REFINING BIOGAS PRODUCED FROM BIOMASS (COW DUNG), BY REMOVING CO_2

BY

SHOKUNBI ADESHINA
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DECLARATION

I Shokunbi Adeshina declare that this research project is solely the result of my work and has never been submitted anywhere for any degree. All literature cited have been dully acknowledged in the reference.

SHOKUNBI ADESHINA DATE

CERTIFICATION

This is to certify that I have supervised, read and approved this project work, which I found adequate both in scope and quality for the fulfilment of the requirement for the award of the Bachelor Degree in Chemical Engineering.

ABDULKAREEM S.A — 05/03/2002

ENGR. S. A. ABDULKAREEM
PROJECT SUPERVISOR — DATE

DR. J. O. ODIGURE
HEAD OF DEPARTMENT — DATE

EXTERNAL SUPERVISOR — DATE

DEDICATION

This project is dedicated to my mother Mrs. Shokunbi A. Abeni for the love, support and encouragement throughout my study.

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My profound gratitude goes to my entire family, for their support financially, morally and spiritually throughout my stay in school. My sincere appreciation also goes to my supervisor Mr. Abdulkareem, S. A. who took his time to guide, review and give useful advice and criticism that led to making this work a success.

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LIST OF ABBREVIATIONS

GCV : Gross Calorific Value.

wt : Weight.

$\triangle H°$: Standard Heat of Reaction.

LIST OF UNITS

CO_2	:	Carbon (iv) oxide
H_2S	:	Hydrogen sulfide
CH_4	:	Methane
H	:	Hydrogen
C	:	Carbon
N	:	Nitrogen
P_2O_5	:	Phosphorous (v) oxide
K_2O	:	Potassium (i) oxide
H_2O	:	Water
K_2CO_3	:	Potassium trioxocarbonate
KOH	:	Potassium hydroxide
$KHCO_3$	:	Potassium hydrogen trioxocarbonate (iv)
$KMnO_4$	:	Potassium tetraoxomanganate (vii)
H_2SO_4	:	Tetraoxosulphate (vi) acid
K_2SO_4	:	Potassium tetraoxosulphate (vi)
$MnSO_4$	:	Manganese tetraoxosulphate (vi)
S	:	Sulphur
O	:	Oxygen
SO_2	:	Sulphur (iv) oxide
CCl_4	:	Carbon tetrachloride
$CHCl_4$	:	Trichloromethane
CH_2Cl_2	:	Dichloromethane
CN	:	Nitroge Cyanide
%	:	Percent
MJ/kg	:	Megajoules per kilogram
kg	:	Kilogram

MJ/m^3	:	Megajoules per cubic metre
l	:	Litre
Cells/ml	:	Cells per millilitre
atm	:	Atmosphere
°c	:	Degree centigrade
g/l	:	Gram per litre
ppm	:	Parts per million
mm	:	Millimetre
KJ/mol	:	Kilojoules per mole
ml	:	Millilitre
g	:	Gram
mol	:	Mole

ABSTRACT

This project is aimed at refining a biogas produced from cow dung by reducing carbon dioxide (CO_2) content of the biogas produced. A known total solid concentration of cow dung (560 grams in 7 litres of solution) was prepared and allowed to digest anaerobically in a laboratory sized digester at a constant pH of 7±0.5 before the on set of the gas production by addition of concentrated sodium hydroxide solution or concentrated hydrochloric acid solution. The resulting biogas produced was refined by absorbing it into different concentrations of KOH and $KMnO_4$ for CO_2 removal. Each of the three samples of biogas collected in the gas collection bags was passed through gas chromatograph to determine the percentage composition (mol % dry) of the biogas mixture in the bag.

The results of the biogas mixture analysis before refinement were 54.09 mole % dry CH_4, 40.20 mole % dry CO_2 and 0.80 mole % dry H_2S which conformed with the literature values of 50 – 65 mole % dry CH_4, 35 – 50 mole % dry CO_2 and 0.1 – 1.0 mole % dry H_2S. The results of the biogas mixture analysis after refinement using different concentrations of 45 %, 50 % and 55 % of KOH and $KMnO_4$ were 54.09 mole % dry CH_4, 4.07 mole % dry CO_2 and 0.04 mole % dry H_2S, 54.09 mole % dry CH_4, 4.01 mole % dry CO_2 and 0.01 mole % dry H_2S and 54.09 mole % dry CH_4, 4.03 mole % dry CO_2 and 0.016 mole % dry H_2S respectively. From these results, for 45% concentration of KOH, 89.88 % of CO_2 is removed, for 50 % concentration of KOH, 90.02 % of CO_2 is removed. Therefore, it is concluded that 50 % concentration of KOH is the best concentration at which high percentage of CO_2 could be removed.

CHAPTER ONE

1.0. INTRODUCTION

1.1. BACKGROUND OF STUDY

Our dependence on fossil fuel began with the industrial revolution in the eighteenth century. Until that time, man's economy was based almost entirely on biomass. With the development of coal as a new and economical source of energy, low-energy biomass based societies were transformed into high-energy fossil fuel energized societies. More recently our energy supplies have become dominated by petroleum and natural gas, which are even more economically produced and utilized more than coal. But petroleum is a non-renewable resource, in the sense that we are using it up faster than it is being made (King and Cleveland, 1980).

Research on anaerobic digestion of human sewage began in the latter half of the 19th century. The septic tank was developed in England by Donald Cameron in 1895. The septic tank is basically a sealed chamber which is allowed to fill with effluent, in which anaerobic fermentation develops. The first municipal plant for anaerobic treatment of sewage was established in Exeter in 1897, using the septic tank principle. Anaerobic digestion is widely used as a treatment for organic wastes. The feed stock may be excrement of human or animal origin, domestic refuse in land fill sites, residues from agriculture and food-processing industries or agricultural crops grown specifically for the purpose of biogas generation. With rising energy costs, however, increasing attention is being devoted to anaerobic digestion as a potential fuel source, albeit after the necessary CO_2 and H_2S removal (Levett, 1990). The removal of CO_2 improves the heat value of the gas. The removal of H_2S eliminates the corrosive action as well as the fouling odour of the gas.

1.2. AIM AND OBJECTIVES.

The objective of this write up is to produce bio gas from cow dung of high thermal content. The project is aimed at the following: -

1. To improve the production rate of biogas from cow dung.
2. To produce a biogas that could serve as a substitute for petroleum based cooking gas by removing CO_2.

1.3. JUSTIFICATION FOR THE PROJECT

A. K. Kivaisi and M. Mtila of the Applied Microbiology Unit, Botany Department, University of Dar es Salaam, Tanzania, and also Afolayan Razak T. and Adigwu Celestina N. of the Department of Chenical Engineering, Federal University of Technology, Minna had worked on the production of biogas from cow dung using anaerobic digesters and not on the refinement of biogas produced from cow dung. The studies on the anaerobic digestion of cattle dung, and waste barnyard and household materials embarked upon by scientists at the India Agricultural Research Institute were also centred on producing methane as a source of fuel and on retaining or improving the qualities of the residual as fertilizers and not on refining the methane produced by removing CO_2 and H_2S. The removal of CO_2 improves the heat value of the gas, and the removal of H_2S eliminates the foul-smelling, poisonous and corrosive action of the gas.

