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Biogas Production from Anaerobic Co–Digestion of Corn Cobs, Pig and Poultry Droppings

Akindele OKEWALE[1], Kamoru BABAYEMI[2], Olusola ADESINA[3]

[1]*Department of Chemical Engineering Federal University of Petroleum Resources, Effurun, Nigeria*
[2]*Department of Chemical Engineering Chukwuemeka Odumegwu Ojukwu University, Uli, Nigeria*
okewale.akindele@fupre.edu.ng/ak.babafemi@coou.com
[3]*Department of Chemical and Petroleum Engineering, Afe Babalola University, Ado–Ekiti, Ekiti State, Nigeria*
adesinao@abuad.edu.ng

Corresponding Authors: okewale.akindele@fupre.edu.ng
adesinao@abuad.edu.ng

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Abstract**:** *Biogas production from anaerobic co – digestion of poultry and pig droppings, and corn cobs was carried out in this study. Buckner flasks (500 ml) connected in series were used as digesters and water displacement method was used to estimate the amount of biogas produced. The pH and temperature ranges for this study were 5.5 – 8.2 and 28ºC – 30ºC respectively within the hydraulic retention time of 52 days. Total solid concentration of 9.10% was used in each of the digesters. The ratio of the percentage distribution of poultry dropping to pig dropping were; (100:0), (50:50), (75:25), (25:75), (0:100) all by weight percent for digesters 1, 2, 3, 4 and 5 respectively. Result showed the Digester 2 had the maximum biogas yield of 313 cm^3 at the end of 52 days of fermentation after which there was no further production. It is suggested that the presence of polycyclic aromatic hydrocarbon, alkanes, sp^3 and methyl functional group in all these substrates used as shown by the Fourier transform infrared spectroscopy carried out make these materials to be viable for biogas production. The GC analysis on the biogas produced in digester 2 showed 66.60 wt.% and 20.75 wt.% for methane (CH_4) and carbon dioxide (CO_2) respectively. Linear kinetic model was used to fit the experimental data which shows that as the retention time increases the biogas yield increases. The net performance of the digesters is digester 2 > digester 3 > digester 1 > digester 4 > digester 5. X – RF analysis showed that poultry dropping has more of these essential elements required for enzymes and microbial metabolism in anaerobic digestion compared to corn cob and pig dropping which makes it to be a very viable substrate for biogas production.*

Keywords: *Retention time, Fermentation, Gas Chromatography, energy, Kinetics, Digester, Methane, Methanogens.*

1. INTRODUCTION

Global prosperity is entrusted in a very reliable, efficient, and cost effective energy. Majority of people in developing countries like Nigeria do not reliably, easily and steadily have access to energy in advanced forms such as constant and stable electricity; therefore, they entirely depend on solid forms of fuels like firewood to meet their basic energy needs for cooking and lighting. 90% of energy consumption in household in developing countries accounts for cooking.

In the developing countries on average over 60% of the total wood is used as fuel wood in form of charcoal, especially in urban areas, as firewood, and sawdust fire in the rural areas mostly. This has resulted in climate imbalance by rapid depletion of forests at a rate faster than it can be replaced. Biogas is composed of 50 – 75% methane, 25 – 50% carbon dioxide, 0 – 10% nitrogen, 0 – 3% hydrogen sulphide, 0 – 1% hydrogen and traces of other gases. Anaerobic digestion suggests the process occurs in the absence of free oxygen and produce methane (CH4) through decomposition of waste in nature thus reducing environmental pollution [1-2]. The anaerobic digestion has a number of advantages for waste conversion and ultimately producing methane and carbon [3]. The process of biogas production is made up of four stages; hydrolysis, acidogenesis, acetogenesis, and methanogenesis which are catalysed by different and specialized microorganisms [4]. The simultaneous digestion of more than one type of wastes in the same unit is referred to as co – digestion. Advantages of co – digestion include better digestibility, enhanced increase biogas production / methane yield arising from availability of additional nutrients, as well as a more efficient utilization of equipment and cost sharing [5-7]. Powdered leaves of some plants and legumes have been found to stimulate biogas production between 18% and 40% [8]. These additives also help to maintain favourable conditions for rapid biogas production in the reactor such as; increased pH, inhibition/promotion of acetogenesis and methanogenesis for the best yield. Alkan-Ozkaynak and Karthikayan [9], has demonstrated a high yield of biogas from the anaerobic digestion of corn stillage. Seeding of co-digested pig waste and cassava with wood ash was reported to result into significant increase in biogas production compared with unseeded mixture of pig waste and cassava peels [10]. Biogas is a readily available renewable energy resource that significantly reduces greenhouse-gas emission compared to the emission of landfill gas to the atmosphere [11]. The use of agricultural wastes like corn cobs for biogas generation offers several benefits such as the production of safe and clean energy resources that can be stored and used more efficiently, the production of stabilized residue which retains the fertilizer value of original material that has superior qualities in nutrient value over the usual organic fertilizer.

