mono-, di- or tri-ethanolamine or aqueous solution of alkaline salts, i.e. sodium, potassium and calcium hydroxides.

#### **2.6.1.4 Polyethylene glycol scrubbing**

Polyethylene glycol scrubbing is like water scrubbing a physical absorption process. Selexol is one of the trade names used for a solvent. In this solvent, like in water, both carbon dioxide and hydrogen sulphide are more soluble than methane. The big difference between water and Selexol is that carbon dioxide and hydrogen sulphide are more soluble in Selexol which results in a lower solvent demand and reduced pumping. In addition, water and halogenated hydrocarbons are removed when scrubbing biogas with Selexol. Selexol scrubbing is always designed with recirculation. Due to formation of elementary sulphur stripping the Selexol solvent with air is not recommended but with steam or inert gas (upgraded biogas or natural gas). Removing hydrogen sulphide on beforehand is an alternative.

### **2.7.2 Adsorption**

In adsorption processes, the solute (CO<sub>2</sub>) in the raw biogas adsorbs into the surface of a solid material usually by means of weak Van der Waal Forces, London Forces etc. Almost all solids can adsorb, however granular solid with large surface area per unit volume are employed as commercial adsorbents. Good adsorbents are capable of removing CO<sub>2</sub>, H<sub>2</sub>S, moisture and other impurities from biogas. Solid adsorbents used for purification of gas include alumina activated carbon, silica, etc., and are referred to as molecular sieves (Richardson, 2002) .Adsorption systems are simple in design and easy to operate. Although they have good moisture holding capacity, the high heat and pressure required make them expensive process.

#### **2.7.2.1 Pressure swing adsorption (PSA)**

With this technique, carbon dioxide is separated from the biogas by adsorption on a surface under elevated pressure. The adsorbing material, usually activated carbon or zeolites, is regenerated by a sequential decrease in pressure before the column is reloaded again, hence the name of the technique. An upgrading plant, using this technique, has four, six or nine vessels working in parallel. When the adsorbing material in one vessel becomes saturated the raw gas flow is switched to another vessel in which the adsorbing material has been regenerated. During regeneration the pressure is decreased in several steps. The gas that is desorbed during the first and eventually the second pressure drop may be returned to the inlet of the raw gas, since it will contain some methane that was adsorbed together with carbon dioxide. The gas desorbed in the following pressure reduction step is either led to the next column or if it is almost entirely methane free it is released to the atmosphere. If hydrogen sulphide is present in the raw gas, it

will be irreversibly adsorbed on the adsorbing material. In addition, water present in the raw gas can destroy the structure of the material. Therefore hydrogen sulphide and water needs to be removed before the PSA-column.

### **2.7.2.2 Adsorption on activated carbon**

Hydrogen sulphide is adsorbed on the inner surfaces of engineered activated carbon with defined pore sizes. Addition of oxygen (in the presence of water) oxidizes  $H_2S$  to plane sulphur that binds to the surface. In order to increase the speed of the reaction and the total load, the activated carbon is either impregnated or doped (by addition of a reactive species before formation of the activated carbon) with permanganate or potassium iodide (KI), potassium carbonate ( $K_2CO_3$ ) or zinc oxide (ZnO) as catalysers. In those cases mostly KI-doped carbon or permanganate impregnated carbon is used because addition of oxygen is not required in the case of KI under reduced loading. While ZnO impregnated carbon is rather expensive,  $H_2S$  removal is extremely efficient with resulting concentrations of less than 1ppm.

### **2.7.2.3 Membrane purification technology**

Membranes for biogas upgrading are made of materials that are permeable for carbon dioxide, water and ammonia. Hydrogen sulphide, oxygen and nitrogen permeate through the membrane to a certain extent and methane passes only to a very low extent. Typical membranes for biogas upgrading are made of polymeric materials like polysulfone, polyimide or poly di methyl siloxane.

These materials show favorable selectivity for the methane/carbon dioxide separation combined with a reasonable robustness to trace components contained in typical raw biogases. To provide sufficient membrane surface area in compact plant dimensions these membranes are applied in form of hollow fibers combined to a number of parallel membrane modules (Nactogroup, 2007). After the compression to the applied operating pressure the raw biogas is cooled down for drying and removal of ammonia. After reheating with compressor waste heat the remaining hydrogen sulphide is removed by means of adsorption on iron or zinc oxide. Finally, the gas is piped to a single- or multi-staged gas permeation unit.

The numbers and interconnection of the applied membrane stages are not determined by the desired bio-methane quality but by the requested methane recovery and specific compression energy demand. Modern upgrading plants with more complex design offer the possibility of very high methane recoveries and relatively low energy demand. Even multi-compressor

arrangements have been realized and proved to be economically advantageous (Nactogroup, 2007). The operation pressure and compressor speed are both controlled to provide the desired quality and quantity of the produced bio-methane stream.

### **2.7.3 Biological process**

Hydrogen sulphide can be oxidized by microorganisms of the species *Thiobacillus* and *Sulfolobus*. The degradation requires oxygen and therefore a small amount of air (or pure oxygen if levels of nitrogen should be minimized) is added for biological desulphurization to take place. The degradation can occur inside the digester and can be facilitated by immobilizing the microorganisms occurring naturally in the digestate. An alternative is to use a trickling filter which the biogas passes through when leaving the digester. In the trickling filter the microorganisms grow on a packing material. Biogas with added air meets a counter flow of water containing nutrients. The sulphur containing solution is removed and replaced when the pH drops below a certain level. Both methods are widely applied, however they are not suitable when the biogas is used as vehicle fuel or for grid injection due to the remaining traces of oxygen. Similar to this study, the efficiency of CO<sub>2</sub> capture of 85% was obtained for 25% of NaOH (Kordylewski, 2013). Therefore, comparing the cost and efficiency of upgrading methods water absorption with 25% caustic will be used.

### **2.8 Boiler**

A boiler is a vessel in which water, under pressure is transformed into steam by the application of heat. Open vessels and those generating steam at atmospheric pressure are not considered as boilers, thus, the primary function of boiler is to generate steam at a pressure above atmospheric pressure by absorption of heat that is produced due to combustion of fuel. Boilers vary significantly in size and in design. According to the relative location of fire and water spaces boilers are classified into two classes. Fire tube Boiler; the gases of the combustion process flow through the tubes and thereby heat the water that surrounds the tubes i.e. Steam is generated outside the tube. Water tube Boiler; Here the water flows through the tubes and is heated by the gases of the combustion process that fill into the furnace and heat the outside metal surfaces of the tubes. Steam is generated inside tubes. Based on burners location boilers are classified as follows. Front fired burner boiler; a boiler plant in which burners are located at the front of the boiler plan. Top fired burners boiler; boilers which have their burners on the top of the boilers.

(Kuiper, 2016) There two boilers at Heineken breweries share company Addis plant. Based on the above two classification the boiler types are fire tube and front fired burner boilers.

### **Fundamentals of Steam Generation**

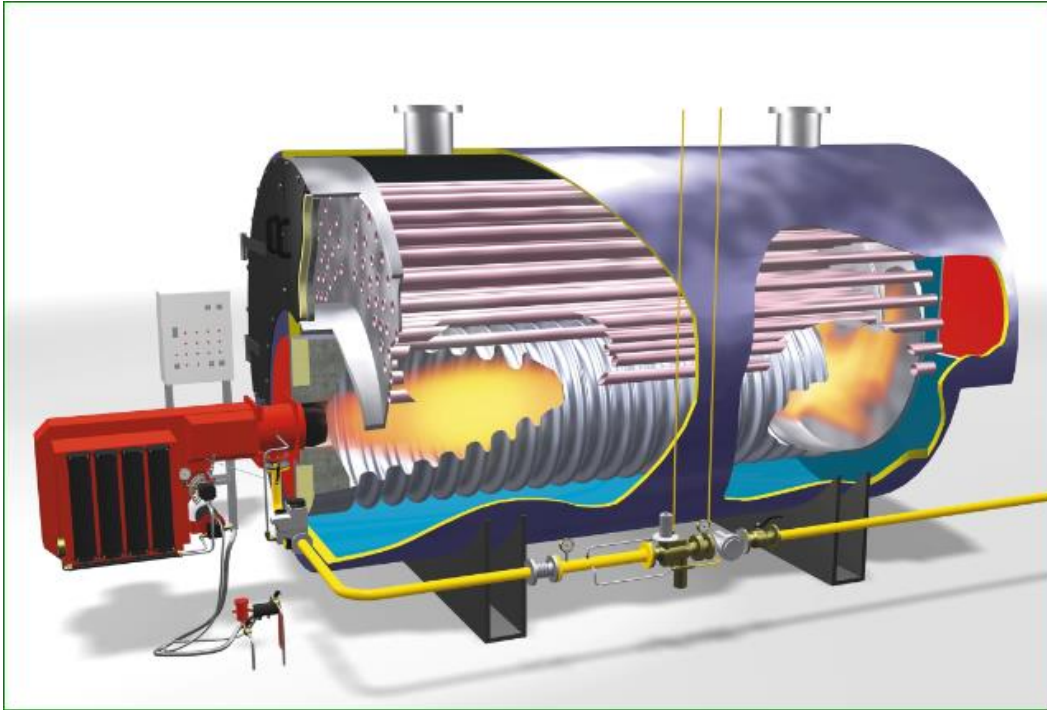
If a given quantity of water is heated the heat raises the water temperature until the boiling temperature (saturation temperature) is reached, for specific pressure. After boiling temperature, instead of raising the water temperature the heat energy from the source is resulted in change of phase from liquid to gaseous state i.e. from water to steam the temperature remaining constant. steam will leave the water at its surface and it passes into what is called the steam space (Kuiper, 2016).The space in the container directly above the water is always wet and will remain wet as long as the water is present. Wet steam is all that is required then the steam is piped out of the steam space away into steam main or steam delivery line.

#### **2.8.1 Process Description**

Boilers commonly called steam generators have a primary function of generating steam by the application of heat from the combustion of fuel with air in a device called a furnace. A furnace or a fire box is a large room like space where air and fuel are mixed for combustion. The fuel oil which is the source of heat energy is preheated and filtered and then pumped to the burner of the boiler. The combustion air is also forced into a furnace by a forced draft blower.

The air then travels to the boiler front where it is forced to the furnace through the air register. The air entering the furnace through the air register mixes with affine fuel oil spray through the atomizer and by using an electrical ignite the mixture of fired fuel oil and air is burned and heat energy is transferred from furnace to the boiler. The product of combustion is made to pass to the rear end of the boiler. The front head of the boiler seals the flue gas to from escaping and directs it to pass through the tubes to move to the rear of the boiler where they exit to the stack. The boiler feed water is preheated and treated and then pumped boiler prior to the combustion (Kuiper, 2016).

**Figure 2:** Fire tube boiler oil burner



## 2.9 Heavy Fuel Oil (HFO)

Heavy fuel oil consists primarily of the residue from distillation or cracking units in the refinery. Historically, fuel oils were based on long residues from the atmospheric distillation column and were known as straight run fuels. However, the increasing demand for transportation fuels such as gasoline, kerosine and diesel has led to an increased value for the atmospheric residue as a feedstock for vacuum distillation and for cracking processes. As a consequence, most heavy fuel oils are currently based on short residues and residues from thermal and catalytic cracking operations. These fuels differ in character from straight run fuels in that the density and mean molecular weight are higher, as is the carbon/hydrogen ratio. (Management, 1998) The density of some heavy fuel oils can be above  $1,000 \text{ kg/m}^3$ , which has environmental implications in the event of a spillage into fresh water or during combustion.

Heavy fuel oils also contain organo-metallic compounds from their presence in the original crude oils. The most important of these trace metals is vanadium. Vanadium is of major significance for fuels burned in both diesel engines and boilers because when combined with sodium (perhaps from seawater contamination) and other metallic compounds in critical proportions it can form high melting point ashes which are corrosive to engine exhaust valves, valve seats and superheater elements. Other elements that occur in heavy fuel oils include nickel, iron,

potassium, sodium, aluminum and silicon. Aluminium and silicon are mainly derived from refinery catalyst fines.

Significant amount of hydrogen sulfide are known to accumulate in the headspaces of storage tanks that contain heavy fuel oils. Appreciable concentrations of polycyclic aromatic compounds (PAC) can be present in heavy fuel oils.

### 2.9.1 Typical properties

Typical properties for heavy fuel oils can vary widely within the specification limits. Typical properties for heavy fuel oils can vary widely within the specification limits for industrial purpose.

**Table 1:** Range of physico-chemical properties for heavy fuel oils adapted from CONCAWE's Petroleum Products and Health Management.

Property	Unit	Typical range
Kinematic viscosity at 100°C	mm <sup>2</sup> /s	6.0 to 55.0
Density at 15°C	kg/m <sup>3</sup>	950 to 1010
Flash point	°C	> 60
Pour point	°C	< 30
Carbon residue	% (m/m)	< 22
Ash	%(m/m)	< 0.20
Water	% (v/v)	< 1.0
Sulphur	% (m/m)	Inland < 3.5 Marine < 5.0
Vanadium	mg/kg	< 600
Aluminum plus Silicon	mg/kg	< 80

Heavy fuel oils can be blended from a wide range of refinery components, the most important of which are:

### 2.9.2 Residual Fuel oils

To produce fuels that can be conveniently handled and stored in industry and to meet marketing specification limits, the high viscosity residue components are normally blended with gas oils or

similar lower viscosity fractions. In refineries with catalytic cracking units, catalytically cracked cycle oils are common fuel oil diluents (Miller, 1996). As a result, the composition of residual fuel oils can vary widely and will depend on the refinery configuration, the crude oils being processed and the overall refinery demand.

Residual fuel oils are complex mixtures of high molecular weight compounds having a typical boiling range from 350 to 650°C. They consist of aromatic, aliphatic and naphthenic hydrocarbons, typically having carbon numbers from C20 to C50, together with asphaltenes and smaller amounts of heterocyclic compounds containing sulphur, nitrogen and oxygen. They have chemical characteristics similar to asphalt and hence, are considered to be stabilised suspensions of asphaltenes in an oily medium. (Miller, 1996) Asphaltenes are highly polar aromatic compounds of very high molecular weight (2000-5000) and in the blending of heavy fuel oils, it is necessary to ensure that these compounds remain in suspension over the normal range of storage temperatures. Long residue is the residue from the atmospheric distillation of crude oil. As mentioned earlier, historically this was a major fuel oil blending component, but it is now mainly used as a feedstock for the vacuum distillation unit or for a thermal or catalytic cracking unit. Short residue refers to the residue from the vacuum distillation of crude oil.

### **2.9.3 Cost**

For heavy oil there are greatly increased costs over gas-fired plants from:

**Oil Storage** – Large storage tanks are required and must be kept full to prevent moisture build up from condensate. Moisture converts the high sulphur content of the fuel to an acidic form which rapidly corrodes metal tanks.

**Heating of stored oil** – Because heavy oil is so viscous it cannot be pumped without pre-heating to allow it to be pumped more readily throughout the pipe work of the power plant. Heat exchangers based on steam pipe work are often used but the contaminated condensate is dumped to the effluent stream.

