GAS CHROMATOGRAPH PLOTS ON DIVERSE COW DUNG ANALYSIS

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ABSTRACT: *Biogas is a gaseous fuel obtained from biomass by the process of anaerobic digestion (fermentation) of garbage, human excreta, organic waste, agricultural waste, animal waste from butchery, vegetable and industrial waste. This research was conducted to produce bio-energy from variety of cow dung. The fresh cow dung which was free from anti-biotics weighing 2 Kg each was obtained from EPZ (export processing zone) Sebore cattle farm, Mayo-belwa from Holstein Friesian, Jersey, and Simmental and White Fulani cows, which were fed with equal amount of concentrates for some weeks. The cow dung was mixed with water in a ratio of 1:1 by volume to form slurry and the mixture loaded into a digester to ferment with HRT (Hydraulic Retention Time) of 9-14 days and mesophilic temperature of 25-35^oC. Human excreta and urine were added into the digester to increase mechanization, micro-organism, microbial and pathogenic activities and also to reduce the retention period. The biogas obtained after 9-14 days was collected and analyzed in a Gas Chromatograph and Integrator. The results showed the percentages and Gas Chromatograph plots for the cow dung of the four (4) selected varieties of cows studied. The results indicated thus: Holstein Friesian cow has methane (84.916% CH_4) and 196.199 cal/m^3 of energy, Jersey cow (69.233% CH_4) and 159.963 cal/m^3 of energy, Simmental cow has (60.459% CH_4) and 149.235 cal/m^3 of energy and White Fulani cow has (85.331% CH_4) with 197.157 cal/m^3 of energy respectively. The results indicate that the White Fulani cow has the higher quantity of methane than the other breeds of cows.*

KEYWORDS: Bio-energy; White Fulani; Holstein; Jersey; Simmental; Cow Dung.

INTRODUCTION

Biogas is a bio-fuel and bio-energy source and a secondary renewable energy source. It is cheap and obtained by anaerobic fementation. Methane which is the main component in the biogas is used as: fuel for kilns, furnaces, domestic fuel for burners used in kitchen, fuel for internal combustion engines to drive pump sets, producing electrical energy from IC Engine Driven Generator sets and for producing mechanical energy by IC engine operated by biogas (Rao and Parulekar, 2007).

Biogas plants convert urban refuse (excreta) and waste (garbage) into useful energy (biogas). In the rural areas, cow dung, agricultural wastes are converted to bio-energy source (biogas). This is possible in Nigeria where agricultural, human, domestic and industrial wastes are in large supply. Proper use and application of these abundant wastes can be used to generate biogas for cooking, lighting and power generation by operating a dual fuel engine. It can replace up to 75% of the diesel (Jawurek et al, 1987and Kumar, 2006).

Biogas as an energy source can be converted to benefit Nigeria domestically and to power our industries and small scale enterprises. This is possible in Nigeria where vegetable waste, agricultural, human, domestic and industrial wastes are in large supply. This research was carried out with the purpose of discovering which breed of cows is most effective for biogas generation, particularly in the West-African sub-region. Past research efforts were largely on the biogas content from cows, but this research is interested in knowing percentages from various and specific varieties of cows. This is to assist the government, individuals and the private sector to concentrate in farming the breed that has the highest content biogas and for meat and milk respectively. In addition, this research narrowed and concentrated on biogas (CH_4) that is available in the local White Fulani breed, which is the predominant breed of cow in Nigeria and the West-African sub-region. The work is intended to boost current research materials in biogas production area and widen academic interest. Proper use and application of the abundant wastes (cow dung) in Nigeria can be used to generate biogas for cooking, lighting and power generation by operating a dual fuel engine. This and other immeasurable uses and benefits developing countries stand to drive from biogas that makes it absolutely necessary to look into this subject.

Methane gas content has been found to vary with feed material and also during a day. And when cattle feed is used in the slurry, the methane gas produced is about 55 to 60% along with 40-45% of carbon dioxide and some quantity of hydrogen sulfide. If human excreta are used, the percentage of methane gas can be about 65%. (Dhillon; 2009, Khemani; 2009 and Habig, 1985).