This work focuses on co - digestion of corn cobs with pig and poultry droppings anaerobically for the production of biogas. The study is aimed at getting the right proportion of pig and poultry droppings that will be co – digested with corn cobs to achieve a maximum biogas production. The kinetic parameters of the linear kinetic model concerning the biogas rate of production for the batch operation on bio-digester were investigated.

2. MATERIAL AND METHODS

The corn cobs were obtained from Ebrumede community, Effurun, Delta State while pig droppings and poultry droppings were procured from piggery and poultry farms respectively in Ugbomro, Effurun, Delta State. Conical flasks (500 ml), mercury in glass thermometer (range between -10 ^oC – 100 ^oC, with an accuracy of ± 0.1 ^oC), digital pH meter (HANNA model pH – 211), delivery tubes, corks, measuring cylinders (200 mL), muffle furnace, Oven (Genlab oven model, Mino/75/f), connecting tubes, mortar and pestle, weighing balance (model BH 600) with an accuracy of 0.01 g, sodium chloride (NaCl), tetraoxosulphate (VI) acid (H_2SO_4), Buckner flasks (500 ml), and distilled water which was procured from Department of Chemistry Laboratory, Federal University of Petroleum Resources, Effurun were used for the biogas production.

2.1 Pre-treatment and characterization of sample

Corncobs were grinded in a mill and sieved into small particle size of 800μm and mixed with water to make slurry. The mixture was boiled at 100^o C for one hour, allowed to cool, filtered and sun dried for two days to remove the moisture content. The pig and poultry droppings were also dried at room temperature for one week. All the substrates were subsequently oven dried at 110°C for 6 hours to remove any residual moisture.

2.2 Fourier Transform Infrared Spectroscopy

Corn cobs, poultry, and pig droppings of 800μm particle size were observed with Fourier Transform Infrared spectroscopy (Buck Scientific model 530) with the range 650 - 4000 cm^{-1} (wavelength).

2.4 X – Ray Fluorescence Analysis

The elemental and chemical analyses of the substrates were investigated to identify the elemental make up of these substrates. The substrates were examined using a Philip (PW1606) X-ray fluorescence spectrometer model.

2.5 Determination of pH

5g of the sample slurry was poured into a beaker. The slurry was agitated and left for 24 hours to stand at room temperature. The pH of the slurry was then measured using the pH meter (HANNA model pH – 211) (ASTM, 1996).

2.6 Determination of moisture content

The moisture content was determined using standard test ASTMD 2867 – 91 (ASTM, 1991).

2.7 Gas Chromatography (GC) Analysis

Agilent GC analyzer model (7890) was used to analyzed the biogas produced.