**Fuel oil additives** – Sulphur and vanadium are present in high concentrations in heavy oil and require the addition of special treatment chemicals to reduce the corrosion effects on boilers and storage tanks.

**Oil pumping** – Increased energy costs associated with continual circulation of the oil in the storage tanks to maintain viscosity.

**Fuel oil atomization** – The oil cannot burn in its normal form but must be atomized into droplets through steam or compressed air which requires high energy inputs.

**Soot blowing of boiler tubes** – The build-up of soot on the fire-side of the boiler reduces heat transfer to the boiler and must be removed daily to maintain efficiency with steam or compressed air and regular manual soot removal must be conducted.

**Additional boiler makeup water** – Water must be preheated before addition to the boiler to prevent thermal shock and reduce oxygen corrosion of metals.

**Additional maintenance** – Higher maintenance costs are the prime economic disadvantage of heavy oil over gas-powered plants. Dirty fuel translates to dirty machinery and soot removal, and general maintenance costs are high.

**Table 2:** Imported product fuels for the year 2015/2016 source Ethiopian Petroleum Enterprise.

Month	Gasoil		LFO		HFO	
	Qty; MT	C&F; USD	Qty; MT	C&F; USD	Qty; MT	C&F; USD
Jul-12	130,764	116,405,133.08	3,558.46	2,582,207.10	15,303.36	10,645,842.21
Aug-12	74,104	71,501,001.93	4,046.59	3,144,247.44	12,232.04	9,137,479.92
Sep-12	129,119.77	129,204,433.98	2,596.38	2,037,995.51	13,594.33	10,255,337.50
Oct-12	73,644.72	71,469,256.55	3,190.80	2,400,650.37	12,251.76	8,850,264.95
Nov-12	90,947.33	86,020,799.60	3,996.58	2,870,468.77	11,095.25	7,636,103.35
Dec-12	106,694.98	100,924,189.15	947.63	678,437.93	6,000.36	4,115,839.62
Jan-13	122,270.94	116,902,587.64	4,085.33	3,013,124.36	11,717.44	8,274,895.34
Feb-13	98,676.89	97,832,247.89	936.08	707,531.39	8,680.80	6,300,915.28
Mar-13	139,915.80	132,626,685.73	4,665.13	3,451,360.40	8,309.06	5,876,641.13
Apr-13	132,859.997	119,826,599.03	2,499.71	-	8,079.000	-
May-13	127,428.84	-	4,000.00	-	10,000.000	-
Jun-13	125,000.40	-	3,500.000	-	8,000.000	-
Total Import	1,351,427.87	1,042,712,934.58	38,022.680	20,886,023.26	125,263.394	71,093,319.29

#### 2.9.4 Environmental Hazard

Heavy fuel oils are composed of residual materials blended with middle distillates, or cutter stocks of lower molecular weight, and their composition is highly variable. As a result, the ecotoxicity associated with these oils varies depending on the nature and proportion of the added middle distillates (center, 2015). While all batches of heavy oil have their own chemical

fingerprint it can be assumed that No. 6 oil contain around 15 per cent paraffins, 45 per cent naphthalenes, 25 per cent aromatics and 15 per cent non-hydrocarbon compounds. Naphthalene is a recognised human carcinogen.

Because heavy oil is blended with cracked and uncracked hydrocarbon residues, it contains elevated levels of polyaromatic hydrocarbons (PAH) of up to five per cent in total. Many PAH's have been identified as carcinogenic in humans and animals. On every other factor, such as ease of handling, toxicity, environmental impacts and plant maintenance costs, heavy oils fails to compete with other fossil fuels such as coal, gas, and distillate. When compared against renewable energy sources the gulf widens even further (center, 2015). Smog producing compounds nitrogen oxides and volatile organic compounds are exhausted during HFO combustion. In the presence of sunlight, these materials combine to produce ground-level ozone, which can exacerbate asthma, causes lung damage irritate eyes, damage plant life.

## Chapter Three

### 3. Materials and methods

#### 3.1 Characterization of brewery waste and cow dung

##### 3.1.1 Materials

In this study, brewery waste was used from Heineken Brewery Share Company. Following parameters were analyzed according to APHA-AWWAPCH, Standard Methods for the Examination of Water and Waste Water. The brewery waste was a combination of wastes from the packaging and brewing departments. Two five liter Jerry cans were used to take waste water samples. Cow dung was taken from local farmers around the brewery and plastic bucket was used to carry it. Electronic balance CPA224 (S0.0001g) was used to measure mass. Spectrophotometer HACH (DR2800) was used to measure COD, Total phosphorous (TP) and Total Nitrogen (TN). COD Heater HACH (DRB200) was used to measure COD. Muffle Furnace (0-1000°C) was used to measure volatile solid (VS). Oven (0-200°C) was used to measure the total solid (TS). BOD incubator was used for measurement of BOD<sub>5</sub> at 20 °C. Distilled water generator was used for distilled water production. Refrigerator was used to keep the brewery waste, cow dung and inoculum at 4°C until used in the experimentation. Desiccator is used to cool crucibles after being heated in the oven or the muffle furnace, Crucible tongs to take crucibles out of oven or muffle furnace. Pipette Evaporating dishes 50ml, Crucibles 100 ml and weighing dishes 100 ml for total solid measurement. Portable pH meter and Portable temperature meter were used to measure pH and temperature of samples. The characterization took place at Heineken Breweries, Kilinto laboratory except for BOD<sub>5</sub> at 20 °C (mg/l) which conducted at Addis Ababa Institute of Technology School of Chemical and Bio engineering.

##### 3.1.2 Methods

The brewery considered in this study Heineken brewery in Kilinto, Addis Ababa .Heineken brewery is producing over three million hectoliter beer per a year which makes it the biggest brewery in Ethiopia. This brewery produces 4,500m<sup>3</sup>/day waste water, the waste effluent from the brewery consists mainly waste from brew house (Brewing, Fermentation, and filtration), and Packaging (Under fills and CIP) .Cow dung was collected from local farmers near the brewery. The inoculum was sampled from Alert Shemachoch located in Alert, Addis Ababa. The

inoculum used in this study was bio slurry of cattle dung which contains active microbes essential for anaerobic digestion process. Cattle slurry as methanogenic bacteria provider was added into the digester as much as 10% v/v total volume. (Budiyono, I. Syaichurrozi, S. Sumardiono, 2014). Methanogens (methane producing bacteria) are the last component in the chain of microbes which degrade natural material and return decay products to the environment while producing biogas (Naz, 2013).

Firstly, characteristics of the brewery waste were determined: BOD<sub>5</sub> at 20 °C (mg/l), COD (mg/l), Temperature (°C), pH, Total Solids (%), Total nitrogen (as N) mg/l, and Total phosphorus (as P) mg/l. Total solid (TS), Volatile Solids (VS), and pH of the brewery waste, Cow dung, and inoculum were also separately characterized.

**BOD:** First pH of the Brewery waste water was adjusted to neutral value 7 using 1M H<sub>2</sub>SO<sub>4</sub> & 1M NaOH solutions. Based on the BOD range of low, medium, and high brewery waste attains high range so 27ml brewery waste sample was taken using overflow measuring. The sample was introduced into bottles of BOD measuring unit with the help of funnel. Then, 3 drops of nitrification inhibitor (Allyl Thiourea, or ATH) was added to inhibit nitrification. The bottle was then sealed with a rubber seal gasket and three drops of KOH was added to react with the CO<sub>2</sub> evolved during the process; and then screwed with a cover which consists of pressure sensor and fitted to electronic system ready for measurement. Finally, the bottle was placed in the bottle rack and the entire unit is kept in thermostat under constant temperature of 20 °C. The data was recorded every 24 hours automatically, the value obtained at the fifth day is called BOD<sub>5</sub> at 20 °C.

**COD:** Sample was taken from the brewery effluent. Turned on the DRB200 Reactor to preheat to 150 °C. Homogenized 100 mL of sample for 30 seconds by shaking the sample. To help ensure that a representative portion of sample is analyzed, poured the homogenized sample into a 250-mL beaker and gently stirred with a magnetic stir plate. Then, carefully pipet 2.0 mL of sample into the vial. Capped and cleaned the outside of the vial. Hold the vial by the cap over a sink. Inverted gently several times to mix. The sample vials became very hot during mixing. Placed the vial in the preheated DRB200 Reactor and closed the protective lid. Heated the samples for two hours. Placed the vial into a rack to cool to room temperature. Installed the Light Shield in Cell Compartment #2. Inverted the vial several times while still hot. Turned off the reactor. Waited for 20 minutes until the vials cooled to 120 °C or less. Inserted the blank into the 16-mm cell

holder A blank is needed for measuring the sample ,the blank is prepared in the same way using 2 ml pure water. Inserted the sample vial into the 16-mm cell holder Press zero. The display showed: 0.0 mg/L COD .Thoroughly cleaned the outside of the vial and selected high range test. Installed the sample in Light Shield in Cell Compartment #2 and pressed read. Results were read in mg/L COD.

**Total Solid(TS):** Crucibles were put in an oven then in desiccator until cooled, weighed and recorded then the crucible with 100ml well mixed sample was weighed and result was recorded according to ASTM D 1037(1991). The crucible with sample was put into the oven heated to 105 °C for 24 hrs. Weighed and recorded afterwards, after cooling in a desiccator. Calculated total solid of the sample by subtracting the before oven and the after and divided by the before oven weight.

**Volatile solid (VS):** Ignited the residue produced by method total solid determination in a muffle furnace according to ASTM D 2017 (1998). Then transferred to desiccator for final cooling in a dry atmosphere. Calculated the volatile solid sample by subtracting the before muffle furnace and the after and divided by the before muffle furnace.

**Temperature:** directly measured by using the portable temperature meter immediately after sampling for brewery waste.

**pH:** for brewery waste directly measured by using the portable pH meter immediately after sampling. For cow dung, measured 25gm cow dung then mixed with 100ml distilled water, stirred the solution thoroughly for 5 minute and measured the PH of the liquid.

**Total Nitrogen (TN):** DRB200 Reactor was turned on and heated to 105 °C. Using a funnel, the contents of one Total Nitrogen Persulfate Reagent Powder Pillow was added to each of the two Total Nitrogen Hydroxide Digestion Reagent vials. Any reagent that got on the lid or the tube threads was wiped off. Sample was prepared by adding 2 mL of brewery waste to one vial. Blank was prepared by adding 2ml deionized water to the second vial. Both vials were capped and mixed vigorously by shaking the samples. The vials were inserted in the reactor and heated for exactly 30 minutes. When the time was over immediately removed from the reactor and cooled the vials to room temperature. The test type was selected to total nitrogen. Caps were removed from the digested vials and contents of one Total Nitrogen (TN) Reagent A Powder Pillow was added to each vial. Then capped and shake for 15 seconds. For the reaction to proceed the timer was pressed for three-minute then the reaction proceeded. After the timer expired, the caps were

removed from the vials and one TN Reagent B Powder Pillow was added to each vial. The tubes were capped and shake for 15 seconds. The solution began to turn yellow. A two-minute reaction then proceeded. Removed the caps from two TN Reagent C vials and 2 mL of digested, treated sample to one vial after 2 minutes. The treated reagent blank was added to the second TN Reagent C vial. Capped the vials and inverted ten times to mix the tubes were warm to the touch. Then a five-minute reaction period began and yellow color intensified. The blank reagent blank was inserted into the cell holder and press zero. The display showed: 0.0 mg/L N. The reagent vial was wiped and inserted into the cell holder and pressed the read button the results were displayed in mg/LN.

**Total Phosphorous(TP):** 5.0 mL brewery sample was added to a reactive phosphorus test 'N Tube Dilution Vial'. The test tube was capped and mixed. The outside of the vial was wiped with a damp towel, followed by a dry one, to remove fingerprints or other mark. The vials were inserted in round cell holder and pressed zero. The display showed 0.00 mg/L  $\text{PO}_4^{3-}$ . Using a funnel, the contents of one PhosVer 3 Phosphate Powder Pillow was added to the vial and immediately capped tightly and shake. The reaction proceeded for two-minute. Read samples between two and eight minutes after adding the PhosVer 3 reagent. The vials were inserted in holder and pressed the read button result showed in mg/L  $\text{PO}_4^{3-}$ .

### **3.2 Optimize biogas production**

#### **3.2.1 Materials**

Digital pH meter was used to measure the pH of the mixture of inoculum, cow dung, and brewery waste water. Erlenmeyer plastic flasks with fitting rubber stopper (500 ml) was used to keep the mixed sample of the inoculum, cow dung, and brewery waste in air tight environment during biogas production. Pneumatic pipe was connected to the fitting rubber stopper at one end and with the gas bag at the other end and was used to transfer the biogas produced from the Erlenmeyer plastic flasks with fitting rubber stopper to the gas bag. Gas valve was used to block gas flow from the flask before the start of biogas production and to replace the full gas bag with a new one. Gas (glucose) bag was used to store the biogas produced from the contents in the Erlenmeyer plastic flasks with the rubber fitting and the stopper passing the pneumatic pipe and gas valve to the gas bag. Water bath was used to keep samples at desired temperature. Digital gas analyzer (Biogas-5000) was used to analyze the composition of biogas produced and the

composition of biogas after upgrading. Gas syringe was used to measure the volume of gas. Weighing balance was used to weigh the amount of cow dung to be mixed with brewery waste. The study was conducted in Environmental Engineering & Bio-innovative research laboratories in school of chemical and Bio Engineering, Addis Ababa Institute of Technology Laboratory scale.

### **3.2.2 Methods**

Brewery waste was major feedstock for this study collected from Heineken Breweries Share Company Kilinto, Addis Ababa. Sample was taken from December 2016 up to August 2017, 54 experiments were finished for sampling two 5 liter of Jerry cans were used. Fresh Brewery waste always collected for one batch was finished at once. The fresh collected samples put in an oven to identify solid content of the waste after knowing the total solid mixing it with cow dung, samples were kept in the refrigerator until the total solid of each component was known. Fresh sample collected was immediately fed to the digester after the total solid value was identified. Sample preparation was done for two different purposes the first was to know biogas potential of brewery waste without mixing with cow dung. The experiment was carried out at optimum temperature range at 35°C which was regulated by water bath and initial substrate pH 7.5 (Halimatun, 2011). Methane composition and volume of biogas was measured by Gas Analyzer and Gas syringe respectively. The substrate was mixed once each day to maintain intimate contact between the microorganisms and the substrate. The second experiment was by mixing brewery waste and cow dung, desired proportion with inoculum. Sample preparation for all the 81 experiments were run by mixing Brewery waste and cow dung in school of chemical and Bio engineering laboratory and adding 10% inoculums at HRT( hydraulic retention time) 10, 15 and 20 days & total solid of 4%, 8% and 12%.