Table I: Biogas composition of different wastes

Components	Household Waste	Waste Water Treatment Sludge	Agricultural Waste	Waste of Agri-Food Industrial
CH_4 % vol	50-60	60-75	60-75	68
CO_2 % vol	38-34	33-19	33-19	26
N_2 % vol	5-0	1-0	1-0	-
O_2 % vol	1-0	< 0,5	< 0,5	-
H_2O % vol	6 (à 40 ° C)	6 (à 40 ° C)	6 (à 40 ° C)	6 (à 40 ° C)
Total % vol	100	100	100	100
H_2S mg/m^3	100 - 900	1000 – 4000	3000 – 10 000	400
NH_3 mg/m^3	-	-	50 – 100	-
Aromatic mg/m^3	0 - 200	-	-	-
Organochlorinated or organofluorated mg/m^3	100-800	-	-	

Source: The Biogas, 2010

Nigeria is tremendously blessed with a variety of energy resources (both conventional and non-conventional). The reserves for animal waste alone which is a viable source for biogas production as at 2005 was estimated to be 61.00 million tonnes/yr and crop residue was put at 83.00 million tonnes/yr. However, 50MW and 400MW of electricity is targeted to be generated from biomass by 2015 and 2025 respectively (Esan, 2008).

There is an on going life cycle as plants and animals die. Plants and animals die and are recycled to keep and sustain life on the planet. In the presence of oxygen, organic material "composts" (undergoes aerobic decomposition) and when decomposition occurs in the absence of oxygen (anaerobic conditions), methane gas is produced, and the liquid remaining is rich in nitrogen and other nutrients. Biogas is a renewable, alternative and sustainable form of energy. Not only does biogas technology help to produce an alternative energy source, but it also helps in maintaining the environment and improving health conditions (Bio Applications Initiative, 2008; and Village Earth, 2010).

The energy in plant vegetation, animals, industrial and domestic waste matter can be released in terms of a useful bio-energy when fermented anaerobically, that is, in the absence of oxygen. The biogas formed after the decomposition of organic wastes is channeled or transported to homes for use for cooking, running engines, electrical power generation and heating, with virtually little or no pollution at all. This gas is now used large scale in many countries. Biogas production and use dates back to 2,000 years and is a mixture of methane, carbodioxide and traces of hydrogen sulpide. Marco Polo mentioned the use of covered sewage tanks. It probably goes back to 2,000-3,000 years ago in ancient Chinese literature (Dekker and Lewis; 1983, Biogas Plants; 2010 and Nijaguna, 2002).

Chemical Processes

The processes are mainly by anaerobic digestion. Digestion refers to the various reactions and interactions that take place among the methanogens, non-methanogens and substrates that are being fed into the digester as inputs. Biogas Chemistry (2010) observed that digestion is a complex physio-chemical and biological process involving different factors and stages of change. This process of digestion (methanization), the breaking down of inputs that are complex organic materials is achieved through three stages, namely hydrolysis, acidification and methanization as described below.

Stage 1: Hydrolysis: The waste materials of plant and animal origins consist mainly of carbohydrates, lipids, proteins and inorganic materials. Large molecular complex substances are solubilized into simpler ones with the help of extracellular enzyme released by the bacteria. This stage is also known as polymer breakdown stage. For example, the cellulose consisting of polymerized glucose is broken down to dimeric, and then to monomeric sugar molecules (glucose) by cellulolytic bacteria.

Stage 2: Acidification: The monomer such as glucose which is produced in Stage 1 is fermented under anaerobic condition into various acids with the help of enzymes produced by the acid forming bacteria. At this stage, the acid-forming bacteria break down molecules of six atoms of carbon (glucose) into molecules of less atoms of carbon (acids) which are in a more reduced state than glucose. The principal acids produced in this process are acetic acid, propionic acid, butyric acid and ethanol (Biogas Chemistry, 2010).