2.8 Determination of the ash content

5 g of each sample was weighed into a porcelain crucible and placed in a furnace that was preheated to 600 ^0C for 2 hours. Thereafter, the crucible was transferred to the desiccator to cool. The final weight was measured after cooling. Ash content was determined by using equation (1);

$$Ash\ content\ (\%) = \frac{final\ weight}{initial\ weight} \tag{1}$$

2.9 Determination of volatile matter

5 g of each of the samples were weighed and placed in crucible (initial weight), transferred to a muffle furnace that has been pre – heated to 600 ^oC for 4 hours. The samples were moved to a desiccator and re – weighed again. The weight lost is now the volatile matter present in the samples calculated using equation (2) below;

$$\%\text{Volatile Matter} = \frac{\text{Initial weight of wet sample+Crucible}-\text{final weight after heating+Crucible}}{\text{final weight after heating+Crucible} - \text{Initial weight of the crucible}} \times 100 \tag{2}$$

2.10 Experimental procedure

The apparatus used were properly washed with soap solution, distilled water, and allowed to dry overnight in the laboratory. Buckner flasks (500 ml) were used as digesters for each of the sample. Another set of Buckner flasks (500 ml) which contained an acidified brine water solution, was connected to each of the digester by means of a connecting tube and also, on the other side, connected to a conical flask by means of a connecting tube. Thus, the biogas produced in the digester by fermented slurry (samples) passed through the connecting tube to the Buckner flask containing acidified brine solution. Acidified brine water solution was displaced on the other side of the conical flask by the pressure of the biogas produced. The amount of water displaced was then measured as the volume of biogas produced. The digester was operated at ambient temperatures. The total solid concentration of 9.10% was used in each of the digester. Digester 1 corncobs, poultry droppings and water were mixed together by mass ratio 10g: 15g: 250g respectively. Digester 2 which consists of corncobs, poultry droppings, pig dungs and water were mixed together by mass ratio 10g: 7.5g: 7.5g: 250g respectively. Digester 3 consists of corncobs, poultry droppings, pig dungs and water were mixed together by mass ratio 10g: 11.25g: 3.75g: 250g respectively. Digester 4 was made up of corncobs, poultry droppings, pig dungs and water were mixed together by mass ratio 10g: 3.75g: 11.25g: 250g respectively. Digesters 5 consist of corn cobs, pig droppings, and water were mixed together by mass ratio 10g: 15g: 250g respectively. The ratio of the percentage distribution of poultry dropping to pig dropping are (100:0), (50:50), (75:25), (25:75), (0:100) all by weight percent for digesters 1, 2, 3, 4 and 5 respectively. The experimental set – up is shown in Figure 1.

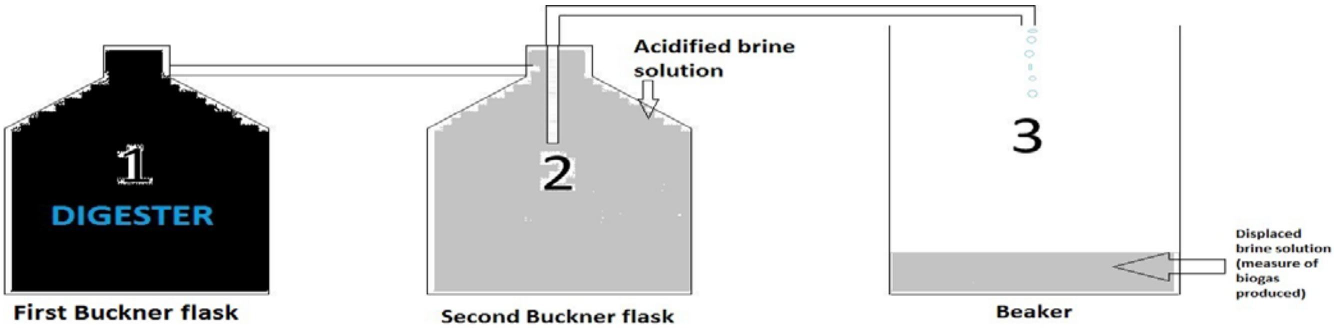

Figure 1. Experimental Set – up for biogas Production.