Anaerobic Digester was setup in the laboratory refer to Appendix one for laboratory anaerobic digester setup. The lab was carried on a batch scale and the Erlenmeyer plastic flasks (digesters) which have a capacity of 500ml were placed containing 300ml sample in the water bath to maintain the fermentation at desired and constant temperature, there are three temperature ranges Pscophilic, Mesophlic, and Thermophilic temperature ranges. Pscophilic below 30 °c, Mesophilic bacteria thrive in temperatures around 30-39°C, and thermophilic bacteria in the

49°C–60°C range. Gas production decreases when the bacteria are subjected to temperature while thermophilic bacteria produce somewhat more gas, often the gas is not worth the energy needed to raise the digester temperature (Kestutis Navickas, 2013). Considering the above from literature, temperature was set at 25 °C, 35 °C and 50 °C.

The amount of time a material substrate spends in the digester obviously has a large effect on the anaerobic digestion process. The longer the HRT, the more likely the substrate will be broken down and stabilized and have proper interactions with the bacteria within the digester. Hence, a longer HRT leads to increased methane production. Having a longer HRT can also affect the size of the digester, as a long time requires a larger digester and has lower turnover rate (Thaniya Kaosol, 2012). Although some studies also looked at the HRT, many set it as a constant ranging from 1 to 20 days. A few studies maintained the digestion until the production of methane fell or leveled off. Therefore, retention time was varied at 10, 15 and 20 days. Total solid has the amount of organic matter contained in a sample and it highly affects the biogas content so three ranges of TS was varied 4%, 8% and 12%.

Using design expert 6.0.8, Response surface 3 level factorial design was used on the experiment in which each numeric factor is varied over 3 levels and duplicated. It is a well-accepted statistical technique able to design and optimize the experimental process that involve choosing the optimal experimental design and estimate the effect of the several variables independently and also the interactions simultaneously (Patrick, 2002). This technique was used in the optimization of Biogas composition and volume of gas production the experiment was applied to obtain optimum operating conditions for the factors involved. In this study three process factors: Total solid, Hydraulic retention time and temperature were studied. The analysis process was done connecting the gas bag of raw biogas to the gas analyzer and pressed the analyze button the gas analyser then takes the sample in and displayed the following samples CH<sub>4</sub> in Vol %, CO<sub>2</sub> in Vol %, O<sub>2</sub> in Vol% and H<sub>2</sub>S in ppm. Volume of Biogas was measured using the syringe.

### **3.3 Upgrade biogas and investigate the CO<sub>2</sub> removal efficiency**

#### **3.3.1 Materials**

25% sodium hydroxide solution, bottle (to hold caustic sample) was used as a scrubbing unit by connecting it to the gas analyser outlet using Pneumatic pipe, gas analyzer (Biogas-5000),

Pneumatic pipe, Gas valve was connected to the gas bag using pneumatic pipe to close the gas bag, gas bag, syringe.

### **3.3.2Methods**

Sodium hydroxide solution was used to perform the upgrading (removing carbon dioxide from raw biogas) simultaneously with gas analyzing by using the outlet of the gas analyzer as an inlet for the upgrading or scrubbing unit. Scrubbing unit consists of a bottle which has 25% sodium hydroxide solution that was closed by a stopper that has an inlet and outlet gas pipe. The inlet gas pipe was longer to the bottom of the caustic holding bottle to increase contact between the solution and carbon dioxide. The outlet gas pipe is short above the level of caustic solution to transfer the upgraded biogas into gas bag. The effluent or upgraded biogas was stored in gas bag and analyzed using the gas analyzer to know the composition of the upgraded biogas in other words the amount of carbon dioxide reacted with sodium hydroxide in the scrubbing unit.

Calculated the amount of energy by using the biogas produced, used the raw biogas composition multiplied by energy stored in  $1\text{m}^3$  biogas .Calculated methane enrichment efficiency subtracting the upgraded from the raw biogas results and divided it by upgraded biogas. Calculated the biogas equivalent energy demand using calorific value of biogas.

## Chapter Four

### 4. Result and discussion

In this section, findings obtained from the biogas production and upgrading experiment. The experimental set up is outlined in Chapter 3. The experiment involves mixing cow dung, brewery waste and inoculum in a lab scale biogas digester at AAiT laboratory. The upgrading unit contains caustic in a bottle for removing carbon di oxide and hydrogen Sulfide by absorption. The experiment uses caustic as an absorbent. Experimental parameters total solid, temperature and hydraulic retention time were investigated to see the effects on the production of biogas and removal of carbon dioxide and hydrogen sulfide using biogas upgrading mechanisms. In the section below, the experiment executed and their results are presented, analyzed and discussed.

#### 4.1 Characterization of Brewery waste and Cow dung

The percentage of inoculum for anaerobic fermentation of the organic waste is approximately 10% of the volume of the feed sample. The pH, total solid and volatile solid of the inoculums were 7.1, 9% and 80.4% respectively. Characterization of the two main components is stated in the following section.

##### 4.1.1 Characterization brewery waste

**Table 3:** Characterization of Brewery Waste

Parameter	Waste water qualities & quantities
COD	4,000 mg/l
BOD <sub>5</sub>	3,000 mg/l
TN	80 mgN/l
TP	30 mgP/l
Temperature	32°C
Ph	5
TS	1%

VS	94%
Volume of biogas at 35°C, 15 day, 10%	0.5L
Methane composition of raw biogas at 35°C, 15 day, 10%	35%

This result implies brewery waste can be used for biogas production but the methane composition is low. The quality and quantity of organic matter available for use in a biogas plant constitutes the basic factor of biogas generation. The volumetric yield of biogas per kilogram (kg) varies from one substrate to another depending on the composition as well as nature of the substrate. In addition, the percentage of methane obtained from the resultant biogas also varies independently according to type of biomass material (Weiland, 2010). Therefore, mixing both wastes will enable to find better biogas volume and composition.

#### 4.1.2 Characterization of Brewery waste and cow dung

Characterization of sample was made by taking Brewery waste, Cow dung and Inoculum without mixing each other in order to know TS and VS of each ingredient to biogas which helps to how much of each should be put in a single reactor to get the desired total solid which is from 4-12%.

Brewery waste feed in the anaerobic digester, and the following factors will be varied TS, Temperature, and Hydraulic retention time. Characteristics of Brewery waste and Cow dung used in the study were determined and the observed results as shown in Table 4.

**Table 4:** Characteristics of Brewery waste and Cow dung used in the study before biogas production.

Type of waste	TS%	VS%	pH
Brewery waste	1	94	5
Cow dung	18.95	81.53	7.5

**Table 5:** Comparison of the characteristics of wastes of this study to other reported elsewhere

Analysis	Brewery waste	Cow dung
Total Solid (%)	2%	19%
Volatile Solid (%)	90%	75.0%
PH	4.8	7.1

Source-Rene Alvarez and Gunnar Liaden, 2007

The cow dung total solid and volatile solid were 18.95% and 81.53% respectively. Other study reported that the total solid content of fresh manure was 16% while its volatile solid content was 79% (Eliyas Jigare, 2011). When compared to the result, this study has slight variation because of several factors which include feeding type of animal, type of on-site sanitation system, way of sampling system and amount of ageing that has taken place. Most of time in Ethiopia animals feed on leaves and grass but in foreign countries buck wheat is used for animal food. Biogas production and methane composition from brewery waste was 0.5L, 35% using 15 days HRT and compared to Cow dung that yielded 3.9L, 65% using 15 days.

**Table 6:** Comparison of the characteristics of brewery waste and cow dung at 35°C, 15 day, 10% Ts

Type of waste	Methane composition (%)	Biogas volume(L)
Brewery Waste	35	0.5
Cow Dung	65	3.9

The cumulative biogas produced during the digestion of the feed stocks for 15 days is presented. From the digestion of Brewery waste total production of bio gas volume 0.5liter at HRT 15 days from 300ml of substrate. The maximum methane composition was 35%. From cow dung biogas volume 3.9liter at 35°C, 15 day, 10% Ts from 300ml of substrate was produced. The maximum methane composition from cow dung was 65%.

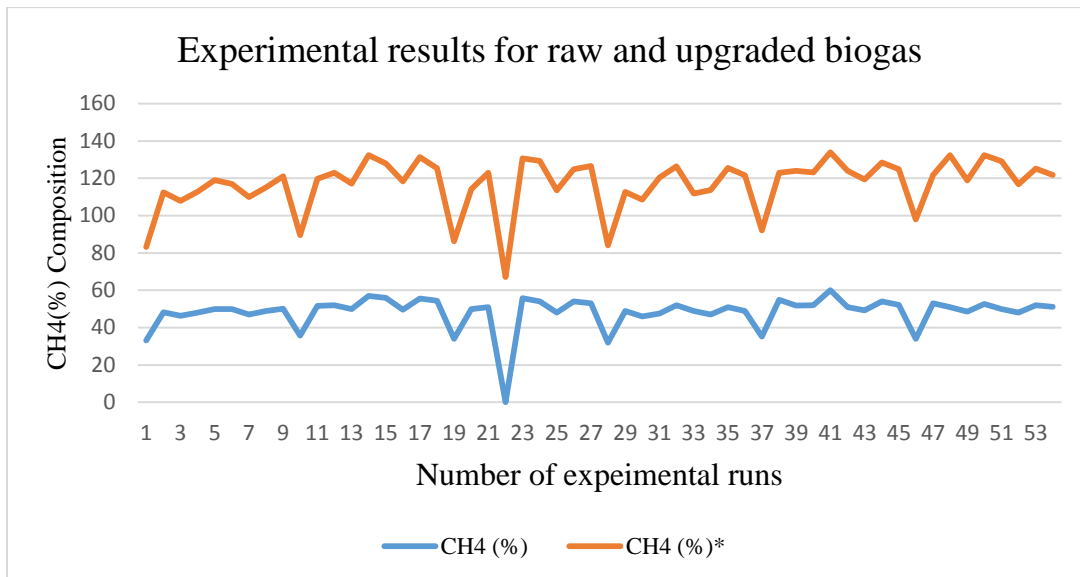
#### 4.2 Raw and upgraded biogas analysis

As prescribed in Chapter 3, the study was conducted in Environmental Engineering & Bio-innovative research laboratories in school of Chemical and Bio Engineering, Addis Ababa Institute of Technology Laboratory. The analysis equipment measures the composition of CH<sub>4</sub>, CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>S and others (sulphide compounds, siloxanes, aromatic and halogenated compounds, oxygen and nitrogen that are outside the main components) of raw biogas and the results are presented in the appendix, as raw biogas composition as a function of HRT, total solid and temperature. The upgraded gas composition was analyzed just before the end of the experiment.

The H<sub>2</sub>S composition was first read in ppm and here converted to vol %. The ‘others’ include sulphide compounds, siloxanes, aromatic and halogenated compounds, oxygen and nitrogen that are outside the main components. Traces of siloxanes may also be found in biogas. These siloxanes mainly originate from silicon-containing compounds widely used in various industrial material or frequently added to consumer products such as detergents and personal care products (R. Scott Frazier, 2015).

As it can be seen from appendix 4 as raw biogas composition as a function of HRT, total solid and temperature, the methane content was very low and carbon dioxide amount is higher especially on retention time 10days. If the retention time is too short, the bacteria in the digester are “washed out” faster than they can reproduce, so that the fermentation practically comes to a standstill (Digest, 1980). This high amount of carbon dioxide decreases the utilization of methane as an energy source. On the other hand, the amount of hydrogen sulfide wasn’t significant so further treatment is not needed for hydrogen sulphide. In order to improve the quality of the biogas energy content, carbon dioxide need to be removed.

**Figure 3 :** Experimental results for biogas of raw biogas and upgraded biogas



### 4.3 Optimization of biogas production

ANOVA for brewery waste and cow dung using quadratic model are shown at appendix. The analysis of variance of the quadratic regression model was a significant model, from evident of Fish's F test with a very low probability value [(P-model > F) =0.0001]. The Model F-value of 92.18 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, A<sup>2</sup>, B<sup>2</sup>, C<sup>2</sup>, BC are significant model terms. The "Pred R-Squared" of 0.9278 is in reasonable agreement with the "Adj R-Squared" of 0.9393. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 31.952 indicates an adequate signal. This model can be used to navigate the design space. The Brewery waste and cow dung appears to be a reliable model for methane percentage (CH<sub>4</sub> %) of biogas composition and biogas volume.

**Table 7:** Analysis of variance (ANOVA) for methane composition

Source	Sum of Square	DF	Mean of Squares	F-value	Prob > F	
Model	914.25	9	101.58	24.13	< 0.0001	significant
A	316.31	1	316.31	75.13	< 0.0001	
B	191.73	1	191.73	45.54	< 0.0001	
C	42.15	1	42.15	10.01	0.0057	
A <sup>2</sup>	120.42	1	120.42	28.60	< 0.0001	
B <sup>2</sup>	78.98	1	78.98	18.76	0.0005	
C <sup>2</sup>	62.89	1	62.89	14.94	0.0012	
AB	105.19	1	105.19	24.99	0.0001	
AC	4.89	1	4.89	1.16	0.2963	
BC	0.30	1	0.30	0.071	0.7928	
Residual	71.57	17	4.21			
Cor Total	985.83	26				

A=HRT B=TS C=Temperature

**Table 8:** Analysis of variance (ANOVA) for methane volume

Source	Sum of Square	DF	Mean of Squares	F-value	Prob > F	
Model	21.03	9	2.34	47.50	< 0.0001	Significant
A	1.96	1	1.96	39.84	< 0.0001	
B	14.51	1	14.51	295.09	< 0.0001	
C	2.15	1	2.15	43.62	< 0.0001	
A <sup>2</sup>	0.050	1	0.050	1.03	0.3255	
B <sup>2</sup>	0.68	1	0.68	13.83	0.0017	
C <sup>2</sup>	0.71	1	0.71	14.47	0.0014	
AB	0.079	1	0.079	1.61	0.2222	
AC	8.421E-003	1	8.421E-003	0.17	0.6842	
BC	0.40	1	0.40	8.08	0.0112	
Residual	0.84	17	0.049			
Cor Total	21.86	26				

A=HRT B=TS C=Temperature

The Model F-value of 47.50 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, B<sup>2</sup>, C<sup>2</sup>, BC are significant model terms.

**Table 9:** Statistical data of design expert for methane composition

Std. Dev.	2.05	R-Squared	0.9274
Mean	49.37	Adj R-Squared	0.8890
C.V.	4.16	Pred R-Squared	0.8158
PRESS	181.61	Adeq Precision	18.349

The "Pred R-Squared" of 0.8158 is in reasonable agreement with the "Adj R-Squared" of 0.8890. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 18.349 indicates an adequate signal. This model can be used to navigate the design space.

**Table 10:** Statistical data of design expert for methane volume

Std. Dev.	0.22	R-Squared	0.9618
Mean	2.13	Adj R-Squared	0.9415
C.V.	10.42	Pred R-Squared	0.9095
PRESS	1.98	Adeq Precision	23.403

The "Pred R-Squared" of 0.9095 is in reasonable agreement with the "Adj R-Squared" of 0.9415. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 23.403 indicates an adequate signal.