1.4. SCOPE

The method of biogas production used in this work is a batch anaerobic digestion using laboratory-sized digester. Substrate of known concentration of animal waste was allowed to digest anaerobically at room temperature. The gaseous product resulting therefrom contains methane, carbon dioxide and hydrogen sulfide and this was analysed using gas analyser. The gas was refined by gas-liquid absorption method of acid-gas

analyser. The gas was refined by gas-liquid absorption method of acid-gas removal.

1.5. RELEVANCE OF STUDY

With rising energy costs and inevitable major shortage of oil in the world sometimes in the future, it is hoped that the biogas obtained from renewable sources could serve as a potential fuel source and a substitute for petroleum-based cooking gas whose source is a non-renewable one, albeit after the necessary carbon dioxide and hydrogen sulfide removal.

CHAPTER TWO

2.0. LITERATURE REVIEW

2.1. BIOGAS AS A FUEL

When organic matter undergoes anaerobic fermentation, the principal off-gases formed by micro-organism are methane (50-70 percent), and carbon dioxide (30-50 percent), with traces of hydrogen sulfide (King and Cleveland, 1980). This natural process has been known for many years. In fact, gas from a septic tank was used for street lighting in Exeter, England as early as 1895 (Levett, 1990). Methane is the term used by organic chemists for the gas originally known as marsh gas or, by coal miners, firedamp and more recently biogas. It occurs naturally by the anaerobic decomposition of vegetation in swampy areas, and by a similar process in the formulation of coal and oil (King and Cleveland, 1980). In the latter case, it constitutes a gaseous hydrocarbon with a high calorific value when burned, and is the major constituent of natural gas.

By 1938-1939, scientists at the India Agricultural Research Institute began studies on the anaerobic digestion of cattle dung, and waste barnyard and household materials, with the objectives of producing methane as a source of fuel and of retaining or improving the qualities of the residual substances as fertilizers (King and Cleveland, 1980). After considerable research and technical work, biogas plants were designed for family and village use which were functional and acceptable for cooking, lighting, and even mechanical power.

In theory, almost any organic residue could be used as the starting point for biogas production. In practice, however, the bulk of it comes from the fermentation of animal manure. In India, in particular, dried cow dung has been-and is still-used as a fuel. Biogas production from manure

gives a much cleaner source of heat, light and power, with an undigested residue suitable for recycling as fertilizer (king and Cleveland, 1980).

2.2. BIOMASS AS A SOURCE OF BIOGAS

Biomass is any material that is directly or indirectly derived from plant life and that is renewable in time periods of less than about 100 years. More conventional energy resources such as petroleum and coal, as well as kerogen and tar sands, are of course, also derived from plant life, but are not considered renewable in the sense that their qualities are usually determined and defined by natural factors and they exist as deposits on the earth in specific quantities (Probstein and Hicks, 1982). Biomass is a renewable bioresource in the sense that it can be produced continuously or replenished by nature, man or both. Several routes in bioconversion processes are shown in figure1. (Probstein and Hicks, 1982). .

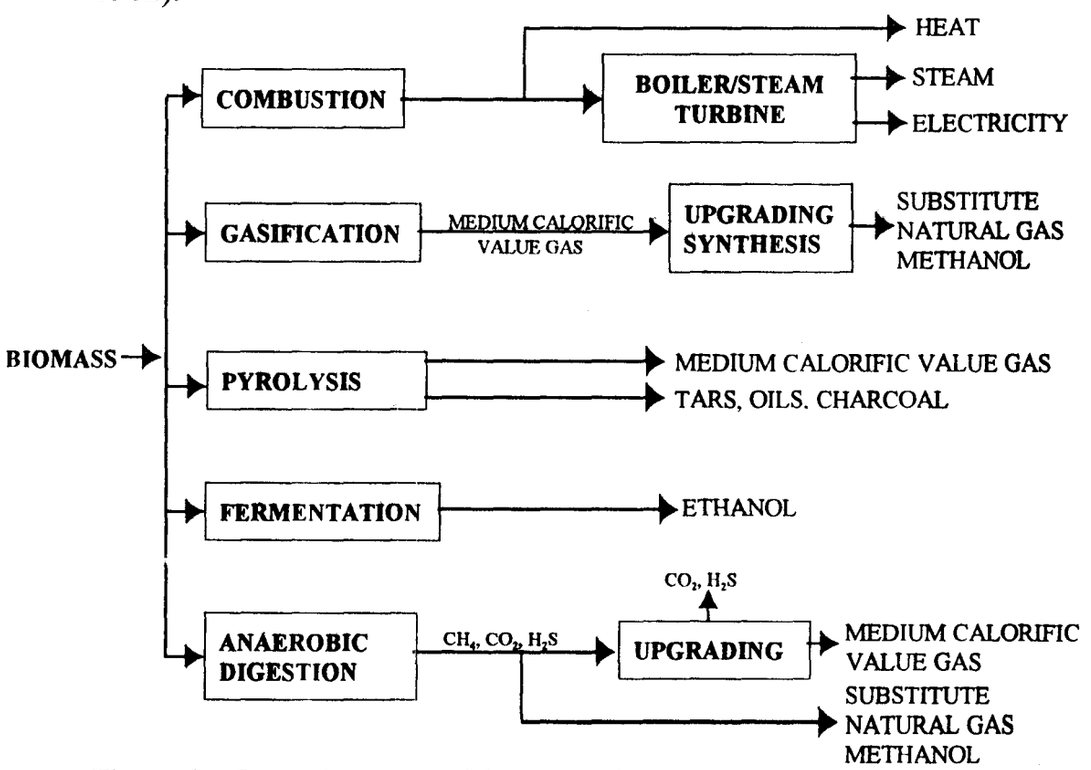


Figure 1:- Several routes in bioconversion process.

GENERAL CONSTITUENTS OF A BIOMASS

1. Polysaccharide.
2. Proteins.
3. Non-protein nitrogenous compounds.
4. Lipids.
5. Volatile fatty acid.
6. Water (if fresh).

Selected properties of representative biomass material are shown below:-

Table 2.0:- Selected properties of representative biomass material (Office of Technology Assessment, 1980 and Solar Energy Research Institute, 1980).