2.11 Linear kinetic model for biogas production

Biogas production rate from co – digestion of elephant grass, poultry and pig droppings, was simulated using linear plot. The rate of biogas production is expressed in equation (3) [12].

$$Y = a + bt \quad (3)$$

where y is biogas production rate in ml/gm/day, t is time in days for the digestion, a (ml/gm/day) and b (ml/gm/day) are constant obtained from the intercept and slope of the plot of y against t in ml/gm/day.

3. RESULT AND DISCUSSION

Characterization of the substrates

Table 1 shows the characterization of corn cob, pig and poultry droppings, poultry dropping had the least volatile solid compared with the other substrates used. It has been reported by El – Mashad and Zhang [13], that biogas production decrease with increase in volatile solids. They opined that methanogenic consortium microorganisms acclimatized very well with substrates that have fewer volatile solids and this enhance easy digestion of volatile solid during anaerobic digestion. It can be seen that poultry dropping has the least C/N ratio which enables it to perform better in terms of biogas production thus corroborating the work of [14], that substrates with very high C/N ratio would produce very low biogas. The pH range of 5.8 – 8.2 as observed in Table 1 also suggest the better performance of anaerobic co – digestion of corn cobs, poultry and pig droppings in biogas production which is in line with Ofoefule *et al.* [15], they opined that physicochemical properties like high volatile solids and sufficient pH range of 6.5 to 8.0 enhances optimization strategies provided by co – digestion to improve biogas production [16-17]. Lee et al. [18] also reported that methanogenesis in anaerobic digester occurs efficiently at pH 6.5 – 8.2 while hydrolysis and acidogenesis occurs at pH 5.5 and 6.5. It was observed that the value of pH ranges of these substrates enhances biogas production.

Table 1: Characterization of corn cob, pig and poultry droppings

Parameters	Corn cob	Pig Dropping	Poultry Dropping
pH	5.9 – 8.2	5.8 – 6.8	5.5 - 7.1
Particle size (µm)	800	800	800
Carbon Content (%)	15.5	14.3	27.25
Nitrogen Content (%)	0.67	0.65	2.19
C:N	23.13	22	12.44
Moisture content (%)	17.05	1.0	7.30
Ash Content (%)	1.95	22.80	35.55
Volatile Solid (%)	98.05	67.95	64.45

The elemental compositions of the substrates used in the fermentation process for biogas production is shown in Tables 2 – 4. The growth of methanogens is dependent on many ions like; nickel, cobalt, iron, zinc, sodium, magnesium, potassium cations, molybdate or tungstate and phosphate anions, and calcium [4]. With the exception of sodium which is required for coupling methanogenesis with ADP phosphorylation, all the other ions are required for the synthesis of enzymes, prosthetic groups, and coenzymes [19-20]. Trace level of these elements is required for the activation and /or functioning of many enzymes and co – enzymes during anaerobic digestion [21-24]. These elements form part of the enzymes that are essential in driving anaerobic fermentation reactions. Iron has been reported to be essential for the growth of almost all microorganisms. The basic physiological function of iron is a cofactor for some proteins, most of which are related to energy metabolism [21]. The nutrient requirement is a major concern for the stable operation of methane fermentation process [25]. The presence of iron element in all the substrates used suggest these materials to be good for biogas production since iron is required in methanogenesis by almost every metalloenzyme involved in the methanogenesis pathway [26]. The magnesium pathway use the synthetase and kinase enzymes complexes of ATP and ADP with Mg^{2+} as substrates and products, this (Mg^{2+}) is predicted to be taken up by the MgtE system [26]. It has been reported that methane formation in cell suspensions of microorganisms is simulated by the gradient of Ca^{2+} ions which is driven by membrane – associated Ca^{2+} ATPase [19]. (Ca^{2+}) calcium ions are required for the synthesis of enzyme Mch and a membrane bound Ca^{2+} ATPase [27-28]. Majority of the methanogenic enzymes function optimally only at high concentration of K^+ ions [4]. The zinc is required for the synthesis of the subunit B of HDR enzyme (involved in CO_2 reduction with H_2 to methane) and RNA polymerases [4]. The Zn^{2+} ions are translocated by the high – efficiency ZnuABC/ZupT transportes in Methanothermobacter marburgensis and M. thermautothrophicus which are regulated by the nickel – responsive transcriptional regulator NikR homolog [19, 29]. Ramansu et al. [4], reported that potassium ions are not directly involved in methanogenesis from CO_2 and H_2O. The presence of the potassium ions in these substrates suggests that methanogenic bacteria will be able to withstand various environmental stresses they may be subjected to. The preponderance of these essential elements in poultry dropping makes it to be a viable substrate for the biogas production compared to the other substrates. Phosphorus in bacterial cells occurs in inorganic form, mostly pi, and in organic form mostly as a component in a number of biomass such as RNA and DNA. It plays a central role in energy metabolism since biochemical energy obtained by the oxidation of substrates is used to synthesize ATP from ADP and Pi [30].

