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The qualitative evaluation of Biogas Samples Generated from Selected Organic Wastes

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ABSTRACT

Biogas generated from various agricultural wastes was subjected to compositional analysis so as to assess the quality of the biogas in terms of the methane, carbon (IV) oxide, and hydrogen sulfide content. On the basis of methane content paper waste has the highest quality biogas with 72.59% this is followed by saw dust with 68.79%, followed by cow dung with 66.00% and then rice husk with methane content of 64.97% the substrate that produced biogas with the lowest percentage methane is millet husk which gave 58.08% . The quality of biogas is also evaluated in terms carbon (IV) oxide content, the higher the carbon (IV) oxide content the lower biogas quality, base on this the highest percentage of CO_2 *of 40.72% was recorded for millet husk this is followed by 33.00% for both cow dung and rice husk., saw dust gave 29.65% making it as substrate with the second best quality biogas after paper wastes which recorded the lowest percentage of* CO_2 *(24.27%) which is the best. The other parameter used as the measure of the quality of biogas is hydrogen sulphide content, based on this, biogas sample from cow dung and millet husk have the lowest value of* H_2S *percentage content and therefore of higher quality compared to biogas from saw dust that contain 1.53 %* H_2S*. Rice husk with* H_2S *content of 2.00% has a better quality compared to biogas sample from paper waste which is poorest in terms of* H_2S *content.*

Key Words: Biogas, Substrate, Digester, biodegradable matter.

INTRODUCTION

Biogas is a flammable gas produced when organic materials are fermented under anaerobic condition. It contains mainly methane and carbon (IV) oxide with traces of hydrogen sulphide and water vapour. It burns with a pale blue flame and it has a calorific value of between 25.9J/m^3

– 30J/m^3 depending upon the proportions of methane and other constituent gases (Zuru, *et al.*, 2000). The gas is called by several other names such as dung gas, marsh gas, Gobar gas, sewage gas and swamp gas (Dangoggo *et, al.* 2004).

Biogas Production Process

The production process of biogas is a naturally occurring process involving the decomposition of organic materials under anaerobic conditions. The organic materials used in the fermentation generally contain volatile solids and ash. The volatile solids are made up of carbohydrates, fats, proteins, tannins etc. The fermentation, process is complex, it involves three main stages. The first stage being the stage in which the facultative micro-organism act on the organic matter and break it down to simpler substances which are soluble in water. Complex organic components such as cellulose, starch or proteins are converted to less complex organic compounds such as glucose and fructose which are soluble monosaccharide reducing sugars (Arian, 1981). At this stage polymers are transformed into soluble monomers through enzymatic hydrolysis.

In the second stage, the soluble monomers are converted into organic acids by a group of bacteria collectively called "acid formers". The soluble organic acids form the substrate for the third (3^{rd}) stage.

The 3rd stage which is the final stage of the fermentation process is strictly an anaerobic process (i.e. there must be no air) it involves the methanogenic bacteria attacking the soluble organic acids and generating methane from them. This process is activated in two alternative ways or mechanization routes. The first route being the fermenting of acetic acid to methane (CH_4) and carbon (IV) oxide (CO_2) and the second route involve the reduction of CO_2 to methane via hydrogen gas or format generated by the action of other bacteria species(Garba, 1999).

Factors Affecting the Production of Biogas

The rate at which biogas is produced and also its quality depends largely on several factors. These factors include; nature of substrate, temperature, surface area, C: N ration, Lignin content, agitation, e.t.c, (Garba, 1999).

Nature of Substrate

Materials of plant origin vary widely in composition. In general, the concentration of water-soluble substances such as sugars, amino acids, proteins and mineral decrease with the age of the plant (Nicholas *et al*, 1980). This is because, substances that are non-water soluble such as lignin, cellulose, hemi cellulose and polyamides (e.g. pectin, gums and mucilage) increase in content with the age of the plant (Nicholas *et al*, 1980). This means that vegetable matter from young plants produce more biogas compared to those from the older plants (Fernando, 1985).