Mass % dry	Wood	Grain	Municipal Solid Waste	Animal wastes (Manure)
Carbon	50-53	45	47.6	35.1
Hydrogen	5.8-7.0	5.8	6	5.3
Nitrogen	0-0.3	2.4	1.2	2.5
Sulfur	0-0.1	0	0.3	0.4
Oxygen	38-44	42.5	32.9	38.7
Volatile Matter	77-87	~80	77	76.5
Fixed Carbon	37641	-	11	0
Ash	0.1-0.2	4	12	23.5
H/C atom ratio	1.4-1.6	1.5	1.5	1.8
GCV, MJ/kg(dry)	19.8-21.0	16.8	19	13.4
Moisture %	25-60	16	20	7-35

2.2.1. Biomass Types

The word biomass is an all encompassing term for recently grown plant and animal materials. The manner in which biomass is utilized is equally broad. Biomass is a renewable bioresource and occurs universally in vast quantities as stated below (King and Cleveland, 1980):

1. Energy Crops: - Wood (sawdust, spent paper-pulping liquor, thinning and logging residues and cotton gin trash), Grain (corn, wheat, rice, barley, and other cereals), Sugar Crops (sugar cane, beet, and sweat sorghum).
2. Farm and Agricultural wastes (straws, corn stover and sugar cane bagasse)
3. Municipal Wastes (sewage sludge, pulp mill sludges and paper residues)
4. Animal wastes (cow dung, poultry droppings)
5. Aquatic biomass (including ocean kelp, and fresh water plants such as algae, water hyacinth, and duckweed)

2.2.2. Advantages of Biomass as A Source of Biogas

1. Biomass is a renewable bioresource.
2. It does not affect atmospheric carbon dioxide concentrations.
3. Biomass fuels are clean burning in that sulfur and nitrogen concentrations are low, and because the hydrogen-to-carbon ratio is generally high.
4. It is cheap and readily available (Probstein and Hicks, 1982).
5. Its use serves in most cases as an environmental pollution control.
6. The by-product from animal waste digestion is suitable for recycling as fertilizer.

7. Small-scale conversion of biomass for domestic or farm application appears most appropriate (King and Cleveland, 1980).

2.2.3. Disadvantages of Biomass as a Source of Biogas

1. The limitations of extensive development of biomass resource are its highland and water requirements, and the competition with food production.
2. From economic stand point, large-scale production of energy from biomass faces competition with the synthetic fuels. In particular, there is currently not a large energy market for ethanol and methanol, the two liquid fuels most readily produced from biomass.
3. Its availability may be periodical and non-commercial quantity wise.
4. The kinetics of reaction of the anaerobic digestion of animal waste are not well known, hence design of digesters using performance equation is not encouraging (Probstein and Hicks, 1982).

2.3. ANIMAL WASTE

Animal wastes are biomass materials in that they are derived either directly or via the food chain, from plants which have been consumed as food (Probstein and Hicks, 1982). They are the undigested parts of food taken by an animal. They are called waste products because they have not been used by the animal for metabolic processes. Animal wastes, or manure, as a source of biomass has the advantage that it is not competitive with other uses for this material (Prostein and Hicks, 1982).

2.3.1 Characteristics of Animal Wastes

Animal wastes are characterised by the constituents of the original food taken by the animal despite the fact that most of the digestible have been digested and the resulting waste deficient in these constituents when compared to the original food (Scott, 1983). Bacteria are generally

present in the animal wastes, and if required conditions are provided, will propagate. Animal wastes (of cattle and poultry) are usually solid under normal conditions while those of pigs are more often than not in slurry form (Scott, 1983).

Animal manures usually contain all the required nutrients. However, the high ammonia concentrations in some animal wastes may lead to ammonia toxicity problems. In this respect, the carbon-to-nitrogen ratio (C/N) is thought to have affect the digestion process (Chen et al, 1980). The rate of carbon consumption is typically about 15 times that for nitrogen. It is found that wastes such as dairy manure with higher than average C/N ratios can be processed at relatively high solid concentrations and require relatively short retention times. Poultry manure, which has high nitrogen content, requires lower solid concentrations and longer residence times. In all cases, the concentration of nitrogen in the solids remaining after decomposition is higher than in the original feedstock. Small-scale conversion on farm appears most appropriate, and could result in animal husbandry operations being self-sufficient in energy. Anaerobic digestion to produce methane is the most applicable technology (Probstein and hicks, 1982).

Table 2.1 below shows the composition of animal wastes.

Material	Hens (2kg)	Pigs (50kg)	Beef cattle 450kg	Dairy cattle 500kg
Total solids (dry wt kg/day)	0.026	0.315	3.48	4.92
Volatile solids (%dry basis)	70	85	80	80

Continuation of Table 2.1

Material	Hens (2kg)	Pigs (50kg)	Beef cattle (450kg)	Dairy cattle (500kg)
Nitrogen (% dry basis)	5	4.5	3.7	5
P_2O_5 (% dry basis)	4	2.7	1.1	2
K_2O (% dry basis)	2	4.3	3	5

Other compounds or elements may be presented in traces due to contaminations. Other constituents likely to be present in minutes quantities are: -

1. Ammonia (Scott, 1983).
2. Urea and Uric acid.
3. Lactic acid.
4. Acetic acid.
5. Moisture.
6. Salts, etc.

2.3.2. Availability of Animal Wastes

Availability of animal wastes could be determined by several factors, the major ones are: -

1. Availability of animals
2. Mode of keeping animals (roaming, grazing or stationed).
3. Accessibility of animal waste sites.

The population of cattle and domestic fowls (poultry) are high in relative to pigs in Nigeria. This is not surprising as the source of animal protein for most Nigerians are beef and chicken. In terms of cost, cow

dung and poultry droppings are relatively cheap when viewed from the facts that they are mostly considered as waste in many circumstances. Although they could also be used as farm manures but the popularity of this practice is fast fading out due to improved performance of chemical fertilizers so much so that about 80% of farmers particularly in Nigeria are now users of chemical fertilizers.

Considering the technological know how involved, biogas production from biomass offers a cheaper production rate when compared with methane derived from petroleum-based resources. The animal waste considered in experimental for methane production are (Scott, 1983): -

1. Domestic fowls (layers, breeder and broilers).
2. Cattle (cow, dairy and beef).
3. Pigs (boars, sows, piglets or litter).

The dung is carefully collected from stables, shelters, and pathways.

2.3.3. Product Yield

Several researches have been carried out on the product yield from animal waste. The product yield of cattle, poultry and pig are given in table 2.2 below: -

Table 2.2: - Methane Yields of Animal Wastes (Probstein and Hicks, 1982)

Animal	Typical experiment yield per kg manure	CH_4 %	CO_2 %	Thermal content MJ/m^3
Cattle	200 - 350 l	57.5	42.5	23
Poultry	550 - 650 l	70.0	30.0	28
Pig	400 - 500 l	65.0	35.0	26

Although the above table shows that the methane yield from pig

waste is second highest, but considering the fact that other factors such as population of animals and physical condition of animal waste militate against its choice, it is therefore obvious that cow dung and poultry droppings are the better choice in Nigeria context.

2.4. BIOCHEMICAL CONVERSION BY ANAEROBIC DIGESTION

Waste containing substantial amounts of fermentable organic components can be treated biologically under anaerobic conditions (Bailey and Ollis, 1986). Anaerobic digestion of organic matter to methane is a widespread process in natural environments (Levett, 1990). Anaerobic digestion is the decomposition of any organic material by the metabolic action of bacteria without the participation of atmospheric oxygen. Methane and carbon dioxide are the main products of the decomposition. The source of the oxygen in the carbon dioxide is the combined oxygen in the organic molecules and in the water (Probstein and Hicks, 1982).