Table 2: Elemental compositions of corn cob

Element	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	Fe_2O_3	Mn_2O_3
Concentrations (wt. %)	0.00	1.182	4.061	44.648	12.051	16.533	3.911	0.263	3.750	0.164

Table 3: Elemental compositions of pig dropping

Element	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	Fe_2O_3	Mn_2O_3
Concentrations (wt. %)	0.00	0.904	6.936	53.159	7.396	2.353	10.118	1.343	5.603	0.118

Table 4: Elemental compositions of poultry dropping

Element	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	Fe_2O_3	Mn_2O_3
Concentrations (wt. %)	1.684	3.391	2.766	11.930	16.913	11.533	40.414	0.231	2.126	0.583

Figure 2 shows the FTIR spectra for poultry dropping, the frequency ($1028.7cm^{-1}$) suggests the presence of primary amine, CN stretch. The broad band with frequency ($3280.1cm^{-1}$) exhibited RO – H (Alcohol) wide rounded band showing the presence of alcohol while the broadband ($1636.3cm^{-1}$) exhibited (C = C) alkenyl stretch. The main functional group (O – H) phenol or tertiary alcohol OH band was seen at broadband ($1408.9 – 1319.5cm^{-1}$). The presence of alkene and phenol suggest poultry dropping to be a good substrate for biogas generation.

Figure 3 shows the FTIR spectra for pig dropping, the broadband ($2851.4 - 2922.2cm^{-1}$) exhibited the major functional group present; SP^3. The broad band with frequency ($3291.2cm^{-1}$) showed the presence of RO – H (Alcohol) wide rounded band showing the presence of alcohol. (C = C) alkenyl stretch was noticed at frequency ($1636.3cm^{-1}$). The broadband frequency of $1461.1cm^{-1}$ revealed the presence of methylene C = H bend. The broadband frequency of $1036.2cm^{-1}$ suggests the presence of primary amine, CN stretch. The presence of SP^3, C-H group and methyl C-H group as the main functional groups shows that pig dropping is a good substrate for biogas production.