Stage 3: Methanization: The principal acids produced in Stage 2 are processed by methanogenic bacteria to produce methane. The reaction that takes place in the process of methane production is called Methanization and is expressed by the following equations.

$$CH_3COOH \rightarrow CH_4 + CO_2$$

(Acetic acid) (Methane) (Carbon dioxide)

$$4CH_3CH_2OH + 2CO_2 \rightarrow 2CH_4 + 4CH_3COOH$$

(Ethanol) (Carbon dioxide) (Methane) (Acetic acid)

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

(Carbon dioxide) (Hydrogen) (Methane) (Water)

The above equations show that many products, by-products and intermediate products are produced in the process of digestion of inputs in an anaerobic condition before the final product (methane) is produced. Obviously, there are many facilitating and inhibiting factors that play their role in the process.

If the fermentation is done in the absence of air, the gas produced may contain the concentration of methane (CH_4) as high as 70 to 75 percent; the remaining gas is mostly carbon dioxide ($C0_2$), hydrogen (H), Hydrogen Sulfide, and traces of nitrogen compounds such as Ammonia (NH_3). When animal, plant vegetation and domestic wastes are allowed time, they are acted upon by anaerobic bacterial to produce a gas which is commonly referred to as biogas. This natural gas or "marsh gas" can be used as a rich source of fuel and power generation (Biogas Plants, 2010).

MATERIALS AND METHOD

Samples of cow dung (2kg each) were obtained from the Jersey, Holstein Friesian, White Fulani and Simmental cows. The cows were all fed with di-calcium, premix, Soya meal, wheat offal, cotton seed, molasses and cotton husk in equal proportion and the dung samples were collected at the same time from each cow. The cows were monitored for two weeks and ensured were in good health conditions and were not treated with antibiotics within the weeks prior to samples gathering. The reason is that the presence of antibiotics in the mixture can affect biogas generation and destroy micro-organism and pathogens that aid biogas production. The fresh cow dung was weighed and mixed with water to form slurry (water and cow dung) in a ratio of 1:1 by volume.

Fresh human excreta, grinded water hyacinth and urine were added to the mixture to hasten the generation of biogas and also served as starter. Also, the generation of biogas is enhanced by the presence of metal ions in the biomass (Geeta et al, 1990 and Obayomi, 2008).

The 263-50 Gas Chromatograph, D2500 Chromato-Integrator and Gas Sampler were used for the collection and analysis of the biogas samples collected from the bio-reactor. Temperature of the substrate is a major factor in the production of biogas. With a mesophilic flora, digestion precedes best at 30 - 40^{0}C. Retention period was reduced due to the application of the human waste or excreta as a starter to enhance quick production of biogas. Within 9-14 days the biogas generation commenced. The pH value of the slurry was kept at a favourable value of about 6.8.

The gas sample was introduced into the 263-50 Gas-Chromatograph which was connected to a D2500 Chromato-Integrator and charged for a period of 13 minutes. The results were plotted on graph by the D2500 Chromato-Integrator and summary given within 13 minutes by the Integrator (see figures 1, 2, 3 &4). The results indicate the presence of Air (Oxygen and Nitrogen), CH_4, CO, N, CO_2 and traces of other gases.The content of the gas was analyzed using the 263-50 Gas-Chromatograph with the results displayed by the aid of D2500 Gas Chromato-integrator.

RESULTS AND DISCUSSION

Table 2 revealed the percentages of biogas collected from White Fulani, Holstein, Jersey and Simmental cows respectively. The table and the gas Chromatograph plots of figures 1, 2, 3 and 4 revealed that 69.233%, 60.459%, 84.916% and 85.331% of CH_4 gas for Jersey, Simmental, Holstein Friesian and White Fulani cows respectively.

Table 2: Moles Percentages and composition of Biogas for White Fulani, Holstein, Jersey and Simmental Cows

Composition of Biogas matter	Chemical Formula	White Fulani (%)	Holstein (%)	Jersey (%)	Simmental (%)
Methane	CH_4	85.331	84.916	69.233	60.459
Carbon dioxide	CO_2	13.011	14.89	22.911	27.991
Nitrogen	N_2	1.596	0.177	7.800	11.484
Carbon monoxide	CO	0.13	0.001	0.001	0.021
Air	(N + O)	0.048	0.010	0.055	0.045
Total	-	100.00	100.00	100.00	100.00

The researcher noticed that even in terms of weights, breeds of cows differ from the other and that can be a contributing factor in the amount of biogas obtained from each of the breeds. Also, the variation in the results according to the researcher has to do with the nature of the cows, feeds and the environment. The White Fulani which is predominantly found in Nigeria and the West-African sub-region in large number feeds most often on green grasses and marine plants grown along river banks which are high density energy plants.