Anaerobic digestion of the cow dung takes place in the digester which is the heart of the process. The purpose of this anaerobic digester is to provide an environment for the bacteria to propagate, to ensure adequate contact between the bacteria and the digestible cow dung, and to hold the mixture for sufficient time for the nearly complete consumption of degradable cow dung. The mixture of dried cow dung, and water, and any added nutrients is called the "substrate". Since the cow dung contains all the required nutrients, there is no need to add any nutrient. Bacteria are generally present in the cow dung, and providing required conditions, will propagate. Those bacteria best able to metabolise the feedstock will, by a process of natural selection, soon dominate. This process of producing a thriving micro-organism population is known as "acclimation". Important variables requiring careful control in acclimating and maintaining a viable

micro-organism population include substrate concentration, temperature and pH, as well as the presence of nutrients and absence of toxicants (Probstein and Hicks, 1982).

2.5. MICROBIOLOGY OF ANAEROBIC DIGESTION

The microbial community involved in anaerobic digestion of cow dung is complex. Methane production is a syntrophic process depending upon the action of several types of anaerobic bacteria. Three interdependent phases of microbial activity are recognised as shown in figure 2 (Levett, 1990). Ideally, each step in the reaction sequence should be conducted in a separate reactor so as to accommodate the specific reaction rates and preferred operating conditions associated with each group of bacteria. In practice, the process is generally carried out in a single reactor vessel, the domestic septic tank being a typical example (Probstein and Hicks, 1982). The three phases involved in the anaerobic digestion of organic matter (cow dung) are shown in figure2 (Probstein and Hicks, 1982).

2.5.1. Phase I - Hydrolysis of Complex Organic Matter

In the first phase, involving fermentative bacteria (e.g, Bacteroides, Clostridium, Eubacterium, Peptococcus and Propioni bacterium), polymers such as proteins, polysaccharides and lipids are hydrolysed to monomers such as amino acids , sugars and fatty acids respectively (Moses and Cape, 1991). The initial stage of hydrolysis is performed by a variety of organisms, chiefly clostridia, which may reach counts of up to 1,000,000,000 cells/ml in the digester contents (Levett, 1990). The monomers formed as a result of the hydrolysis of proteins, polysaccharides and lipids are fermented to a variety of short-chain organic acids (fatty acids), alcohols and esters, together with carbon dioxide and hydrogen.

This second stage or step is known as acidogenesis (Moses and Cape, 1991).

2.5.2. Phase II - Acetogenesis (Production of Acetate)

In the second phase, hydrogen producing acetogenic bacteria (Peptococcus, Propioni bacterium, Syntrophobacter and Syntrophomonas) convert the products of the first phase into acetic acid, hydrogen and carbon dioxide. Desulphovibrio changes lactate and hydrogen to acetate and sulphide. The second phase or third stage (acetification) is the result of metabolism of fatty acids by H_2- producing acetogenic bacteria. The ability of the acetogens to release hydrogen requires a very low partial pressure of hydrogen (10^{-6} atm) in the medium. This is dependent on the removal of hydrogen by the hydrogenotrophic methanogens and by Desulfovibrio. This is known as interspecies hydrogen transfer (Moses and Cape, 1991). Some hydrogen is converted to acetate by H_2-consuming acetogens (homoacetogens), such as Acetobacterium woodii, Acetogenium kivui, Clostridium thermautotrophicum and C. formicaceticum (Levett, 1990).

2.5.3. Phase III - Methanogenesis (Production of Methane)

In the third phase, two distinct groups of bacteria are involved. The acetoclastic methanogens (Methanosarcina, Methanospirillum and Methanothrix) produce methane and carbon dioxide from acetate and the hydrogenotrophic methanogens (Methanobacterium and Methanobrevibacterium) produce methane from hydrogen and carbon dioxide (Moses and Cape, 1991). About 70% of the methane generated by the anaerobic digestion of organic matter is produced from acetate by the acetoclastic methanogen, the remainder is derived from H_2 and CO_2 by the action of hydrogenotrophic methanogens (Levett, 1990).

The interactions between the groups of bacteria are only partially understood but the information available is useful in operating anaerobic digesters to its best advantage. The hydrolytic fermenters (bacteria) and acetogens (hydrogen producing acetogenic bacteria) can grow much faster (doubling times about 30 minutes and 1-4hrs respectively) than the hydrogenotophic methanogens (doubling times about 8-10hrs). The acetoclastic methanogens are very slow growing (doubling times 2-3days) and thus a high retention time is necessary for maximum methane production. The sudden changes in the medium composition can cause surges of hydrogen production, exceeding the capacity of the methanogens to remove it. The partial pressure of hydrogen rises, leading to a change in the metabolic pattern of the acetogens which produce lactate, propionate, butyrate, valerate and caproate instead of acetate, the amount of hydrogen produced falls, but the products cannot be utilised by the methanogens. This shows that sudden changes in load must be avoided and that fermenter function can usefully be monitored by measuring hydrogen concentration, pH and the types of organic acid present (Moses and Cape, 1991). Successive stages in anaerobic waste digestion are shown in figure 2 below.

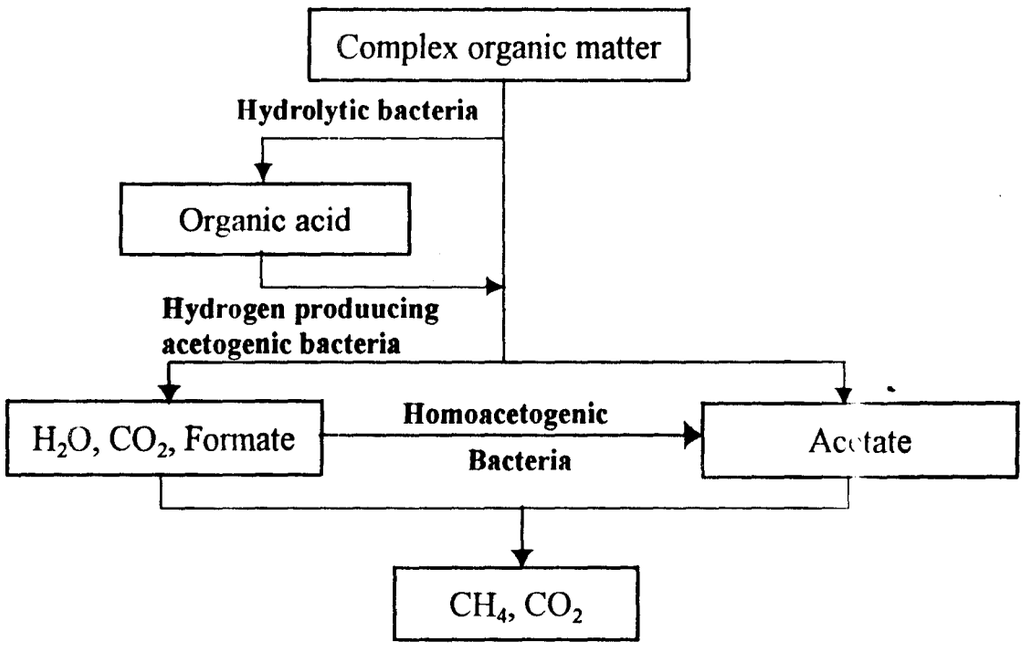


Figure 2:- Successive stages in anaerobic digestion (Probstein and Hicks, 1982).