For the waste products from animals, the type and age of the animal, its feeding and living condition, the age and storage of the waste product before use are all factors that can affect the quantity and quality of the biogas produced. In general finely ground waste products produce more biogas than lumps of waste materials due to large surface area of content with the bacteria (Maheshwari and Vasudevan, 1981). In this paper we determine the quality of biogas produced from various wastes by assessing its composition.

Purification of Biogas:
Biogas being a mixture of methane, carbon (IV) oxide, hydrogen sulphide and trace amounts of water vapour needs purification if the gas is to be used as a fuel especial in internal combustion engines. This is because of the fact that of all the gases produced, only methane is combustible, carbon (IV) oxide and hydrogen sulphide actually reduce the fuel efficiency of the biogas and therefore need to be removed or significantly reduced to the bearest minimum. The hydrogen sulphide is known to be corrosive and can damage metal surface if present at high levels.

Removal of Carbon (IV) Oxide (CO_2)
Different workers have used various methods for the absorption of CO_2. The absorption of CO_2 by the passage of biogas through concentrated alkaline solution such as KOH, NaOH, $Ba(OH)_2$ or $Ca(OH)_2$ is the most convenient method. Methane which neither reacts nor dissolves under this condition passes on.

$$CO_{2\,(g)} + 2\,NaOH_{(aq)} \longrightarrow Na_2CO_3 + H_2O \qquad (1)$$

Removal of hydrogen sulphide (H_2S):
Hydrogen sulphide may be eliminated from biogas by passing it through a concentrated solution of acidified lead (II) acetate or lead (II) nitrate. The acidified lead acetate solution absorbs the H_2S gas according the following equation.

$$(CH_3COO)_2\,Pb_{(aq)} + H_2S_{(g)} \longrightarrow PbS + 2CH_3COOH. \qquad (2)$$

The H_2S can also be removed from biogas as a precipitate of metallic sulphide. Since H_2S can precipitate many metallic ions from their solutions. Salts such as copper (2) sulphate, iron (II) sulphate iron (III) chloride, lead nitrate etc may be used and the reactions are according to the equations 3 - 6.

$$CuSO_4 + H_2S \longrightarrow CuS + H_2SO_4 \qquad (3)$$
$$FeSO_4 + H_2S \longrightarrow FeS + H_2SO_4 \qquad (4)$$
$$2FeCl_3 + H_2S \longrightarrow 2\,FeCl_2 + 2HCl + S \qquad (5)$$
$$Pb\,(NO_3)_2 + H_2S \longrightarrow PbS + 2HNO_3 \qquad (6)$$

Removal of Water Vapour
It is difficult to obtain completely dry biogas but the moisture content can be reduced to the barest minimum by passing the gas through a drying agents. The drying agents commonly used for drying biogas are silica gel or calcium chloride (Garba 1998).

MATERIALS AND METHODS

The materials used in this investigation as substrates were cow dung, paper waste, saw dust and residue from cereals such as, millet husk and rice husk.

The waste materials were all obtained from various locations around Sokoto metropolis. The paper waste was a mixture of various types of papers, such pure white, newspapers, cardboard, tissue and packaging papers of different types. The cow dung was collected fresh and sun dried for ten days before use. The millet husk was collected from Shama village near the main campus of Usmanu Danfodiyo University Sokoto. The rice husk was collected from a rice mill near the Kara market in Sokoto. The sawdust was obtained from the wood market (Timber shade) in Sokoto.

Treatment of Samples

The cow-dung, millet and Rice husk, paper waste and saw dust were each air-dried before drying the representative sample in an oven at 110^0C for 24 hours. The dried samples were grounded using wooden pestle and mortar, and stored in black polythene bags until required (Garba, 1999).

Preparation of slurry

From the oven dried crushed samples of the substrates, a known weights (600g) were taken in separate beakers and 3000 cm^3 of water was added to the substrate and mixed thoroughly before transferring in to the digester.

Generation and Collection of Biogas:

For the generation and collection of total gas produced, the digesters were fed with the slurry, prepared above and then sealed before the end of the PVC tube from the digester was connected to the inlet of a Buckner flask containing some quantity of silica gel, which served as a drying agent. The digesters were then jacketed in polyurethane form to minimise the temperature changes in the digester. Another PVC tube was connected to the outlet of the Buckner flask and the other end of the tube was connected to separate inverted 1000 cm^3 capacity measuring cylinders which was filled with water. The downward displacement of water in each measuring cylinder was taken as a measure of the volume of biogas produced for each digester, and the volume of daily biogas production for each digester was recorded separately.