In figures 1, 2, 3 and 4, the percentage of carbon dioxide (CO_2) in the biogas are 22.911% for Jersey, 27.991% for Simmental, 14.896% for Holstein and White Fulani is 13.011%. These values agreed with the 35-45%. Air was relatively low from figures 1, 2, 3, and 4 with a proportion of 0.055% for Jersey cow, 0.045% for Simmental cow, 0.010% for Holstein Friesian cow and 0.048% for White Fulani cow. With additional bleeding, the air can be totally removed out of the digester. The values for Nitrogen are in the same range with the 7.800% in Jersey, 11.484% in Simmental, 0.177% in Holstein and 1.596% in White Fulani (Nijaguna, 2002 and Obichigha (2005).

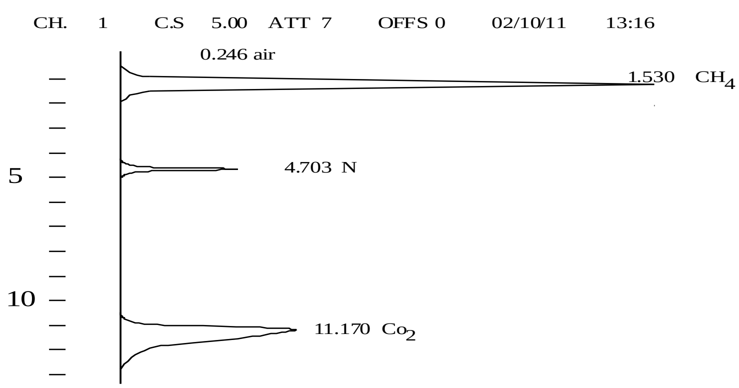

Figure 1: Jersey Cow

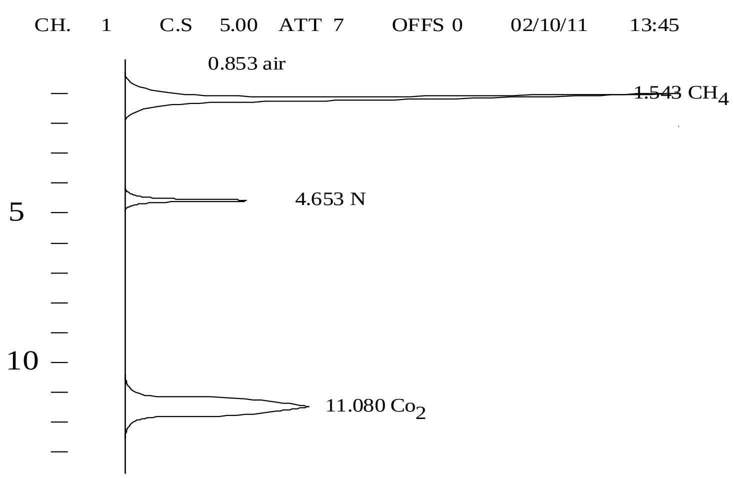

Figure 2: Simmental Cow

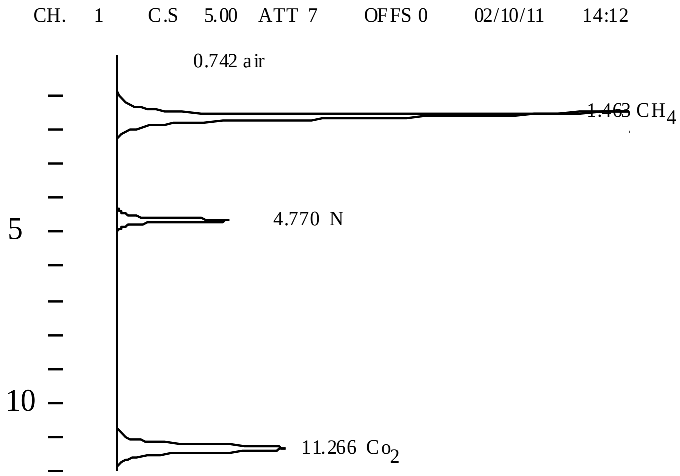

Figure 3: Holstein Friesian Cow

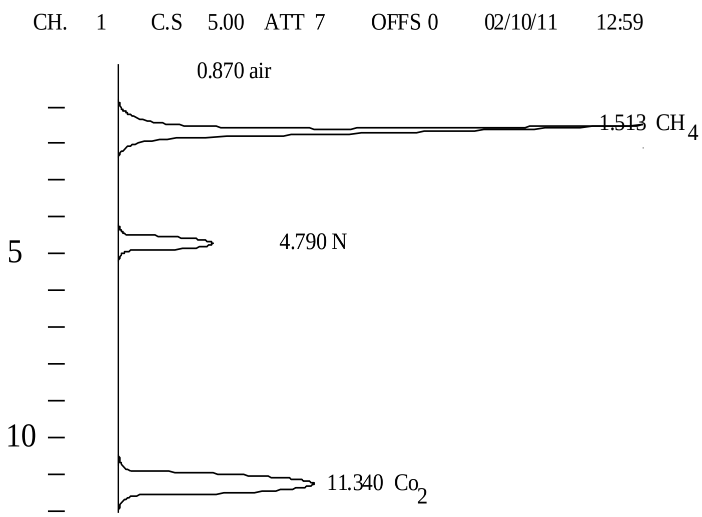

Figure 4: White Fulani Cow

The analysis in figures 1, 2, 3 and 4 showed the order in which the gases are eluted, with White Fulani having 85.331% of CH_4 gas, 0.048% of air, 0.13% carbon monoxide, 1.596% of nitrogen and carbon dioxide 13.011% respectively. This was followed by Holstein Friesian which has 84.916% of CH_4, 0.010% of air, 0.001% of CO and 0.177% N_2 which appeared to be the lowest and 14.89% CO_2. Jersey has 69.233% CH_4, 0.055% of air, which is the highest so far, 0.001% CO, 7.800% N_2 and 22.911% CO_2 which is the highest. The Simmental cow has 60.459% of CH_4 gas the lowest percentage in the four (4) cows analyzed, 0.045% of air, 0.021% CO, 11.484% N_2 and 27.484% CO_2 which is the highest amongst the four cows studied.

It is the opinion of the researchers, that further research into the variations in composition of CH_4, CO_2, CO, air, Nitrogen and other gases for the varieties of cows is necessary to ascertain the primary cause of the differences.

From table 2, the percentages of CH_4, CO_2, N_2, CO and air (O +N) in each of the four cows were arranged as eluted by the Chromatograph and plotted by the D2500 Gas-Integrator.