2.6. PRODUCTS OF ANAEROBIC DIGESTION OF COW DUNG

When organic matter (cow dung) undergoes anaerobic fermentation, the principal off-gases formed by micro-organisms are:-

2.6.1. Methane

The methane generated by anaerobic waste digestion ("biogas") can be used for cooking, heating, generation of steam or electricity or compressed for use as a vehicle fuel. If it is to be transported through pipe-lines hydrogen sulphide, which is corrosive, must be removed. If it is to be compressed it is usually necessary to remove carbon dioxide and water. The low liquefaction temperature (-70°c) means that liquefaction is usually uneconomic on a small scale. Methane is very inert. Its boiling and melting points are -162°c and -183°c respectively. It does not react at ordinary temperatures and pressures with fuming sulphuric acid, concentrated nitric acid, alkalis, bromine water, potassium permanganate

solution, or phosphorus pentoxide (Moses and Cape, 1991).

2.6.2. Carbon dioxide

Carbon dioxide in the gas is objectionable because it lowers the heating value of the gas. Hence, there is the need to refine the biogas by removing the carbon dioxide present. It reacts with hydroxides forming carbonates and bicarbonates. Thus solutions of alkalis absorb carbon dioxide readily and are used either to remove it from a mixture or to reveal how much of it is present by the contraction which takes place on shaking (Austin, 1984). The carbon dioxide is absorbed by concentrated potassium hydroxide solution forming the soluble carbonate:

$$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

and subsequently the hydrogen carbonate:

$$K_2CO_3 + H_2O + CO_2 \rightleftharpoons 2KHCO_3$$

2.6.3. Hydrogen sulfide

Traces of hydrogen sulfide are present in the gas. Hydrogen sulfide is objectionable in biogas because it causes corrosion and also form air-polluting compounds when burned. The odour of hydrogen sulfide is very annoying to household customers. Hence, there is the need for its removal from the biogas (Austin, 1984). The hydrogen sulfide is absorbed by acidified potassium permanganate solution. The purple solution of the acidified potassium permanganate changes to a colourless solution with pale yellow precipitate of sulphur according to the reaction below:-

$$5H_2S+2KMnO_4+3H_2SO_4 \rightarrow K_2SO_4+2MnSO_4+8H_2O+5S\downarrow$$

Hydrogen sulfide on combustion gives:-

$$2H_2S + 3O_2 \longrightarrow 2SO_2 + 2H_2O$$

2.7. INHIBITORY CONDITIONS OF ANAEROBIC DIGESTION

Important variables requiring careful control in acclimating and maintaining a viable micro-organism population include:-

2.7.1. Substrate Concentration Effect

The concentration of biomass in the substrate is limited by the toxicity of the components present. The substrate has to be relatively dilute, equivalent to a solid concentration of 7 - 12 percent of the original biomass material and thus a considerable supply of water is required to provide the necessary dilution. Acetate concentrations above 2g/l and ammonia concentrations in excess 3g/l are toxic and will decrease or arrest the methane production rate (Chen et al, 1980). Oxygen is highly toxic to methanogenic bacteria, while trace metals and antibiotics may be trouble some (Probstein and Hicks, 1982). When substrate overloading occurs the digester pH falls as volatile fatty acids accumulate in excess, and both acetogenesis and methanogenesis are inhibited. This imbalance can be corrected by stopping the flow of substrate into the digester until the flora has equilibrated and methanogenesis recommences. Inhibition due to overloading is costly both in terms of labour and lost methane production (Levett, 1990)

2.7.2. Temperature Effect

The digestion process is only mildly exothermic, and heat may have to be supplied to the substrate to achieve the optimum operating temperature. Apart from their decompositional activity, bacteria can be grouped according to the temperature at which they thrive. Temperature ranges are 0°c to 20°c for psychophilic bacteria, 20°c to 45°c for

mesophilic bacteria, and 45°c to 65°c for thermophilic bacteria (Probstein and Hicks, 1982). While the temperature range is fairly broad for each group, an established population requires much narrower confines of temperature for optimum performance. The temperature of thermophilic processes should be controlled within 5°c, and to within 2°c for mesophilic processes. The selection of an operating temperature not only determines the group of bacteria that will dominate, but also affects the degree of conversion, residence time, and cost.

Thermophilic processes generally have the highest decomposition rates and hence have reduced residence times (Probstein and Hicks, 1982). The associated reduction in capital costs must, however, be weighed against the increased operating costs incurred in heating the substrate. While mesophilic decomposition rates are lower, there is evidence that these bacteria achieve a greater degree of conversion with some feedstocks. Decomposition rates at psychophilic temperatures are too slow for practical application. Depending on the biomass, residence times may range from 5 to 10 days for thermophilic processes, 10 to 15 days or longer for mesophilic process. Small-or-farm-scale processes will probably operate under mesophilic conditions, while with larger-scale processes it may prove economical to incorporate more extensive heat recovery systems for operation at thermophilic temperatures (Probstein and Hicks, 1982).

2.7.3. pH Effect

The pH of the substrate should be maintained between 6.6 and 7.6, and preferably between 7.0 and 7.2 (Chen et al, 1980). Within the digester, acidogenesis occurs at an optimum rate in the range pH4.0-6.5 while methanogenesis occurs at optimum rate in the pH6-8. Methanogens

are susceptible to inhibition by a variety of organic pollutants (including CCl_4, $CHCl_3$, CH_2Cl_2, CN) and heavy-metal ions, at concentrations as low as 1 parts per million(ppm). Formaldehyde, SO_2 and H_2S are also toxic at higher concentrations (50-400ppm). In addition, ammonia may be inhibitory unless time is allowed for the digester flora to adapt to higher ammonia levels (Levett, 1990).

Although it is necessary to maintain a mildly acidic regime there is usually a tolerance around the neutral value of pH scale. A highly acidic medium will tend to hydrolyse the cellulose and hemicellulose in substrate into hexosans (glucose) and pentosans (xylose), while a highly basic medium will have an accelerated hydrolysis of cellulose into glucose and xylose (Probstein and Hicks, 1982). In order to maintain a satisfactory environment for both acid formers and the methane bacteria, digester is operated at a pH7 (Bailey and Ollis, 1986).

2.7.4. Mixing Effect

Mixing is used to enhance contact between the bacteria and substrate. It has, however, been argued that while mixing may increase conversion rate, it is not energy efficient (Probstein and Hick, 1982). Mixing is also provided to prevent high local concentrations of acids from developing (Bailey and Ollis, 1986).

Without mixing, the rate of methane production is reduced. This as a result of overcrowding of micro-organisms. It will also make slurry region at which digestion has started to be highly digested without in-coming new substrate for the acting bacteria. The bacteria activities will also be reduced due to poor escape of gaseous products (Probstein and Hicks, 1982).

2.8. REFINEMENT OF BIOGAS

Biogas produced from cow dung contains components that may be categorised as desirable and undesirable primarily from a process viewpoint. A desirable component should be present in the end product and an undesirable one should be absent. The main desirable component in biogas is methane while carbon dioxide and hydrogen sulfide are undesirable components. When the biogas is freed from such undesirable components to an extent, it is said to undergo refinement (ref: - Kohl and Riesenfeld, 1974).