An empirical relationship between the response and the input test variables in actual units can be expressed by the following equation:

$$\text{CH}_4 \text{ Composition} = -124.42182 + 8.07483 * \text{HRT} + 16.21742 * \text{TS} + 1.55280 * \text{Temperature} - 0.17920 * \text{HRT}^2 - 0.60870 * \text{TS}^2 - 0.021727 * \text{Temperature}^2 - 0.23530 * \text{HRT} * \text{TS} + 0.010144 * \text{HRT} * \text{Temperature} + 4.99030\text{E-}003 * \text{TS} * \text{Temperature}$$

An empirical relationship between the response and the input test variables in actual units can be expressed by the following equation:

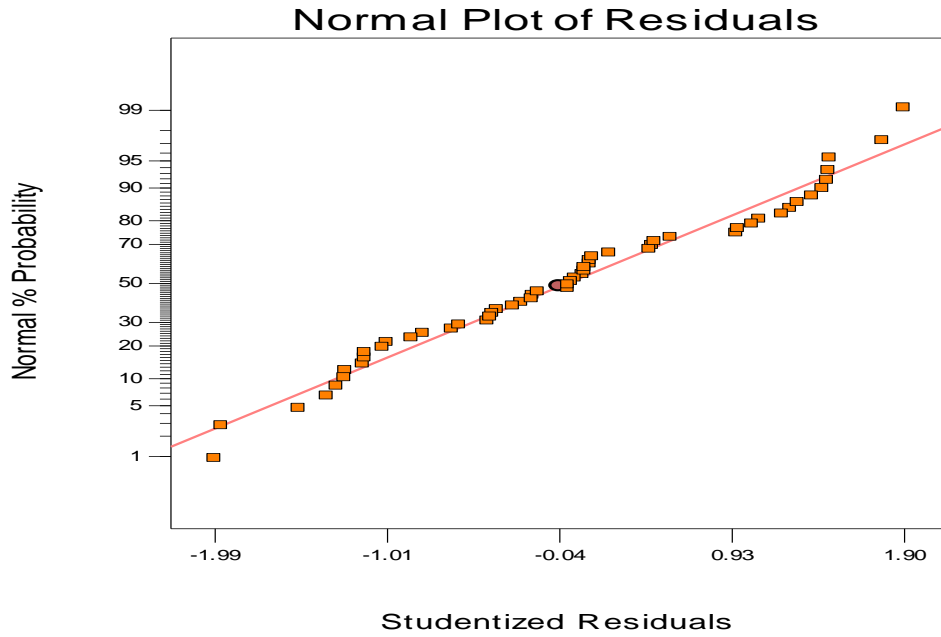
$$\text{CH}_4 \text{ Volume} = -10.62708 + 0.22189 * \text{HRT} + 1.31466 * \text{TS} + 0.14012 * \text{Temperature} - 3.66667\text{E-}003 * \text{HRT}^2 - 0.056481 * \text{TS}^2 - 2.31111\text{E-}003 * \text{Temperature}^2 - 6.44737\text{E-}003 * \text{HRT} * \text{TS} + 4.21053\text{E-}004 * \text{HRT} * \text{Temperature} + 5.74792\text{E-}003 * \text{TS} * \text{Temperature}$$

### 4.3.1 Diagnostic Model

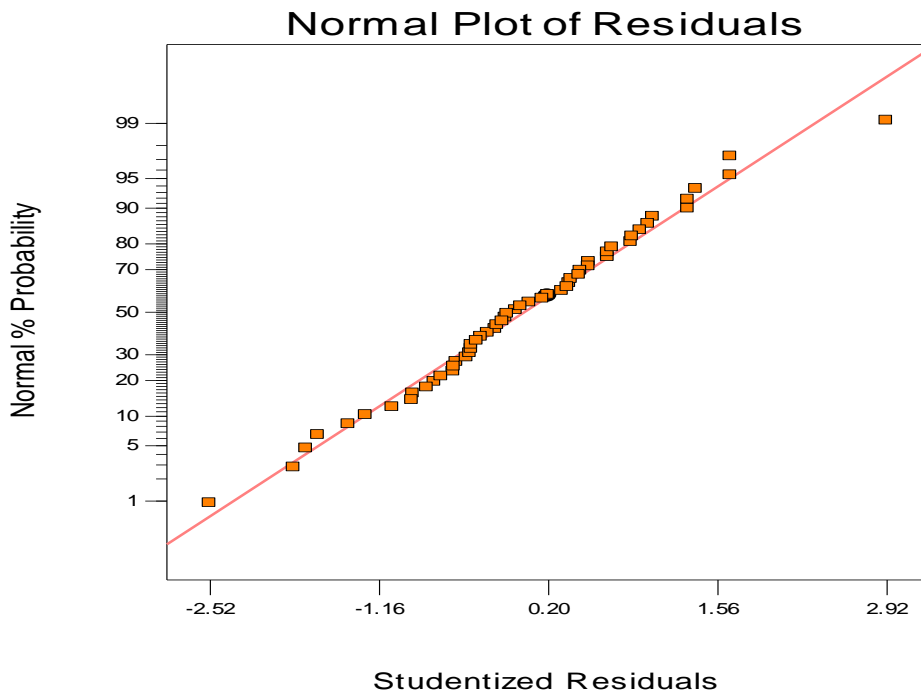
Before accepting any model, the satisfactoriness of the adopted model must be checked by an appropriate statistical analysis. The experimenter handbook by (Kraberet *al.*, 2002) stated that a good normal probability plot should show a linear straight line. The handbook also mentioned that good residuals versus predicted response plot should be random scatter whereas a bad plot of the kind will show a megaphone shape. A review on the normal probability plot for biogas yield as illustrated in Figure 3 revealed that the residuals generally fall on a straight line implying that the errors are distributed normally. On the other hand, the residuals versus predicted response as shown in Figure 20 revealed that they were random scattered without obvious pattern and unusual structure. This general impression implied that the model proposed was adequate and

there was no reason to unsure any violation of the independence or constant variance assumption.

**Figure 4:** Normal probability plot of residuals for methane composition



**Figure 5:** Normal probability plot of residuals for Biogas volume





### 4.3.2 Optimal production

The numerical optimization finds a point that maximizes the Desirability function. The following data presents the specific optimum conditions of methane composition by considering HRT, Total solid & temperature and our goal is at optimum conditions to obtain maximum methane composition and Biogas volume. Table showed that the suitable optimum HRT is 16.76 total solid is 10.28% and temperature 42.3 with the highest desirability of 0.967 have high value of methane composition and biogas volume per feeding volume selected.

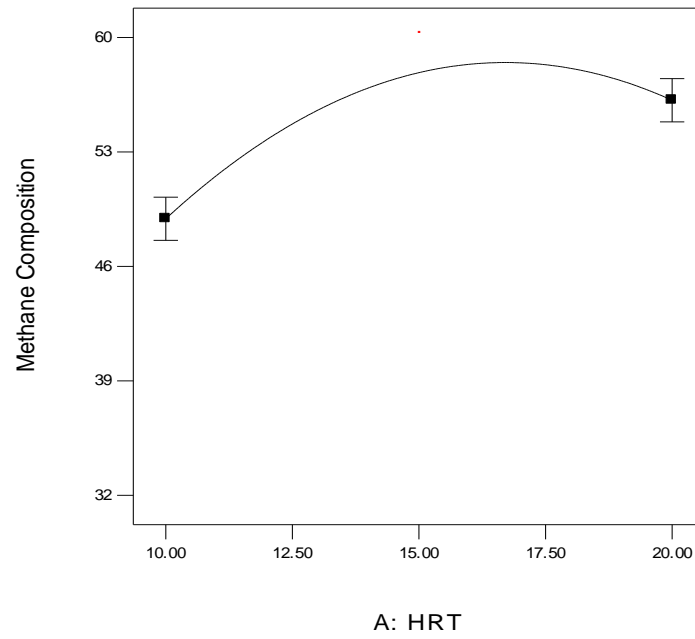
#### Solutions

No	HRT	TS	T	CH <sub>4</sub> Composition	Biogas vol	Desirability
1	<u>16.76</u>	<u>10.28</u>	<u>42.30</u>	<u>58.215</u>	<u>3.39818</u>	<u>0.967</u> <u>Selected</u>

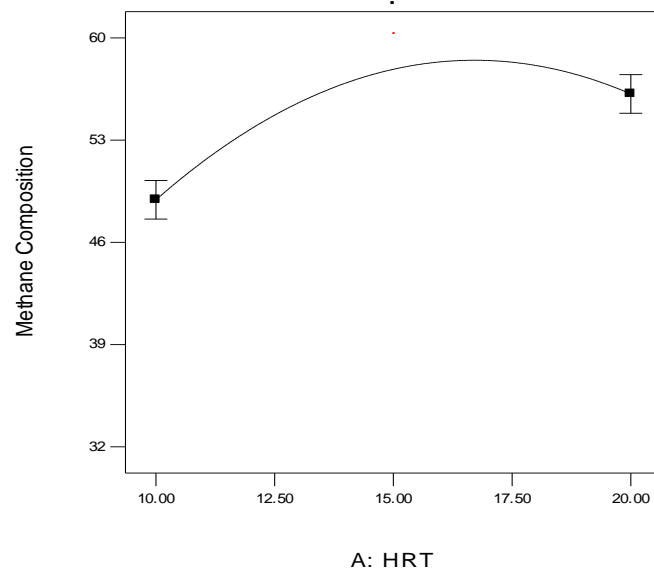
#### 4.3.2.1 Optimum Hydraulic retention time (HRT)

The effect of retention time on biogas composition for brewery waste and cow dung increased up to the optimum HRT 15 days then started to decline. The experimental results in this study demonstrated that the suitable HRT for anaerobic co-digestion is 15 days with the maximum biogas volume 3.4L and the average maximum methane composition of 60 %. In other researches, the best performance for biogas production is the anaerobic co-digestion with 15 days of HRT (Ezekoye, 2011). An initial increase in biogas production during the first to 15 day is observed, then a somewhat constant rate for 16 - 17.5 days then the final decline. From the graph, it was deduced that as retention time increased, the cumulative biogas composition and volume equally increased until it reached the optimum point. Retention time increase is expected because of the conversion of the volatile solid to monosaccharides, polysaccharides, amino acids etc. (A.H. Igoni, 2008).

**Figure 8:** Biogas composition versus HRT at selected at temperature 37.5 °C and Total solid 8%



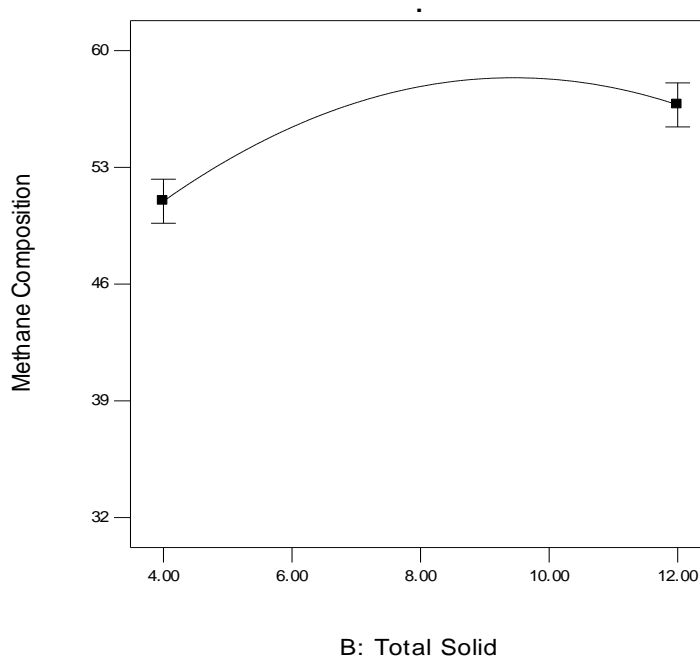
**Figure 9:** Biogas composition versus HRT at selected at temperature 37.5 °C and Total solid 8%



It can be concluded that the longer a substrate is kept under proper reactor conditions the more biogas composition and volume will become. Retention time has a significant effect on the digester's performance. But, the reactor rate will decrease with increasing residence time. The disadvantage of a longer retention time is the increasing reactor size needed for a given amount of substrate to be treated. A shorter retention time will lead to a higher production rate per reactor volume unit, but a lower overall degradation. These two effects have to be balanced in the design of the full scale reactor (BTG, 2003).

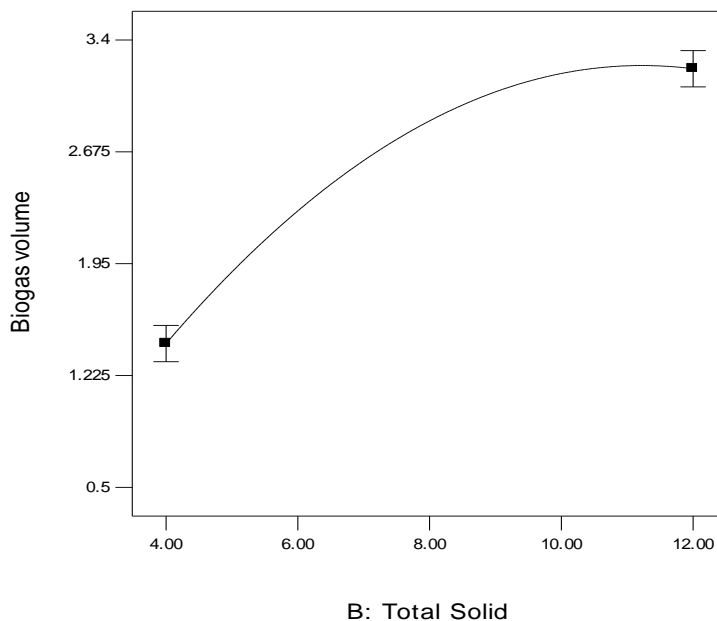
#### 4.3.2.2 Optimum Total solid (Ts)

**Figure 10:** Biogas composition versus Total solid at selected at temperature 37.5 °C and HRT 15days



The effect of retention time on biogas composition for brewery waste and cow dung increased up to the optimum 10% then started to decline. The experimental results in this study demonstrated that the suitable total solid for anaerobic co-digestion is 10% with the maximum biogas volume 3.4L and the average maximum methane composition of 60 %. The experimental results show that the reactor with 10% of total solid content yielded higher biogas compared with other reactors (Paramaguru, 2016).