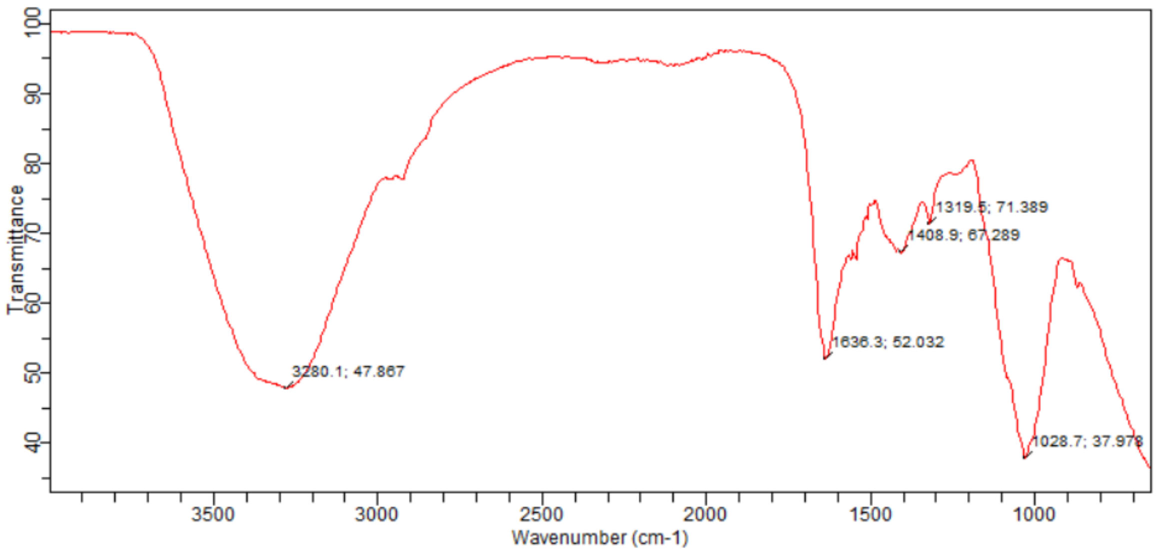

Figure 2. FTIR spectra for poultry dropping

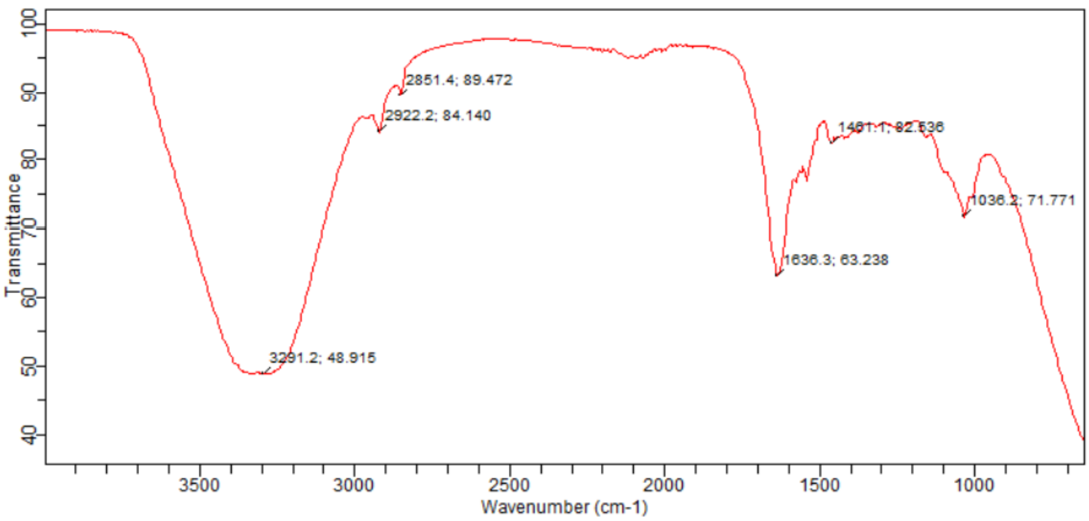

Figure 3. FTIR spectra for pig dropping

Figure 4 shows the FTIR Spectra for corncob, RO – H (Alcohol) wide branded band was shown with frequency (3678.9 -3272.6 cm^{-1}) indicating the presence of alcohol. SP^3, C – H band was revealed in (2922.2cm^{-1}) frequency while 2105.9 cm^{-1} and 1640.0 cm^{-1} frequency corresponds to C≡C (alkyne) and (C = C) alkene groups respectively (Coates, 2000). SP^3, C – H band was observed in (1151.7 – 1017.6 cm^{-1}) frequency. The functional group (O – H) phenol or tertiary alcohol OH band was exhibited at broadband (1364.2 – 1241.2 cm^{-1}). The frequency of broadband (2046.3cm^{-1}) suggests the presence of (–NSC) isothiocyanate. The presence of saturated hydrocarbon functional group in corn cob suggests it to be suitable for production of biogas.