2.8.1. Need for Refinement of Biogas

The necessity of refine biogas of its undesirable components is dictated by:-

1. Their potential danger to human, animal and plant life.
2. Loss due to corrosion mainy from acidic oxides in the atmosphere.
3. The need to improve the heating value of the gas (Austin, 1984).

2.8.2. Acid Gas Removal

Of the two acid gases it is the hydrogen sulfide which presents the most difficult removal problem since it cannot be vented to the atmosphere and must be collected, with sulphur recovery generally the end step. In the particular case where the gas containing the hydrogen sulfide is to be used as a fuel gas, an alternative procedure would be to burn the gas, converting the hydrogen sulfide to sulfur dioxide, and then to remove the sulfur dioxide by stack gas scrubbing procedure.

Acid gas removal processes generally fall into one of the following categories:-

2.8.2.1. Absorption into a liquid

This the most important gas purification technique. It

involves the transfer of a substance from the gaseous to the liquid phase through the phase boundary. The absorbed material may dissolve physically in the liquid or react chemically with it (Probstein and Hicks, 1982). This process was used to refine the biogas by absorbing carbon dioxide into concentrated potassium hydroxide solution and hydrogen sulfide into acidified potassium permanganate solution before collecting the gas over water. Desorption, or stripping, represents a special case of the same operation in which the material moves from the liquid to the gaseous phase (Probstein and Hicks, 1982). This is the most common procedure or process used to remove carbon dioxide and hydrogen sulfide from a mixture of gases.

2.8.2.2. Absorption into a solid

This is a procedure of limited use and it involves the transfer of a substance from the gaseous to the solid phase. The absorbed material diffuses throughout the absorbent and may react chemically with it (ref:- Probstein and Hicks, 1982).

2.8.2.3. Adsorption on a solid

In this procedure the impurities are removed from the gas stream by concentration on the surface of a solid material. The quantity of material adsorbed is proportional to the surface area so that the adsorbents generally are granular solids with a large surface area per unit mass (Probstein and Hicks, 1982).

2.8.2.4. Chemical conversion to another compound

Here the impure gaseous contaminant is converted to a compound which is not objectionable or which can be subsequently removed with greater ease than the original compound. This is most

often carried out in the presence of a solid catalyst (Probstein and Hicks, 1982).

2.8.3. Factors Controlling the Choice of Acid Gas Removal Process

Factors controlling the choice of acid gas removal process are:-

1. The gas flow rate.
2. The concentration of acid gases.
3. The need to remove carbon dioxide as well as hydrogen sulfide.
4. The presence of other impurities.
5. The gas pressure.
6. The solvent selectivity.
7. The energy requirement (Probstein and Hicks, 1982).

2.8.4. Bulk Acid Gas Removal by Liquid Absorption

For large gas volumes containing high concentrations of carbon dioxide mixed with hydrogen sulfide, a likely but by no means unique sequence of treatment is shown in figure 3. Most of the carbon dioxide and hydrogen sulfide are removed in a regenerable liquid absorbent which is continuously circulated.

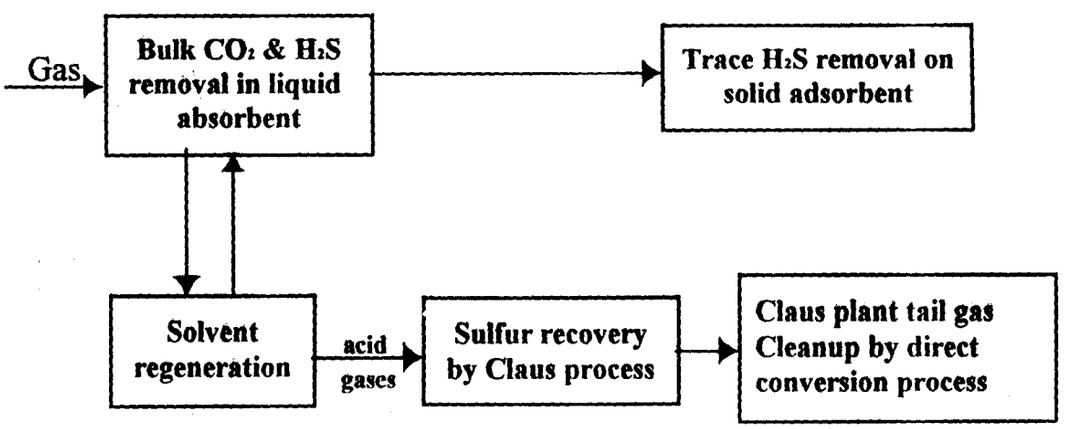


Figure3:-Possible treatment sequence for removal and recovery of acid gases from a high volume gas stream (Probstein and Hicks, 1982).

Final trace of hydrogen sulfide which, for example, might poison down stream catalyst are removed in a solid adsorbent. The solid adsorbent is regenerated intermittently or discarded. Concentrated gas from the regeneration of the liquid absorbent is treated for bulk recovery of elemental sulfur by the Claus process. Most currently practised large-scale bulk-acid-gas removal procedure are indirect ones in which the acid gases are selectively dissolved in a liquid, passed counter current to the gas. In a separate vessel the absorbing liquid is stripped of its gas content and thereby regenerated. It is then recycled back to the absorber. Direct conversion processes remove hydrogen sulfide by chemically converting it to sulfur. Indirect conversion processes simply remove the hydrogen sulfide molecules from the gas. The Claus process is the principal method by which sulfur is recovered from separated hydrogen sulfide. It is not a gas purification process in the usual sense, since its purpose is to recover sulfur from a gas stream which itself is a porduct of a previous gas purification process.

The Claus process is usually carried out in two stages, a thermal stage where part of the hydrogen sulfide is burned to elemental sulfur and sulfur dioxide, and a catalyst stage where the remaining hydrogen sulfide is reacted with sulfur dioxide in the presence of an aluminium oxide catalyst to form additional sulfur. The stoichiometry for the formation of the element alsulfur and sulfur dioxide in the thermal stage can be represented by the exothermic reactions:-

$$2H_2S + 3O_2 \longrightarrow 2H_2O + 2SO_2 \qquad \Delta H^\circ \approx -520KJ/mol$$

$$2H_2S + SO_2 \rightleftharpoons 2H_2O + 3S_{(g)} \qquad \Delta H^\circ \approx -88KJ/mol$$

The heats of reaction are only approximate, since the exact values will depend on the type and state of sulfur that is formed. The elemental sulfur which is formed is condensed out by cooling effluent gases from the furnace by heat recovery (Kohl and Riesenfeld, 1974).

CHAPTER THREE

3.0. MATERIALS AND METHODS

3.1. MATERIALS

3.1.1. Chemicals

1. Concentrated Hydrochloric acid solution (50%).
2. Concentrated Sodium hydroxide solution (50%).
3. Concentrated Potassium hydroxide solution (45%, 50%, 55%,).
4. Potassium tetraoxomanganate (vii) solution (45%, 50%, 55%).