**Figure 11:** Biogas volume versus Total solid at selected at temperature 37.5 °C and HRT 15days

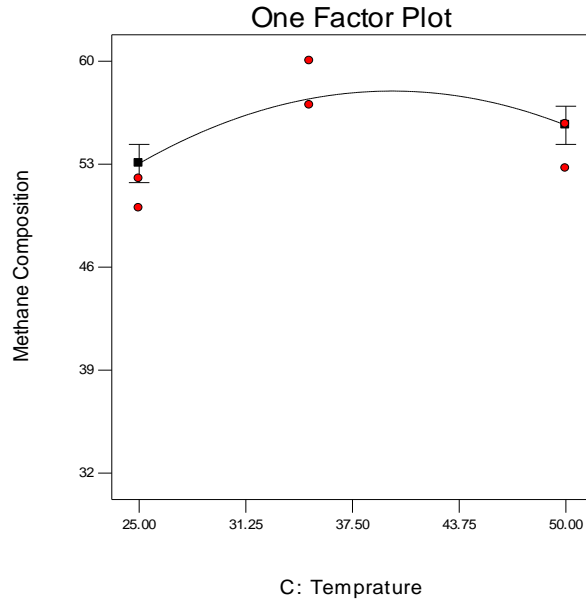


An initial increase in biogas production during from 4% to 10% total solid is observed, then a somewhat constant rate up to 11% to then then starts to decline. From the graph, it was deduced that as total solid is increased from 4% to 10 %, the cumulative biogas composition and volume equally increased until it reached the optimum point. Therefore, it can be concluded that total solid has a significant effect on the digester's performance

#### **4.3.2.3 Optimum Temperature**

This study was conducted in psycophilic, Mesophilic and Thermophilic temperature ranges and input ranges minimum and maximum temperature value from 25 °C to 50 °C to the factorial general Design Expert software which was chosen at 25 °C, 35 °C, and 50 °C and methane composition at these temp point presented at Appendix. Methane composition and Volume of biogas at controlled HRT and Total solid are shown in Figure 12 and Figure 13.

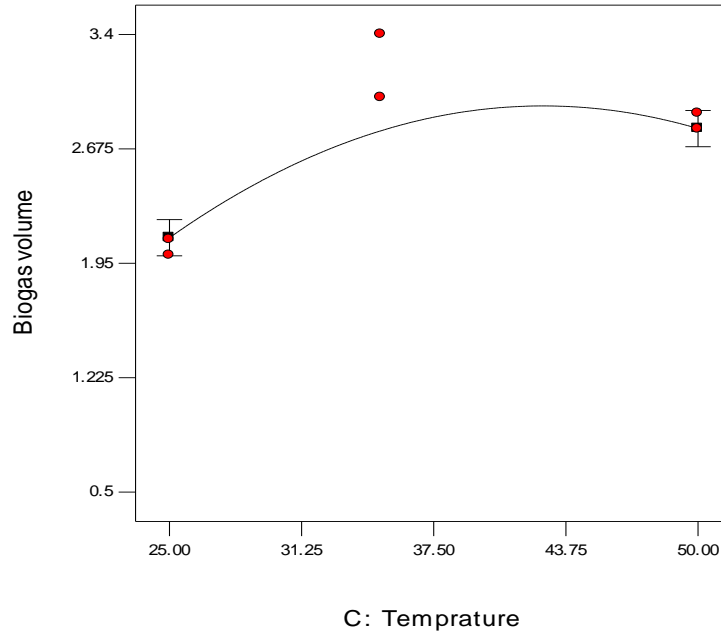
**Figure 12:** Methane Composition versus temperature at selected at HRT 10 days and Total solid 8%



Researches have suggested that the gas production during anaerobic digestion is correlated to temperatures (K.J, 2008). It can be maintained at psychrophilic 16-25 °C, mesophilic 35-45 °C, and thermophilic Conditions 45-60 °C (Kestutis Navickas, 2013). The optimum digester temperature setting, considering both the potential biogas yield and energy value, is one of the most critical factors for the economically viable digester operation in modern countries. This is the reason 25 °C, 35 °C, and 50 °C are chosen to do the experiment.

In this study, the optimal methane composition and biogas volume at temperature 35 °C was found and 60% and 3.4L; in other words this temperature range is mesophilic temperature range which is recommend range in literatures (Kestutis Navickas, 2013).Both on the methane composition and biogas volume the optimum was found when temperature was set in the mesophilic region then decreases as it goes to the termophilic region

**Figure 13** : Biogas volume versus temperature at selected at HRT10 days and Total solid 8%



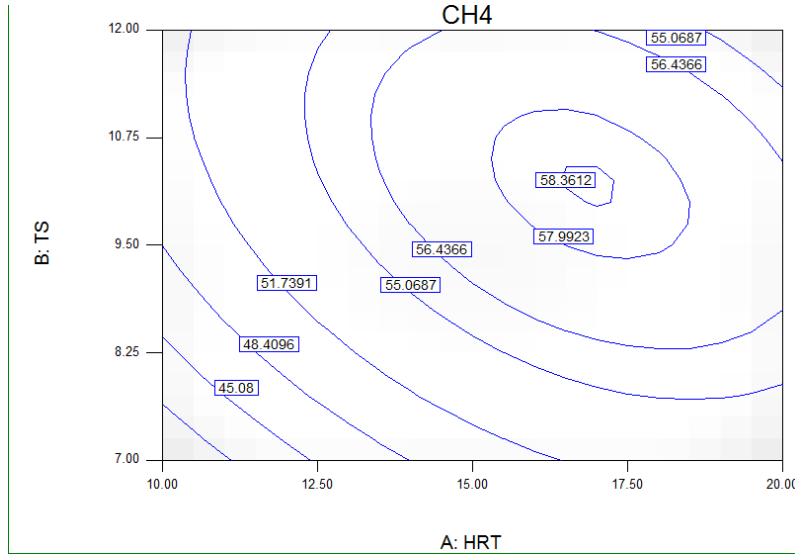
Researchers suggest that an increase of the temperature results reduction of the biogas composition due to the increased inhibition of free ammonia ( $\text{NH}_3$ ) which increases at elevated temperatures (Hutnan M., 2003). Digesters operating at lower temperatures are considered to be more stable systems (Hutnan M., 2003). At the same time the thermophilic process results in a larger degree of imbalance and a higher risk for ammonia inhibition. Ammonia toxicity is intensifying with temperature increase (Kestutis Navickas, 2013). The experimental result also shows at psychocopic temperature range the methane composition and biogas volume show decreased result relative to mesophilic range. Temperature in psychocopic ranges are not suitable for anaerobic digestion and it takes long HRT for digestion and low gas production because the degradation of long-chain fatty-acids is often rate limiting. If long-chain fatty-acids accumulate, foaming may occur in the reactor and so inhibit process continuity (Tchobanoglous G, 2003). Refer appendices 6 and 7 to see the interaction effect of all the parameters the interactions show that the optimum vale for optimum biogas production and yield is 15day, 35 °C, and 8%.

### Interaction effect on CH<sub>4</sub> composition

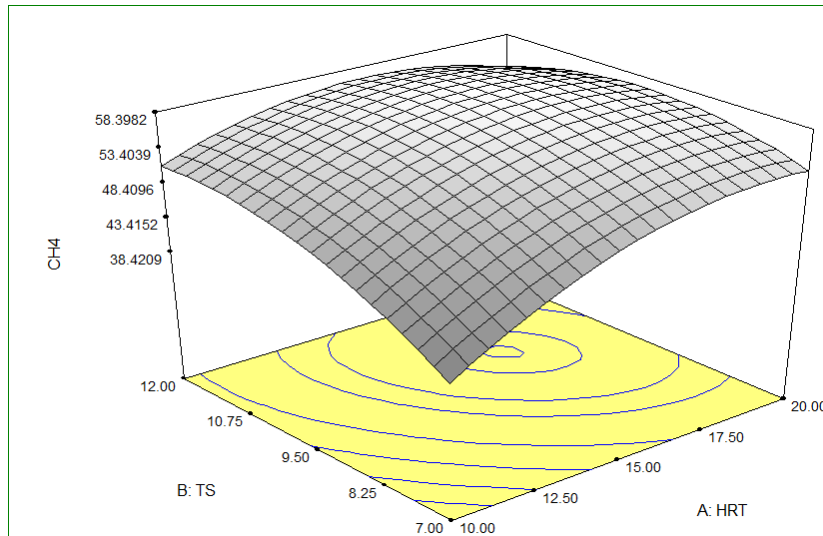
The interaction effects of HRT and TS as seen from the figure it shows as the HRT increase up to 17.5 °C, CH<sub>4</sub> composition increases then starts to decline, as well as TS increase up to TS 8 the CH<sub>4</sub> composition also then starts to decline.

**Figure 14:** Interactions effects of HRT and TS on CH<sub>4</sub> composition

#### A. Contour diagram



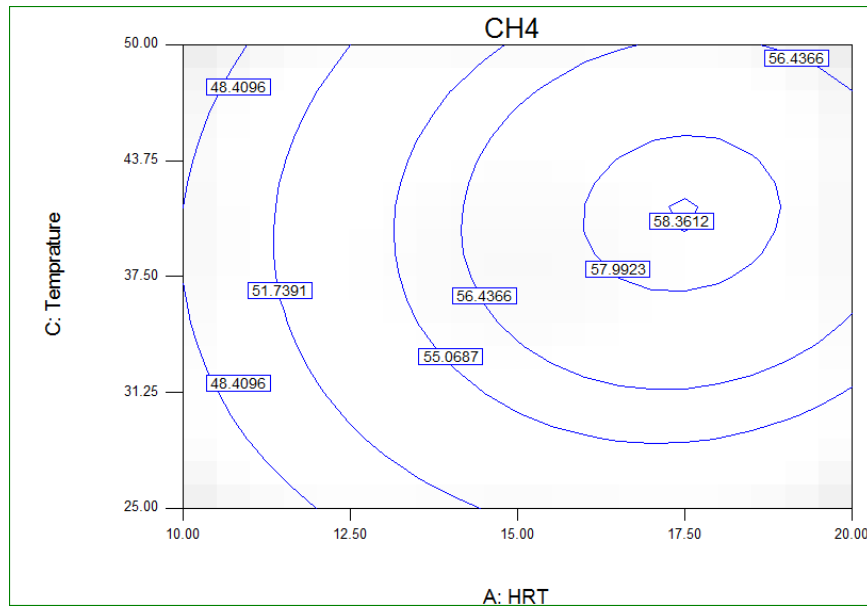
#### B. 3D diagram



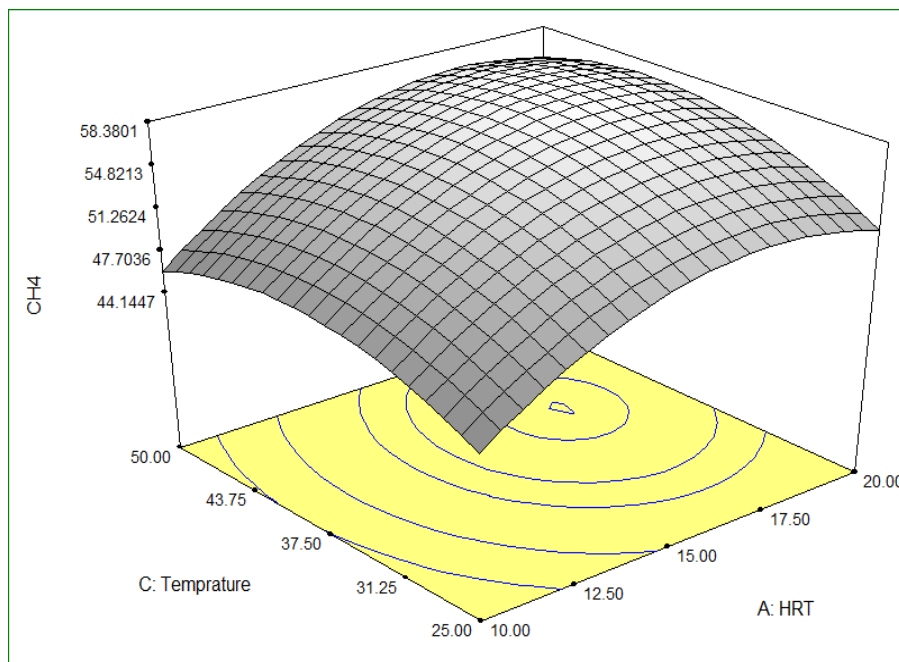
The interaction effects of HRT and temperature as seen from the figure it shows as the HRT increase CH<sub>4</sub> composition increases up to HRT 17.5 then starts to decline. In the case of temperature maximum CH<sub>4</sub> composition is produced around 43.75 degree Celsius then starts declining.

Figure 15 : Interactions effects of HRT and temperature on CH<sub>4</sub> composition.

A. Contour diagram



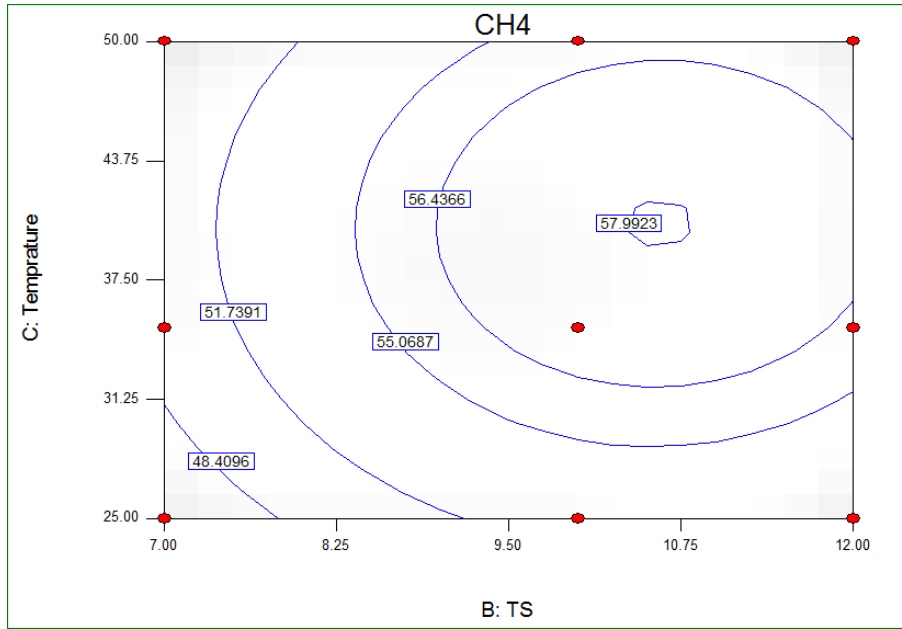
B. 3D diagram



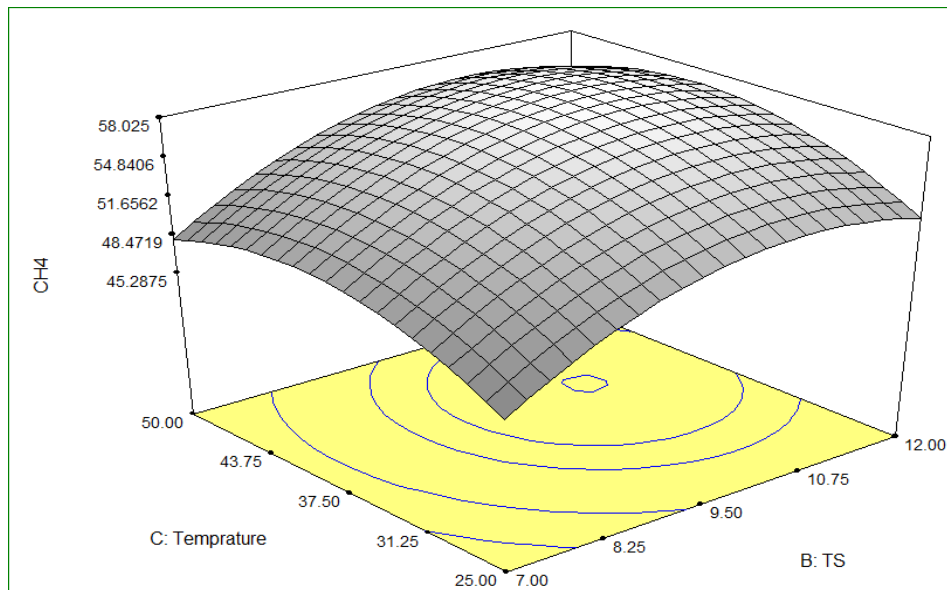
The interaction effects of TS and temperature as seen from the figure it shows as TS increase up to 10.75 CH<sub>4</sub> composition increases then starts to decline. In the case of temperature maximum CH<sub>4</sub> composition is produced around 43.75 degree Celsius.