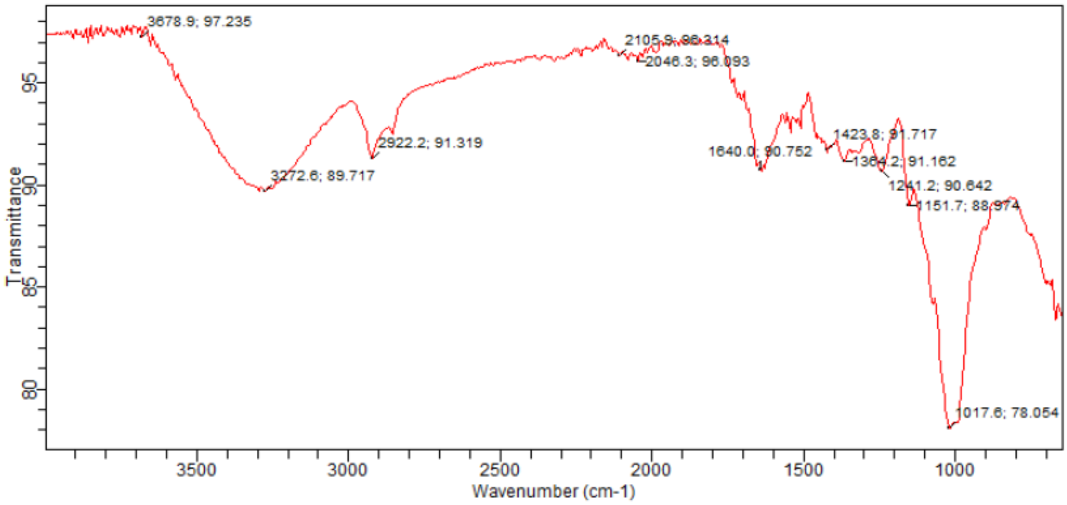

Figure 4. FTIR Spectra for corncob

The cumulative biogas produced for 52 days of anaerobic fermentation by digesters 1, 2, 3, 4, and 5 respectively is depicted in Figure 5. There was no production in all the five digesters for the first four days of fermentation this period of no activity can be explained to be due to the metamorphic growth process of the methanogens by consuming methane precursors produced from the early activity as suggested by [31-33]. Biogas production started on the 8th day in all the digesters except for digester 1 (100 wt.%, poultry and 0 wt.% pig droppings) that started production on 12th days of fermentation. There was a steady increase in biogas production for all the digesters within a retention time of 20 – 40 days. This sudden increase in biogas production can also be said to be as a result of an exponential increase in micro-organism which enhance an increase in rate of fermentation that subsequently leads to a corresponding increase in production of biogas. The initial stages of the overall biogas production process, acid forming bacteria produce Volatile Fatty Acids (VFA) thereby resulting in pH declining and diminishing the growth of methanogenic bacteria and methanogenesis [34-35]. It can also be explained that the non-activity during this period can be as a result of the inoculum that is in either methanogens or lag phase. It has been reported that plant-based biomass is highly lignocellulosic in nature, thereby hindering production of biogas. Co – digesting with poultry and pig manures tends to lower the C/N mixing ratio of the mixture, thus enhancing easy digestion due to the more presence of microbes resulting from these manures. It also provides a positive synergetic effect which is mainly attributed to more balanced nutrients and increased buffering capacity, bacterial diversities in different wastes and supply of missing nutrients by the co – substrates [30]. Digester 2 (50 wt. % poultry, and 50wt % pig droppings) was noticed to generate the highest quantity of biogas, this can be explained as a result of relative low content of lignin, moderate carbon to nitrogen ratio brought by these two livestock manures. This result also corroborated the findings of [14, 30]. Digester 5 (0 wt. % poultry, and 100wt % pig droppings) had the least volume of biogas produced. This can be attributed to the high presence of lignin in corn cob and high C/N ratio in these substrates which would have led to the increase in acid formation thereby retarding the methanogenesis activity and subsequently reduced the methane yield thus corroborating the assertion made by [36]. It can also be attributed to the accumulation of volatile acids (VFAs), and the lack of biodegradable soluble organic substances. The pH of the slurries in the digesters range is between 5.5 – 8.2. This observed change in pH may be due to the high volatile solids in the corn cob which were transformed into volatile fatty acids and other acidic metabolites during acidogenesis due to the activities of the aerobes and facultative aerobes that were subsequently metabolized by the methanogenic bacteria to generate biogas [37-39]. The pH value was observed to increase in all the digesters as fermentation days is increased. Production of biogas increase as retention time and pH increases. This increased in yield of biogas suggests an increase microorganism's metabolic activity present in the digesters. There was no significant variation in temperatures of the slurries in the digesters.