Compositional Analysis of Biogas

For the determination of the constituent gases in biogas i.e. H_2S, CO_2 and CH_4 from the total biogas produced in each digester, parallel sets containing the same and equal quantities of slurry were made. The digesters were separately connected to the inlet of a Buckner filter flask containing some quantity of silica gel that dry the biogas. The outlet of the flask was connected to another Buckner flask containing lead acetate solution in 3M Ethanoic acid. Lead acetate absorbs the H_2S gas from the biogas passing through it, forming black precipitates of lead sulphide as shown in equation (1);

$$H_2S + Pb(COOCH_3)_2 \longrightarrow PbS + 2CH_3COOH \qquad (1)$$

From the buckner filter flask containing lead acetate the remaining gas after the absorption of H_2S gas passed into another Buckner flask containing 10% NaOH solution, which absorbs carbon (IV) oxide in the biogas, as shown in the equation (2);

$$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O \qquad (2)$$

The remaining gas coming out from the second Buckner flask is mainly methane (CH_4) gas collected by the downward displacement of water. The average weights of CO_2 and H_2S absorbed in each set up were respectively determined and converted to volumes using the Vander

Waals equation (3). The weight of the absorbed gas was calculated by subtracting the weight of the absorbent before absorption from its weigh after the absorption process ended.

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \quad (3)$$

Where P is pressure of the gas, V is the volume of the gas, n is the number of moles of the gas, R is the universal gas constant (8.314 j $mol^{-1}K^{-1}$), 'a' and 'b' are constants related to the gas (Atkin and Paula, 2002).

RESULTS

Table1: Compositional Analysis of Biogas Produced from Each Substrate (cm^3)

Substrate	**Total biogas** (cm^3)	**CH_4** (cm^3)	**CH_4** (%)	**CO_2** (cm^3)	**CO_2** (%)	**H_2S** (cm^3)	**H_2S** (%)
Cow dung	8545	5639.85	66.00	2830.50	33.00	74.65	1.00
Millet husk.	6525	3790.00	58.08	2657.20	40.72	52.26	1.00
Rice husk.	1386	900.50	64.97	462.12	33.00	22.40	2.00
Saw dust	974	670.00	68.79	288.83	29.65	14.93	1.53
Paper waste	476	345.54	72.59	115.53	24.27	14.93	3.14