**Figure 16:** Interactions effects of TS and temperature on CH<sub>4</sub> composition

A. Contour diagram



B. 3D diagram

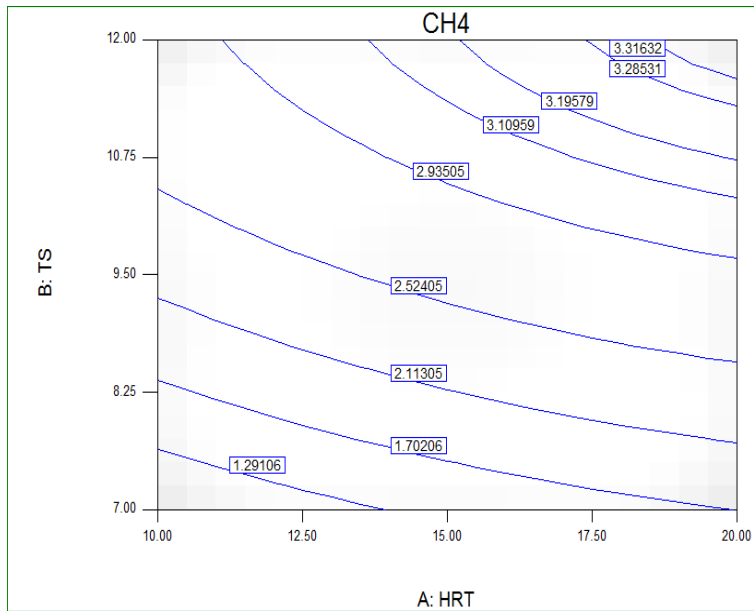


### Interaction effects on CH<sub>4</sub> volume

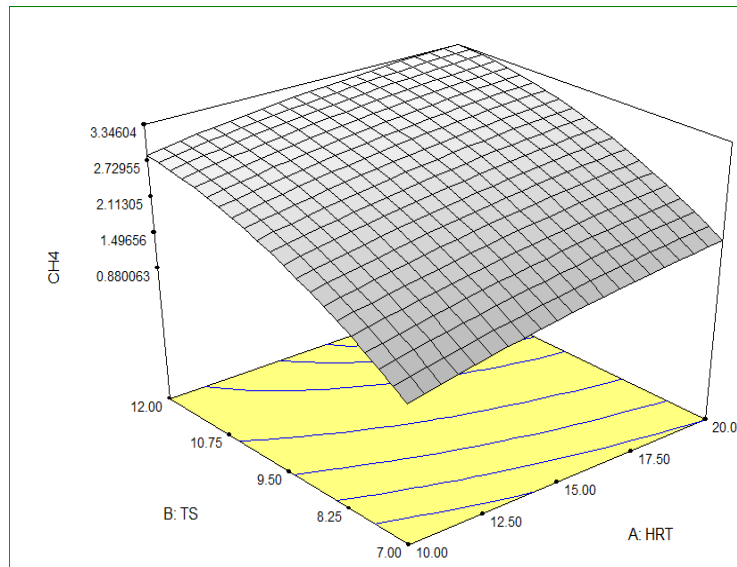
The interaction effects of HRT and TS as seen from the figure it shows as the HRT increase CH<sub>4</sub> volume increases, as well as TS increase the CH<sub>4</sub> volume increases so their interactions exactly affects CH<sub>4</sub> volume.

**Figure 17:** Interactions effects of HRT and TS on CH<sub>4</sub> volume

#### A. Contour diagram

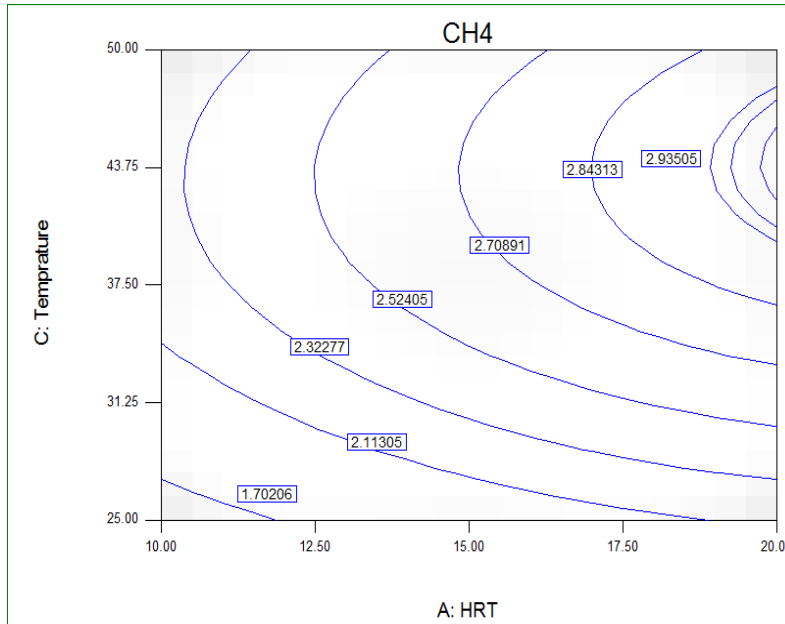


#### B. 3D diagram

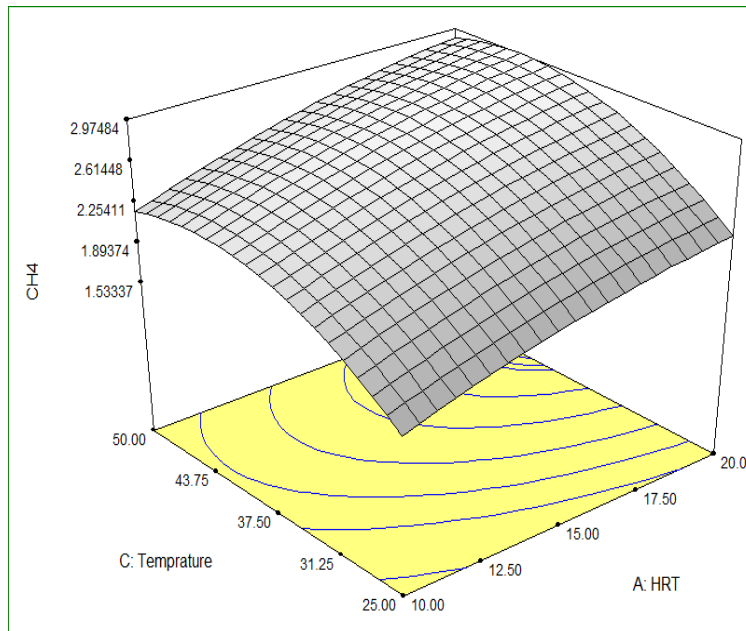


The interaction effects of HRT and temperature as seen from the figure it shows as the HRT increase CH<sub>4</sub> volume increases. In the case of temperature maximum CH<sub>4</sub> volume is produced around 43.75 degree Celsius then starts declining.

**Figure 18** Interactions effects of HRT and temperature on CH<sub>4</sub> volume  
A. Contour diagram

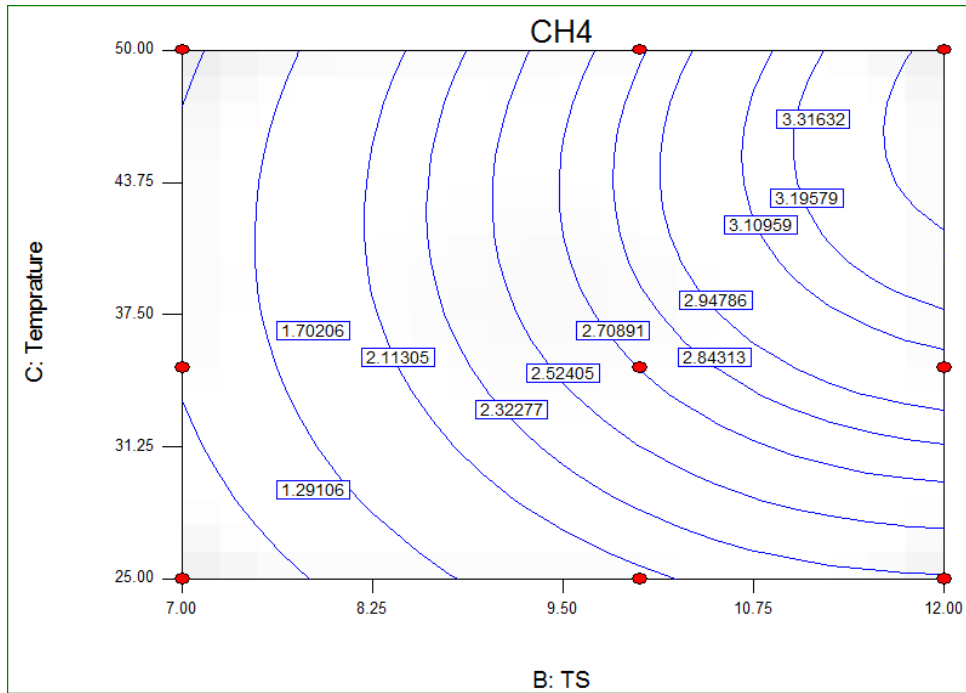


B. 3D diagram

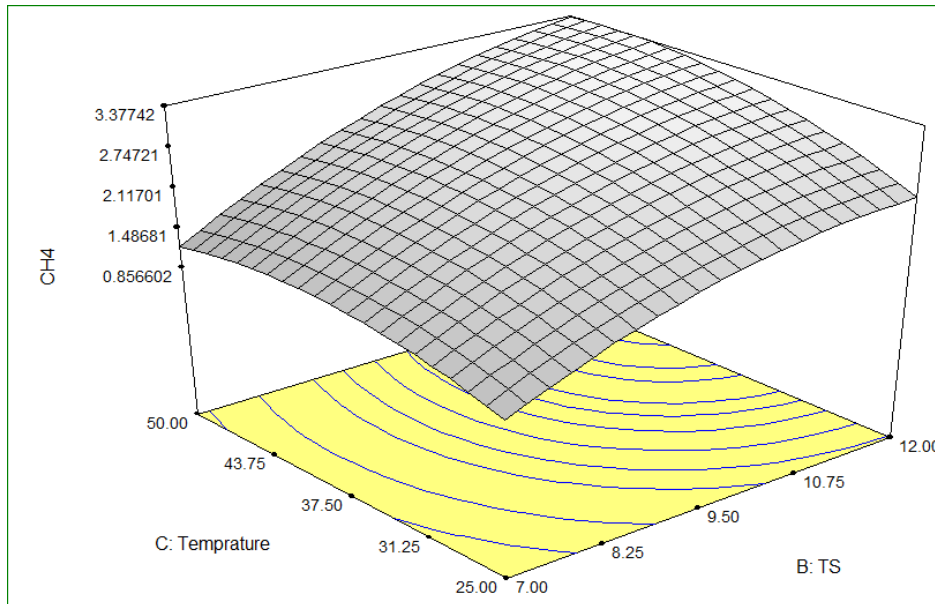


The interaction effects of TS and temperature as seen from the figure it shows as TS increase CH<sub>4</sub> volume increases. In the case of temperature maximum CH<sub>4</sub> volume is produced around 43.75 degree Celsius.

**Figure 19:** Interactions effects of TS and temperature on CH<sub>4</sub> volume  
 A. Contour diagram



B. 3D diagram



#### 4.4 Upgrade biogas and investigate CO<sub>2</sub> removal efficiency

Similar to this study, the efficiency of CO<sub>2</sub> capture of 85% was obtained for 25% of NaOH (Kordylewski, 2013). While high proportion of carbon dioxide (over 83.1% removal efficiency), was observed in this study resulting in CH<sub>4</sub> enriched biogas.

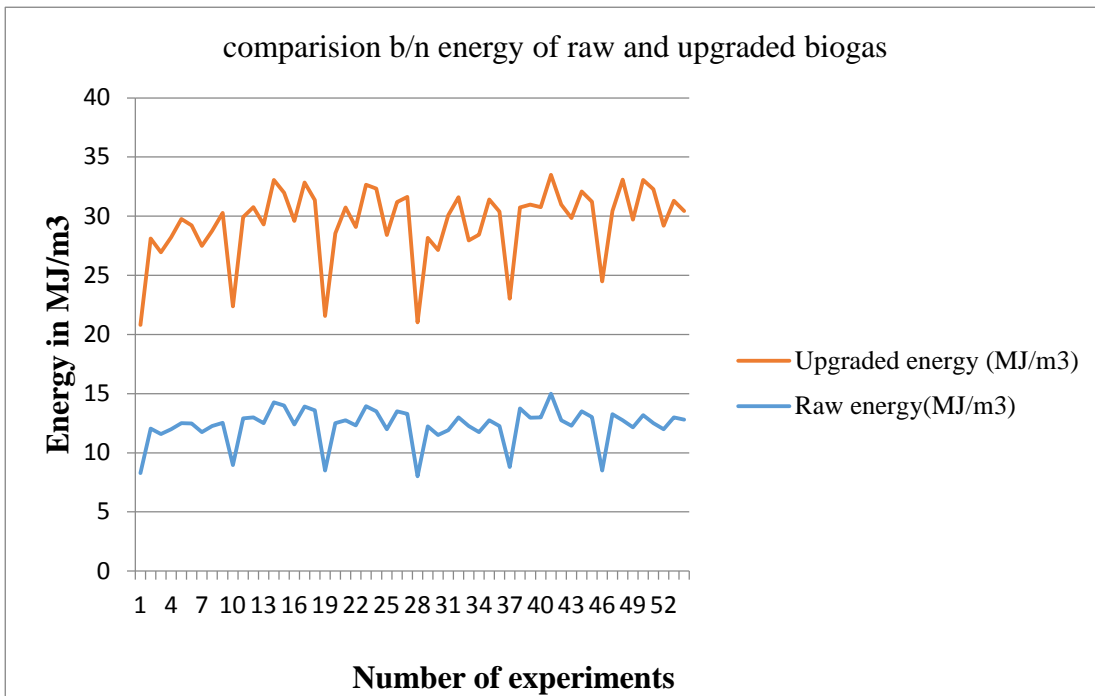
**Table 11** : Methane enrichment and carbon dioxide removal efficiency