3.1.2. Equipment

1. 500ml volumetric flask.
2. 500ml beaker.
3. 1000ml measuring cylinder.
4. 1000ml conical flasks (3).
5. 2 litres capacity gas collection bags (5).
6. Delivery tubes (3).
7. Rubber cork stopper (4).
8. pH meter.
9. Oven.
10. Muffle furnace.
11. Top loading balance.
12. Plastic fermenter (10 litres).
13. Stainless steel evaporating dish.
14. Ceramic mortar and pestle.
15. Thermometer.
16. Desicator.

3.2. METHODS

3.2.1. Experimental Method

3.2.1.1. Preparation of reactor

Known total solid concentration of 560 grams per 7 litres of solution was prepared using the sieved cow dung. The 10 litres laboratory-sized batch digester having working capacity of 7.5 litres was filled to the maximum working capacity after the slurry was warmed using steam bath to remove air bubbles with constant stirring.

pH was maintained at 7±0.5 before the on set of the gas production (constant pH) by addition of concentrated sodium hydroxide solution or concentrated hydrochloric acid solution. Delivery tubes were connected from the digester to three, 100ml conical flasks containing 100ml concentrated potassium hydroxide solution for CO_2 absorption and potassium tetraoxomanganate (vii) solution for absorbing H_2S. Using different concentrations of 45%, 50%, and 55% for the liquid absorbents, three samples of biogas were collected in gas collection bags connected to the flask containing water.

3.2.2. Analytical Method

3.2.2.1. Determination of total solids

These includes non-filterable residue i.e. the portion of the total residue retained by a filter and the filterable residue i.e. the portion of the total residue that passes through the filter.

Procedure:

The 100ml capacity evaporating dish was washed clean using detergent solution, brushed, rinsed and ignited for one hour at

550°c±10°c in a muffle furnace. It was allowed to cool to room temperature and then transferred into a desicator to stand there for one hour and thereafter, weighed using top loading balance and left there until ready for use.

The wet animal waste was sun dried, pulverized using mortar and pestle and sieved to have a maximum particle size of 1mm discarding the dried grass. The 25g sieved sample was then transferred to the pre-weighed evaporating dish and weigh altogether. It was then dried at 105°c in the oven for two hours. The dish with its content was cooled in the desicator to room temperature and weighed using top loading balance. This cycle of drying was repeated until a constant weight was obtained.

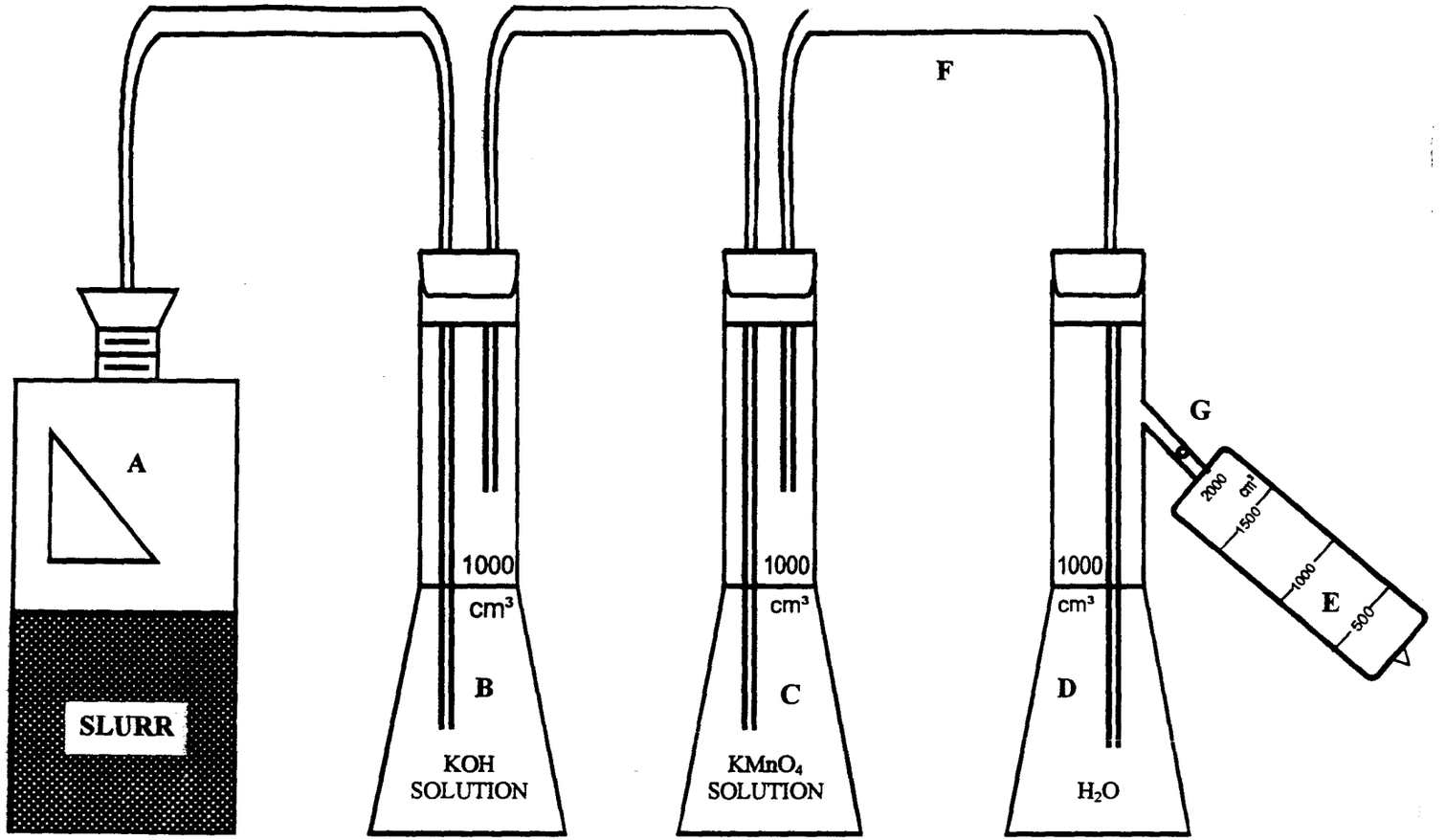
3.2.2.2. Determination of volatile solids

Procedure:

The dried sample was transferred to the muffle furnace and ignited at 500°c±5°c for two hours. The loss in weight was calculated and these represent the volatile solids.

3.2.2.3. Determination of Biogas Composition

Each of the three samples of biogas collected in the gas collection was passed through gas chromatography to determine the percentage mole composition of the biogas in the bag.



A - DIGESTER CONTAINING SLURRY
B - FLASK CONTAINING KOH
C - FLASK CONTAINING $KMnO_4$
D - FLASK CONTAINING H_2O
E - BAG FOR COLLECTION OF PURIFIED GAS
F - DELIVERY TUBE
G - RUBBER CLIP

Figure 4: LABORATORY SCALE EXPERIMENTAL SET UP FOR REFINEMENT OF BIOGAS

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION OF RESULTS

4.1 RESULTS FOR COW DUNG ANALYSIS

Table 4.1: - Values of Total solids, Volatile solids and Moisture content in the cow dung sample

Cow dung analysis	**g**	**%**
Total solids	5.18	20.72
Volatile solids (dry basis)	4.57	88.22
Moisture content	19.82	79.28

4.2 RESULTS FOR BIOGAS ANALYSIS

Table 4.2:- Percentage composition before and after refinement of biogas.