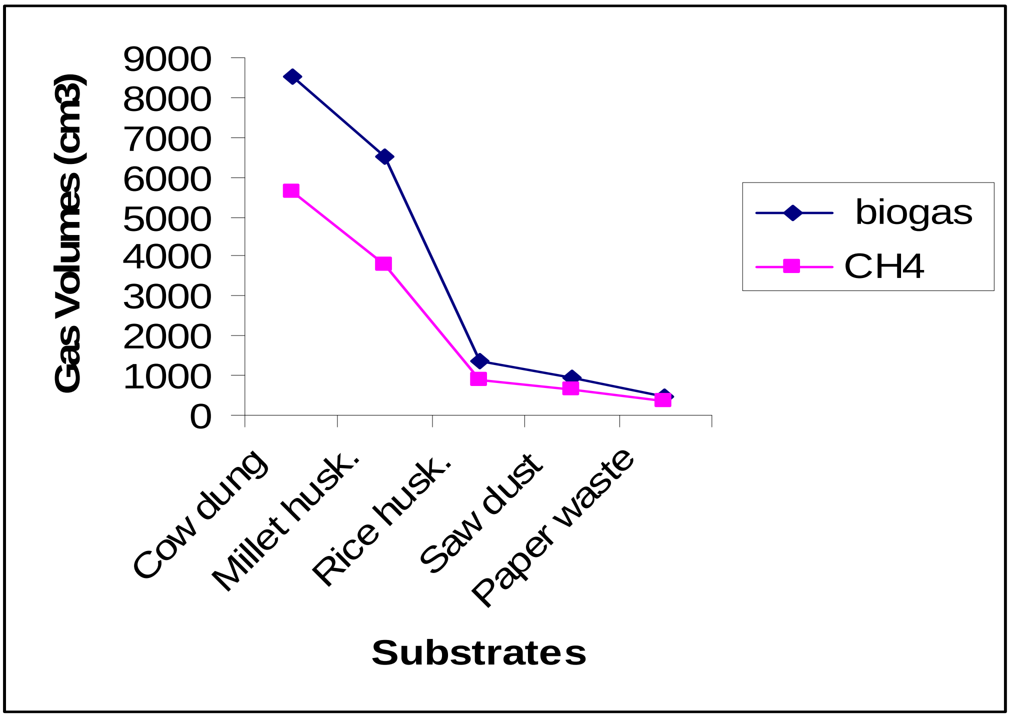

Figure1: Relative proportions of methane in biogas samples from various substrates

Table 2: Correlation of the total volume of biogas and methane content

Substrate	Average volume of biogas (Cm^3)	Volume of methane. (Cm^3)
Cow dung s	8545	5639.85
Millet husk.	6525	3815.54
Rice husk.	1386	901.48
Saw dust	974	670.24
Paper waste	476	345.54

Table 3: Percentage composition of biogas produced

Substrate	% of CH_4	% of CO_2	% of H_2 S	Total yield (100%)
Cow dung	66.00	33.00	1.00	8545
Millet husk.	58.08	40.72	1.00	6525
Rice husk.	64.97	33.00	2.00	1386
Saw dust	68.79	29.65	1.53	974
Paper waste	72.59	24.27	3.14	476

DISCUSSION

Quantitatively cow dung has a greater potential for biogas production since it gave the largest volume of biogas during the retention period compared to all the substrates under investigation. The volume from cow dung was 8545 cm^3 this is followed by millet husk which gave 6525 $cm^{3,}$ and the next best in terms of quantity is rice husk and then saw dust and least potential is found paper waste.

The compositional analysis carried out on the gas produced from each substrate, have shown that the biogas produced from all substrates are of high quality. The quality of biogas is in the order, PW >SD > CD >RH> MH. The percentage of methane was taken as a measure of the quality of biogas and in that sense the biogas generated in each substrate such as paper waste (72.59%), saw dust (68.79%) cow dung (66.00%), rice husk (64.97%) and millet husk (58.08%). Figure 1 gives the relative methane content of all the substrates under investigation. The carbon (IV) oxide content of the gas samples are generally low ranging from PW with 24.27%, which is lowest followed by SD 29.65%, CD and RH with 33.00% and the highest being that of MH which was calculated as 40.72%. The quality of the biogas samples in terms of the percentage of CO_2 is of the order, PW > SD > RH = CD > MH. Since the higher the percentage of CO_2 the lower the quality of the biogas generated because the CO_2 fraction of biogas does not contribute combustion in fact it retards the combustibility of the biogas. The absorption of carbon (IV) oxide takes place because of the presence of NaOH solution which reacts with CO_2 according to the equation;

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O \qquad (4)$$

The levels of H_2S gas recorded for each digester is also indicative of the quality of the biogas produced from all the substrates under study. It showed that in all the digesters the H_2S was between 1.00 - 3.14% of the total biogas produced. The only exception was in paper waste digester where the record indicated a higher percentage of the H_2S gas (3.14%). This may be attributable to the presence of additive sulphite especially inorganic sulphites introduced during the process of paper making especially during the pulping process. The absorption of H_2S was possible because of the reaction between H_2S and Lead ethanoate that led to the formation of the precipitate. The equation for the reaction is given as;

$$(CH_3OO)_2 Pb + H_2 S \longrightarrow PbS + CH_3COOH \quad (5)$$

CONCLUSION

From the results it could be conclude that biogas generated from paper waste have highest percentage of methane followed by that of saw dust and then biogas from cow dung is the third. Based on methane content only it could be concluded that Biogas from Paper waste is of best quality compared to others. But in terms of CO_2 content and H_2S percentage content, the paper waste and saw dust are the worst because of high percentages of diluents gasses and also the lower biogas production rate of the two substrates. On the basis of yield cow dung is the most suitable substrate for biogas production.

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