HRT(D)	Ts(%)	T(C)	CH <sub>4</sub> (vol. %)	CH <sub>4</sub> (vol. %)*	Upgrading efficiency (%)	CO <sub>2</sub> (vol. %)	CO <sub>2</sub> (vol. %)*	CO <sub>2</sub> removal (%)
10	4	25	33.1	50.1	51.36	39	22	43.58
15	4	25	48.2	64.3	33.40	30.8	14.7	52.27
20	4	25	46.3	61.5	32.83	27	11.8	56.29
10	8	25	48	64.9	35.21	38.8	21.9	43.55
15	8	25	50	69	38	35.3	16	54.67
20	8	25	49.9	67	34.27	26.6	17.9	32.71
10	12	25	47	63	34.04	27	11	59.26
15	12	25	49	66	34.69	34.3	9.4	72.59
20	12	25	50.1	71	41.71	25.4	4.3	83.07
10	4	35	35.8	53.7	50	36.1	18	50.13
15	4	35	51.67	68.07	31.74	34.03	17.63	48.19
20	4	35	52	71	36.54	25	6	76
10	8	35	49.99	67.19	34.41	29.71	12.51	57.89
15	8	35	57	75.3	32.11	23.3	4.7	79.83
20	8	35	56	71.9	28.39	28	12.1	56.78
10	12	35	49.6	68.8	38.71	30.6	11.4	62.75
15	12	35	55.67	75.7	35.98	24.33	4.03	83.44

#### 4.5 Energy difference between raw biogas and upgraded biogas

As mentioned in literature, biogas consists of 48-75% methane gas, 30-45% carbon dioxide gas, 2- 8% water vapor and traces of hydrogen. Comparing this with natural gas which contains 75-90% methane, the energy content mainly depends on the content of methane gas. High methane content would be more desirable. A presence of carbon dioxide and water vapor content is unavoidable, but content of sulphur must be minimized particularly when used in engines. The average calorific value of biogas is about 22-24.5 MJ/m<sup>3</sup>, so that 1 m<sup>3</sup> of biogas corresponds to 0.55-0.65diesel fuel which is about 6 kWh.

**Figure 20:** Comparison between energy of raw and upgraded biogas.



#### 4.6 Biogas equivalent energy demand

Daily waste generated from Heineken breweries Kilinto, Addis Ababa

**Table 12 :** Average amount of waste from Heineken breweries Kilinto, Addis Ababa

Parameter	Maximum	Average
Waste water quantity	4000 m <sup>3</sup> /day,4450.5 Kg/day	
Peak flow	120 m <sup>3</sup> /h	80 m <sup>3</sup> /h
COD-load	5700 kg/d	4000 kg/d
Concentration COD	3000mg/l	2100 mg/l
TS	3%	1%

**Table 13:** HFO Consumption at Heineken Brewery, Kilinto

	Annually	Daily
HFO fuel consumption	3,125,063L/y	8680.7 L/day
HFO cost	39,728,905.93birr/y	110,358.072birr/day

On average, cow dung around the factory has total solid of 18%.Based on total solid of the brewery waste and cow dung on average 4197kg /day cow dung is required to make a total of 8000kg/day the amount of bio gas that can be produced from daily waste is equal to 1881.56 m<sup>3</sup> /day and amount of methane that can be produced per day is 1531.58m<sup>3</sup> /day.

##### 4.6.1 Calorific Value and Energy Equivalent of Biogas

To Determine Calorific value of Biogas generated by experiment contains 81.4% of methane. Calorific value of 100 % methane is 8560 KCal / m<sup>3</sup> (Sasse., Kellner, & Kimaro, 1991).

##### Determination of Calorific Value of Biogas

Calorific Value of Pure Methane = 8560 Kcal / m<sup>3</sup>

% of Methane in Biogas = 81.4 %

Calorific Value of Biogas = 8560Kcal/m<sup>3</sup> x 0.814= 6967.84Kcal / m<sup>3</sup>

Caloric Value of Bio Gas =6967.84 kcal/m<sup>3</sup>

Energy Equivalent of Produced Biogas is Equal to

1kwh=859.85kcal then value  $6967.84/859.85$  (kwh/m<sup>3</sup>) =8.1kwh/m

Therefore 1m<sup>3</sup> biogas=8.1kwh

Electrical conversion efficiency = 35% and Boiler conversion efficiency = 85% (Richardson's, 2003) .

Therefore, for electricity application 1m<sup>3</sup> biogas = 8.1\*0.35=2.8 kWh (elec) and

For Boiler application 1m<sup>3</sup> biogas =8.1\* 0.85=6.88kwh (Boiler).

Total energy produced for boiler

1m<sup>3</sup> biogas =8.1kwh

Daily=8.1kwh\*1881.56\*0.85=12,954.54kwh

From Heineken Brewery Kilinto biogases have a capacity to generate power is equal to:

Total produced biogas m<sup>3</sup> per day=1881.56m<sup>3</sup>/day CH<sub>4</sub>=1531m<sup>3</sup>

Total energy generate per day= 1881.56day \*8.1kwh =15,240.636kwh/day

Total energy generate per day=15,240.636 kwh/day

#### **4.6.2 Energy potential of HFO & Percentage substitution by biogas**

In order to Calculate the energy value of liter of furnace oil to kWh per m<sup>3</sup> as follows

1kwh=859.85kcal that is and 1kg furnace oil=10,500 kcal

1Kg of furnace oil =10,500/859.85kwh =12.21kwh changes to kWh per m<sup>3</sup>. Then calculate Energy value of one kilogram of furnace oil in terms of kWh/ m<sup>3</sup>

Density=mass/volume;V=1kg/0.92gm/cc=10.86\*10KWh/m<sup>3</sup>=12.21kwh/10.86\*10<sup>-4</sup>  
=11,243kwh/m<sup>3</sup>

Also from the literature heavy fuel oil 11.4kwh/lit .From this we have quantified daily energy consumption of boiler for steam generation in the form of kWh by considering conversion efficiency of HFO when used or applied on Boiler is 80%.Hence amount energy capacity of

8680.7 lit/day of furnace oil is= 8.6807 m<sup>3</sup>/day \*11,243kwh/m<sup>3</sup>

=97,597.11 kWh /day.

=0.8\*97,597.11 kWh/day

=78,077.68Kwh/day

Amount of Biogas to carry out Boiler energy consumption or substitute HFO

Energy conversion efficiency of Biogas on Boiler=0.85

Amount of Boiler energy consumption=78,077.68Kwh/day

0.85\*Amount of Energy generated from Bio Gas=78,077.68Kwh/day

Amount of Energy required to be generated from Biogas=91,856.1 kwh/day to substitute HFO

Determination of volumetric value of biogas required covering HFO as follows

$1\text{m}^3=8.1\text{kwh}$  for boiler based on conversion efficiency

Required amount of energy demand from Biogas= 91,856.1 kwh/day

Volume of biogas demand for boiler= $91,856.1\text{ kwh/day} / 8.1\text{m}^3=11,340.2\text{m}^3$

Total energy that can be generated from the use of biogas

Total energy generate per day=15,240.636 kwh/day

Total energy required to run the boiler=91,856.1kwh/d

% that can be covered by Biogas= Total energy generated by biogas/ Total energy required by HFO.

= $15,240.636\text{ kwh/day} / 91,856.1\text{kwh/d} * 100\%$

=16.6%

Therefore, biogas produced can cover 16.6 % of HFO for boiler which can save 6,591,764.508 birr/year from  $4000\text{ m}^3/\text{day}$  of brewery waste water and  $4197\text{kg} / \text{day}$  of cow dung.

## Chapter Five

### 5. Conclusion and Recommendation

#### 5.1 Conclusion

Conversion of waste into energy is a technology that has the potential of producing cleaner energy and greener alternative fuel. Anaerobic digestion technology is considered to be a practical method to reduce and treat waste at the same time produce energy fuel, methane. Parameters influencing the anaerobic process and reactions involved to attain methane and optimum conditions to enhance satisfactory methane yields.

This research on optimization and upgrading of brewery waste for boiler emphasizes on production of biogas from brewery waste and cow dung focusing on the optimization of process parameters such as temperature, HRT and TS for the maximal biogas production. Optimization of those variables was carried out by General factorial Design Expert software. Firstly, the characteristics of each of the two items were investigated in detail comparatively. The results obtained can be summarized as follows: Biogas production from brewery waste was 0.5L, 35% using 10 day, 35 °C, 1%Ts and compared to Cow dung that yielded 3.9L, 65% using 10 day, 35 °C, 8%Ts. Therefore, to increase the amount of methane composition and yield brewery waste and cow dung were mixed base on the recommendation from literature Total solid of 4%, 8% and 12%, Temperature at 25°C, 35 °C, 50°C and hydraulic retention time at 10, 15, and 20 days.

From the experiment, all three parameters had significant effects on bio gas volume and composition. The optimum conditions for maximizing the biogas yield and composition were 10 day, 35 °C, 8%Ts a in which maximum biogas yield of 0.3 lit /gm. Out of which 60% is methane then upgraded to 81.41% which gave the calorific value 6967.84Kcal / m<sup>3</sup> which has energy generating potential of 8.1kwh/m<sup>3</sup>. Efficient use of energy resources is an important aspect of energy management. Upgrading raw biogas to high methane content is one form in which biogas energy resource can be efficiently used, and in a sustainable manner. The methane was upgraded to 80% methane using 25% caustic water absorption process. During upgrading the carbon dioxide content reduced below 22%.

While this waste has a potential to generate 15,240.636 kwh/day of energy which could cover 16.6% of HFO consumption it can generate energy equal to 12,954.54 kwh/day and save 6,591,764.508 birr/year of its budget. In addition, there is a benefit for the environment and human health. At the same time, the most beer factories have a future expansion plan and applying this for these factories will have significant contribution in cost reduction.

## 5.2 Recommendation

This study on optimization and upgrading of biogas from brewery waste with cow dung for boiler suggested that Heineken should use bio gas for steam generation to reduce the cost of energy and minimize its discharge of pollutant wastes to the environment, to reduce foreign currency of the country and to find a sustainable energy source. It recommended that the government should give attention for avoiding the direct disposal emission of the waste to the environment any treatment so this biogas technology is the best remedy.

Due to its potential and feasibility for cooking, electricity generation and different other purposes the biogas needs to be purified for easy storage into cylinders and prolong the efficiency of various equipment's. Depending on the methane standards applied in different countries, upgraded biogas could be used in several biogas applications. The findings from the experiment upgrading system adds to the evidence that biogas may be used as a renewable energy source and a substitute for fossil fuels. However, biogas enrichment will be much improved if further research work is conducted .In this research the absorption column used was not designed according to the desired concentration output of  $\text{CH}_4$ ,  $\text{CO}_2$  and  $\text{H}_2\text{S}$ . So that in order to get desired output concentration of the gases, calculations should be made from the mass transfer equations and the minimum flow rate of water from the given raw biogas flow rate and also the minimum contact area required to get the mass transfer should be determined.

Government should encourage investors in food and agro processing because its suitability to produce anaerobically digestible organic waste. And set strict standards to limit the exhaust from polluting the environment. In industry parks combining different kinds of industry so that the wastes generated when combined give the desired range for biogas production. This will ensure a form of sustainability in energy usage.

## References

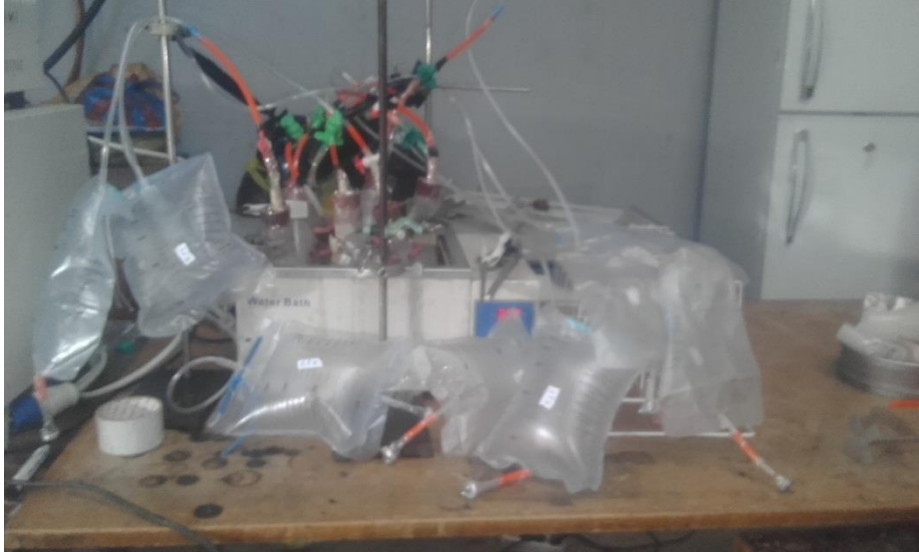
- A.H. Igoni, M. A. (2008). Effect of Total Solids. *Agricultural Engineering International*.
- African, G. D. (2010). *Draft research project to run Gfleet*.
- Ahrens. (2007). *Stabile Prozessführung und Biogasgewinnung bei anaerober*.  
Abwasserklarttechnik: Brauwelt .
- Amigun, M. J. (2011). Biofuels and sustainability in Africa. *Renewable and Sustainable Energy Review*, 1360-1372.
- Anderson, a. (2002). *Designing Experiments that Combine Mixture Components with process factors*.
- APHA-AWWAWPCH. (1998). *Standard Methods for the examination of water and water resources*. APHA Washington D.C.: American Public Health Association.
- Barroso, J. (2003). Behavior of a high-capacity steam boiler using Heavy fuel oil. *ELSEVIER*, 85-105.
- BTG, B. t. (2003). Anaerobic Digestion. A. 1 – 4.
- Buchhauser, U. (2006). Alternativen zu Öl und Gas. *Brauindustrie* 6, 55-57.
- Budiyono, I. Syaichurrozi, S. Sumardiono. (2014). Effect of Total Solid Content to Biogas Production Rate from Vinasse . *International Journal of Engineering*, 177-184.
- center, H. e. (2015). *Healthcare environmental resource center*. Retrieved October 20, 2017, from Healthcare environmental resource center: [www.boiler%20impact.htm](http://www.boiler%20impact.htm)
- de Mes, A. S. (2010). *Methane production by anaerobic digestion of wastewater and solid wastes*.
- Dennis. (2000). *Brewing Science and Practice*. Boston: wodhead publishing limited.
- Digest, B. ((1980)). Information and Advisory Service on Appropriate Technology (Isat) Biogas Basic.
- Djuragic, O., Levic, J., & Serdanovic, S. (2010). Use of new feed from brewery by-products for breeding layers. *Romanian Biotechnol. Lett.* 2010, 15,, 5559–5565.
- Euroserv-er. (2008). *Biogas upgrading -An Introduction Proceedings of the International*. HANAU.
- Ezekoye, V. (2011). Effect of Retention Time on Biogas Production from Poultry. *Nig J. Biotech.* .