From table 2 and Fig 4, the research showed that White Fulani cows are the most effective in terms of production of biogas among the four (4) cows studied. This is probably attributed to the nature of the feed (mainly green grasses) the local White Fulani breed feeds on. Therefore, government and individuals interested in biogas generation need to harness and take this advantage to enhance biogas production.

In conclusion, the research looked into the effect of biogas production from variety of cows. The White Fulani, a predominant variety in Nigeria and the West-African sub-region content the highest percentage of biogas. The methods and materials used prove that the white Fulani has the highest percentage of bio-energy as compare to other breeds studied. The shortage of energy for cooking, lighting and power generation, which is a problem in the developing nations of Africa, especially West-Africa, can solved by the abundance of this local breed of cows. The methane from the White Fulani cows can be used to ameliorate the energy crisis, improve standard of living, generate employment and reduce incidences of deforestation in West-Africa. Therefore, Nigeria as a nation need to be really committed to bio-energy production by utilizing the numerous sources of energy available to it and engage in production of bio-fuel which source is readily available. The government and private sector need to mobilize energy resources in cow dung, particularly the White Fulani and other wastes to ensure energy is provided to Nigerians. Also, the researcher believes that further research into the variation in the percentages of biogas production for each breed will go a long way in enriching energy production capacities of nations.

Finally, it is the opinion of the researchers that with adequate financial grants from the government and private sector to support further research work in this area, the financial inadequacies he faced can be ameliorated, thereby enhancing the exploitation of bio-resources for energy generation in Nigeria.

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