Constituents of biogas mixture	**Percentage composition before refinement (mol % dry)**	**Percentage composition after refinement 45 % concentration absorbents (mol % dry)**	**Percentage composition after refinement 50 % concentration absorbents (mol % dry)**	**Percentage composition after refinement 55 % concentration absorbents (mol % dry)**
CH_4	54.09	54.09	54.09	54.09
CO_2	40.20	4.07	4.01	4.03
O_2	0.05	0.02	0.02	0.02
NH_3	0.98	0.05	0.05	0.06
H_2S	0.80	0.04	0.01	0.016
H_2	0.50	0.50	0.50	0.50
N_2	3.29	3.12	2.54	2.67
Others	0.09	38.11	38.78	38.614

4.3 DISCUSSION OF RESULTS

Analysis was carried out on 25 g of the raw cow dung sample to determine the amount of total solids, volatile solids and moisture content therein. A known concentration of cow dung was digested anaerobically at room temperature in a laboratory sized digester. The resulting biogas produced was passed through gas chromatograph to determine the percentage composition (mol % dry) before and after refinement. The biogas was refined by gas – liquid absorption method of acid gas removal.

For the cow dung analysis, the values of total solids, volatile solids and moisture content in the cow dung sample are 5.18 g, 4.57 g and 19.82 g respectively as shown in table 4.1. The results obtained for biogas mixture analysis before refinement are 54.09 mole % dry CH_4, 40.20 mole % dry CO_2 and 0.80 mole % dry H_2S which conform with the literature values of 50 – 65 mole % dry CH_4, 35 – 50 mole % dry CO_2 and 0.1 – 1.0 mole % dry H_2S (Probstein and Hicks, 1982). The biogas mixture analysis after refinement shows that for 45 % concentration of KOH and $KMnO_4$, it contains 54.09 mole % dry CH_4, 4.07 mole % dry CO_2 and 0.04 mole % dry H_2S. For 50 % concentration KOH and $KMnO_4$, it contains 54.09 mole % dry CH_4, 4.01 mole % dry CO_2 and 0.01 mole % dry H_2S. For 55 % concentration of KOH and $KMnO_4$, it contains 54.09 mole % dry CH_4, 4.03 mole % dry CO_2 and 0.016 mole % dry H_2S.

From these results, for 45 % concentration of KOH, 89.88 % of CO_2 is removed, for 50 % concentration of KOH, 90.02 % of CO_2 is removed and for 55 % concentration of KOH, 89.98 % of CO_2 is removed. The reasons for variation in the values of CO_2 removed are the solubility of CO_2 in 45 %, 50 % and 55 % concentrations of KOH respectively, the hydrodynamic regime in the digester, equilibrium and process rate during chemisorption (Kohl and Riesenfeld, 1974). Within the time limit for removing and replacing the solvents, for 45 % concentration of KOH, the CO_2 absorbed favours the formation of potassium carbonate and water, and this water aids in diluting the solvent for 89.88 % CO_2 to be removed at equilibrium. For 50 % concentration of KOH, the CO_2 absorbed favours the formation of potassium carbonate and water. In this case, more water was formed which helps in diluting the solvent for 90.02 % CO_2 to be removed at equilibrium. But for 55 % concentration of KOH, the CO_2 absorbed favours the

formation of potassium hydrogen carbonate, and as a result there is little or no water in diluting the solvent. Hence, the percentage of CO_2 removed drops to 89.98 % at equilibrium (Kohl and Riesenfeld, 1974).

Therefore, it can be deduced that 50 % concentration of KOH is the best concentration at which high percentage of CO_2 could be removed.

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The cow dung sample contains 5.18 g of total solids, 4.57 g of volatile solids and 19.82 g of moisture content. The results of the biogas mixture analysis show that for 45 % concentration of KOH, 89.88 % of CO_2 is removed, for 50 % concentration of KOH, 90.02 % of CO_2 is removed, and for 55 % concentration of KOH, 89.98 % of CO_2 is removed.

Therefore, it is concluded that 50 % concentration of KOH is the best concentration at which high percentage of CO_2 could be removed.

5.2 RECOMMENDATIONS

1. To achieve better results in future, a well designed and constructed reactor and gas purification arrangement that must exclude the access of oxygen and provide a means of collecting and delivering the biogas should be installed.
2. The technological operating conditions (concentration of substrate, temperature of substrate, pH of substrate, hydrogen ion concentration, C: N ratio, etc) inside the reactor and of the gas purification arrangement (that is, the presence of other impurities apart from CO_2 and H_2S, gas pressure, solvent selectivity, energy requirements, etc) should b selected in such away as to obtain optimum, performance and reduce costs.
3. Hot potassium carbonate process of CO_2 and H_2S removal is recommended because it is very effective in removing large quantities of CO_2. Although it can remove CO_2 down to 0.01 % by volume in the gas being purified it is generally more economical at purity levels of 1 % or greater. By absorbing CO_2 under pressure in hot solution close to its boiling point and regenerating it at the same temperature but at near atmospheric pressure, steam consumption is reduced and heat exchangers are eliminated.

APPENDIX

COW DUNG ANALYSIS

Parameters used:-

★ Weight of dish (A) = 92.04g

★ Weight of di sh + sample before drying (B) = 117.04g

★ Weight of dish + sample after drying (C) = 97.22g

★ Weight of dish + sample after ashing (D) = 92.65g

TOTAL SOLIDS CALCULATIONS

Total solids = (C - A)g

= (97.22 - 92.04)g

∴ Total solids = 5.18g

$$\% \text{ Total solids} = \frac{(C - A) * 100}{(B - A)}$$

$$= \frac{(97.22 - 92.04) * 100}{(117.04 - 92.04)}$$

$$= \frac{5.18 * 100}{25.00}$$

∴ Total solids = 20.72%

VOLATILE SOLIDS CALCULATIONS

Volatile solids = (C - D)g

= (97.22 - 92.65)g

∴ Volatile solids = 4.57g

$$\% \text{ Volatile solids} = \frac{(C - D)}{(C - A)} * 100$$

$$= \frac{(97.22 - 92.65)}{(97.22 - 92.04)} * 100$$

$$= \frac{4.57}{5.18} * 100$$

$$\therefore \text{ Volatile solids} = 88.22\%$$

MOISTURE CONTENT CALCULATIONS

$$\text{Moisture content} = (B - C)g$$

$$= (117.04 - 97.22)g$$

$$\therefore \text{ Moisture content} = 19.82g$$

$$\%\text{Moisture content} = \frac{(B - C)}{(B - A)} * 100$$

$$= \frac{(117.04 - 97.22)}{(117.04 - 92.04)} * 100$$

$$= \frac{19.82}{25.00} * 100$$

$$\therefore \% \text{ Moisture content} = 79.28\%$$

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