- Fărcaș, A., Tofană, M., Socaci, S., Mudura, E., Scrob, S., Salanță, L., & Mureșan, V. (2014). Brewers' spent grain—A new potential ingredient for functional foods.. 2014, 20, 137–141. *J. Agroaliment. Proc. Technol*, 137-141.
- Hilkiah Igoni. (2010). *Designs of anaerobic digestors for production of biogas*.
- Hutnan M., H. M. (2003). Anaerobic treatment of wheat stillage. *Chem. Biochem. Eng.*, 233-241.
- K.J, C. (2008). The effects of digestion temperature and temperature shock on the biogas. *Bioresource Technology*, 1-6.
- Kanagachandran, K. J. (2006). *Utilization potential of brewery waste*. J. Inst. Brew.
- Kapad S., V. V. (2004). Biogas Scrubbing, Compression and storage: perspective and prospectus in Indian context.
- Kestutis Navickas, K. V. (2013). INFLUENCE OF TEMPERATURE VARIATION ON BIOGAS YIELD FROM INDUSTRIAL. *ENGINEERING FOR RURAL DEVELOPMENT*, 406-408.
- Kordylewski, W. (2013). LABORATORY TESTS ON THE EFFICIENCY OF CARBON DIOXIDE CAPTURE FROM GASES IN NaOH SOLUTIONS. *Journal of Ecological Engineering*, 50-370.
- Kuiper. (2016). Boiler Manual. In Kuiper.
- Management, P. P. (1998). *Heavy Fuel Oil*. Brussels: Prepared by CONCAWE's.
- Miller. (1996). *HAZARDOUS AIR POLLUTANTS FROM THE COMBUSTION OF AN EMULSIFIED HEAVY FUEL OIL IN A FIRETUBE BOILER*. Washington: U.S. Environmental Protection Agency.
- Munch, P., Hofmann, T., & Schieberle, P. (1997). Comparison of key odorants generated by thermal treatment of commercial and self-prepared yeast extracts: Influence of the amino acid composition on odorant formation. *J. Agric. Food Chem.*, 1338–1344.
- Mussatto. (2014). *S.I. Brewer's spent grain: A valuable feedstock for industrial applications*. J. Sci. Food Agric.
- Nactogroup. (2007). *Acid Gas (CO<sub>2</sub>) Separation Systems with Cynara Membranes*.
- Naz, A. K. (2013). Isolation and Characterization of Microbial Community in Biogas Production from Different Commercially Active Fermentors in Different Regions of Gujranwala. *International Journal of Water Resources and Environmental Sciences*.
- NRC, (R. (2010). *Energy Efficiency Opportunities in the Canadian brewing industry*.
- Olajire, A. A. (2012). The brewing industry and environmental challenges. *ELSEVIER*, 1-21.
- Olajire, A. A. (2012). The brewing industry and environmental challenges. *cleaner production*.

- Paramaguru, G. (2016). Effect of total solids on biogas production through anaerobic digestion. *desalination and Water Treatment*.
- Patrick, M. J. (2002). Designing Experiments that Combine Mixture Components.
- Persson, J. O. (2003). Biogas as transportation fuel.
- Persson, M. J. (2006). *Biogas upgrading to vehicle fuel standards and Grid injection*.
- Petroleum. (2016). *Yearly Fuel Consumption*. Addis Ababa: Enterprise of Ethiopian petroleum.
- R. Scott Frazier, P. N. (2015). *Biogas Utilization and Clean up*. Kansas City: extension .org.
- Rajeshwari, B. K. (1999). *Anaerobic digestion for industrial waste water treatment*.
- Richardson, C. a. (2002). *Particle technology and Separation process*. Woburn, : utterworth-Heinemann.
- Richardson's, C. (2003). *Chemical Engineering Design*. Burlington: An imprint of Elsevier Science.
- Rozzi. (2000). *Start up and automation of anaerobic digesters with automatic bicarbonate*.
- Sasse., Kellner, C., & Kimaro, A. (1991). *Improved biogas unit for developing countries*.
- SEP, E. A. (2004). *Guidance on gas treatment technologies for landfill gas engines*.
- Speece. (1996). *Anaerobic Technology for Industrial Wastewaters*. USA: Archae Press.
- Tchobanoglous G, B. F. (2003). *Waste-water Engineering treatment and reuse Fourth*. New Delh: Tata McGraw-Hill Publishing Company Limited.
- Thaniya Kaosol, N. S. (2012). Influence of Hydraulic Retention Time on Biogas material. *nternational Journal of Environmental, Chemical, Ecological, Geological and Geophysical Engineering* , 303-305.
- Wainwright, T. (1998). *Baic Brewing Science*. South Africa : Magicprint (Pty) Ltd.
- Weiland, P. (2010). Biogas production current state and perspectives,.
- Wilkie AC, W. (2008). Bioenergy: Biomethane from biomass, Biowaste and Biofuel. pp195-199.
- Yitayal. (2012). Enhancement and Optimization mechanisms of Biogas production for rural Household.

## Appendices

### Appendix 1: Pictures taken during laboratory



### Appendix 2: Gas analyzer and scrubbing unit of the experiment



**Appendix 3: Quantity and amount inquired for HFO at Heineken breweries Share Company**

Entrance Date	Quantity(L)	Amount(birr)
1/13/2016	1914	26808.53
1/14/2016	8055	112822.73
1/14/2016	8314	116450.43
1/14/2016	3233	45283.17
1/14/2016	7440	104208.71
1/14/2016	7134	99922.7
1/14/2016	7332	102696
1/14/2016	3128	43812.48
1/14/2016	6864	96140.94
1/14/2016	6675	93493.7
1/14/2016	3739	52370.48
1/14/2016	8575	120106.14
1/15/2016	7971	111646.18
1/15/2016	8870	124238.07
1/15/2016	8891	124532.21
1/19/2016	8465	118565.42
1/19/2016	8023	112374.52
1/19/2016	8872	124266.08
1/19/2016	8325	116604.5
1/25/2016	8434	116866.36
1/25/2016	8265	114524.6
1/25/2016	8097	112196.7
1/30/2016	7926	126289.29
1/30/2016	8518	135721.95
1/30/2016	5049	80448.47
1/30/2016	7987	127261.23
1/30/2016	8648	137793.31
1/31/2016	8673	138191.65
1/31/2016	11522	183586.32
2/3/2016	7843	114995.93
2/8/2016	7843	112060.24
2/8/2016	7080	101158.55
2/8/2016	7646	109245.51
2/8/2016	7260	103730.37
2/8/2016	6732	96186.35
2/8/2016	2207	31533.46
2/8/2016	2717	38820.31

2/8/2016	9325	133234.95
2/8/2016	7067	100972.8
2/8/2016	7614	108788.3
2/8/2016	9034	129077.16
2/22/2016	4913	62844.47
2/22/2016	3920	50142.55
2/22/2016	1790	22896.72
2/22/2016	7315	93569.58
2/22/2016	6582	84193.43
2/22/2016	8955	114547.58
2/22/2016	9042	115660.44
2/22/2016	8822	112846.32
2/26/2016	9265	118512.94
2/26/2016	5018	64187.58
2/26/2016	7892	100950.25
2/26/2016	8968	114713.87
2/26/2016	7590	97087.23
2/27/2016	6543	83694.56
2/28/2016	7396	94605.69
2/28/2016	8777	112270.7
2/28/2016	3754	48019.16
3/11/2016	2127	26777.01
3/11/2016	7572	95324.64
3/11/2016	8460	106503.75
3/11/2016	4317	54347.13
3/11/2016	6839	86096.83
3/11/2016	8619	108505.42
3/11/2016	7859	98937.71
3/11/2016	3890	48971.58
3/11/2016	8268	104086.65
3/18/2016	8043	100409.23
3/18/2016	7715	96314.46
3/18/2016	7280	90883.9
3/18/2016	8260	103118.27
3/18/2016	6228	77750.68
3/18/2016	1541	19237.92
3/18/2016	7909	98736.37
3/18/2016	4460	55678.87
3/22/2016	41200	514342.94

3/24/2016	6926	86464.54
3/24/2016	7635	95315.74
3/24/2016	6677	83356.01
3/24/2016	3994	49861.3
3/24/2016	4458	55653.9
3/24/2016	7178	89610.52
3/24/2016	6393	79810.54
3/24/2016	5264	65716.05
3/27/2016	8628	107979.98
3/27/2016	7909	98981.65
3/27/2016	4932	61724.3
4/19/2016	1352	16800.18
4/19/2016	6258	77762.96
4/19/2016	5450	67722.62
4/19/2016	7473	92860.75
4/19/2016	7583	94227.63
4/19/2016	5299	65846.26
4/19/2016	7099	88213.37
4/19/2016	5924	73612.62
4/19/2016	11805	146690.91
4/19/2016	7197	89431.13
4/19/2016	7608	94538.29
4/19/2016	7366	91531.15
4/19/2016	4342	53954.42
4/19/2016	6193	76955.26
4/19/2016	8159	101385.11
4/19/2016	6288	78135.75
4/23/2016	7739	96122.32
4/23/2016	6163	76547.6
4/23/2016	7135	88620.34
4/23/2016	2878	35746.23
4/23/2016	6715	83403.72
4/23/2016	6781	84223.48
4/23/2016	8020	99612.49
4/23/2016	6096	75715.43
4/23/2016	7396	91862.09
5/12/2016	2878	35511.24
5/12/2016	6715	82855.44
5/12/2016	6781	83669.81
5/12/2016	8020	98957.66
5/12/2016	6096	75217.69

5/12/2016	7396	91258.21
5/12/2016	8347	102992.46
5/12/2016	2343	28909.95
5/23/2016	1131	13955.25
5/23/2016	6532	80597.43
5/23/2016	8546	105447.9
5/23/2016	5792	71466.68
5/23/2016	7859	96971.1
5/23/2016	8379	103387.31
5/23/2016	5860	72305.72
5/23/2016	2886	35609.95
5/23/2016	6921	85397.25
5/23/2016	7983	98501.12
5/23/2016	7552	93183.07
5/23/2016	7841	96749
5/23/2016	7589	93639.61
5/23/2016	7152	88247.53
5/23/2016	6213	76661.34
5/23/2016	6058	74748.81
5/23/2016	9107	112370
5/23/2016	8638	106583.07
5/23/2016	7345	90628.93
5/23/2016	7712	95157.29
5/25/2016	7741	94983.18
5/25/2016	1351	16576.96
5/25/2016	7284	89375.72
5/28/2016	8545	104385.46
5/28/2016	7377	90117.21
5/28/2016	7190	87832.82
5/28/2016	8348	101978.91
6/2/2016	8348	101607.32
6/2/2016	7855	95606.8
6/2/2016	3899	47456.51
6/2/2016	5384	65531.12
6/2/2016	5610	68281.87
6/2/2016	8022	97639.43
6/15/2016	5859	71159.36
6/15/2016	7599	92292.2
6/15/2016	7009	85126.47

**Appendix 4 :** Feed biogas composition as a function of Hydraulic retention time, total solid and temperature

HRT(D)	Ts(%)	T(C)	CH4 (vol. %)	CO2 (vol. %)	O2 (vol. %)	Others (vol. %)	H2S (vol. %)*	CH4(vol.L)
10	4	25	33.1	39	5.9	22	0	0.5
15	4	25	48.2	30.8	6	15.4	0	1
20	4	25	46.3	27	4.2	22.5	0	1.2
10	8	25	48	38.8	5.8	7.3	0.0001	1.6
15	8	25	50	35.3	5.2	9.5	0	2
20	8	25	49.9	26.6	5.7	17.7	0.0001	2.2
10	12	25	47	27	7.1	18.9	0	2
15	12	25	49	34.3	5.2	11.3	0.0002	2.2
20	12	25	50.1	25.4	5.3	19.2	0	2.4
10	4	35	35.8	36.1	6.1	22	0	0.8
15	4	35	51.67	34.03	3.8	10.5	0	1
20	4	35	52	25	3.8	19.2	0	1.5
10	8	35	49.99	29.71	7	13.3	0.0001	2
15	8	35	57	23.3	5.2	14.5	0	3
20	8	35	56	28	4.8	11.2	0	3.3
10	12	35	49.6	30.6	3	16.8	0	3
15	12	35	55.67	24.33	5.2	14.7	0.0001	3.1
20	12	35	54.33	30.97	4.7	10	0	3.1
10	4	50	34	44.1	9.6	12.3	0	0.9
15	4	50	50	31	8.7	10.3	0	1.2
20	4	50	51	25	9	12	0.0001	1.5
20	8	50	54	28.4	6.1	11.5	0	3.2
10	12	50	48	27.7	5.3	19	0	3.1
15	12	50	54	25.9	3.2	16.9	0	3.3
20	12	50	53.12	31.82	4.3	17	0	3.4
10	4	25	32	67.39	4.9	23	0.0002	0.6
15	4	25	48.9	50.1	6	16.5	0	1
20	4	25	46	52.9	4.2	21.4	0	1.1
10	8	25	47.6	51.2	5.8	6.5	0	1.2
15	8	25	52	45.9	5.2	8.4	0	2.1
20	8	25	49	48.89	5.7	16.7	0.0001	2.1
10	12	25	47	51.1	7.1	15.2	0	1.9
15	12	25	51	46.9	5.2	10.3	0	2.1

20	12	25	49	48.7	5.3	17.4	0	2.3
10	4	35	35.2	63.79	6.1	20	0.0001	1
15	4	35	55	43.8	3.8	11.5	0	1.2
20	4	35	51.9	47	3.8	17.2	0	1.1
10	8	35	52	45.9	2	14.3	0	2.1
15	8	35	60	36.59	5.2	15.1	0.0001	3.4
20	8	35	51	45.69	4.8	10.2	0.0001	3.3
10	12	35	49.2	47.8	3	16.3	0	3
15	12	35	54	43	5.2	15.4	0	3
20	12	35	52.1	44.8	4.7	9	0	3.1
10	4	50	34	65.2	3.6	12.6	0	0.8
15	4	50	53	45.9	4.7	9.9	0	1.1
20	4	50	51	47.6	3	11.5	0	1.4
10	8	50	48.6	49.4	2.9	11.9	0	2
15	8	50	52.7	44.5	3.6	16.8	0	2.8
20	8	50	50	46.89	2.1	11.8	0.0001	3.1
10	12	50	48	49	5.3	17.9	0	3
15	12	50	52	44.79	3.2	16.6	0.0001	3.2
20	12	50	51.2	45.5	4.3	15.2	0	3.3

## **Declaration**

I the undersigned, hereby declare that the work contained in this Thesis entitled “Optimization and Upgrading of Biogas from Brewery Waste for Boiler” is my original work and has not been presented for any degree in any university and all the resource of materials used for the Thesis have been duly acknowledged.

**Tigist Zegeye**

Name

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signature

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date