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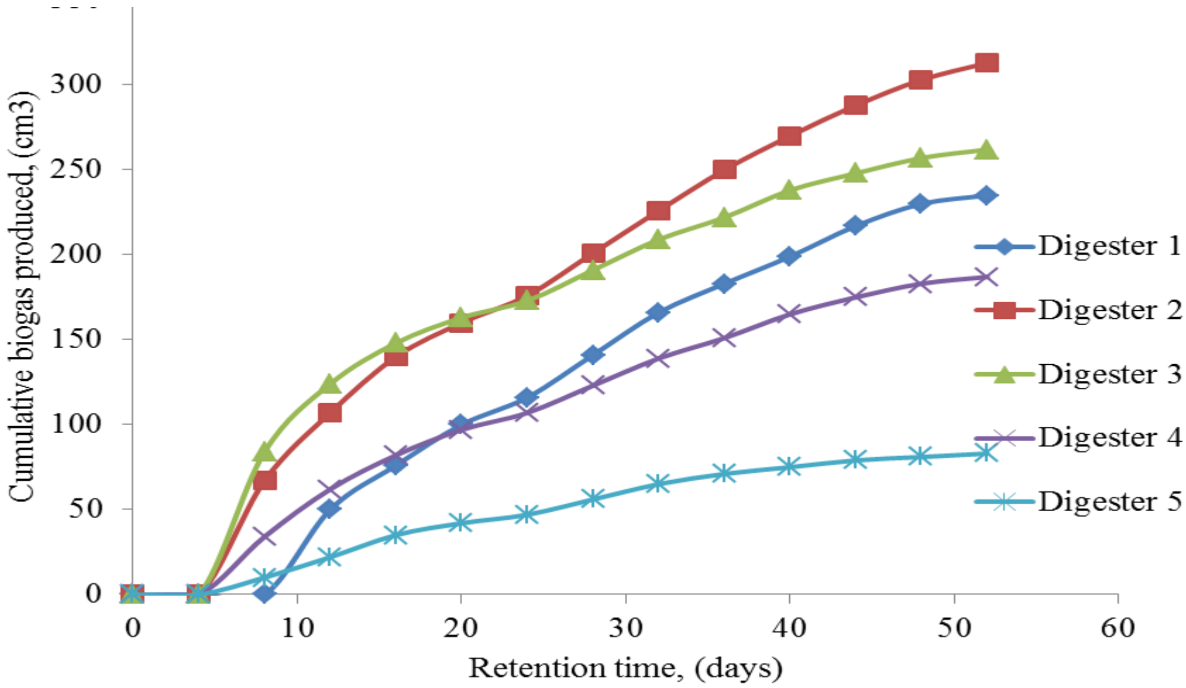

Figure 5. Cumulative biogas produced with retention time

Figure 6 shows the Linear model for the produced biogas, it was observed that as the retention time is increased the rate of biogas production increased. The coefficient of determination (R^2) ranges from 0.9533 to 0.9857 for the five digesters which showed good agreements with the experimental value of biogas produced with the retention time of fermentation. The value of constants a and b were; (0.0517cm^3/gm/day and -0.1231cm^3/gm/day), (0.0551cm^3/gm/day and 0.4313cm^3/gm/day), (0.0384cm^3/gm/day and 0.78cm^3/gm/day), (0.0342cm^3/gm/day and 0.2286cm^3/gm/day), and (0.0165cm^3/gm/day and 0.0599cm^3/gm/day) for digesters 1, 2, 3, 4, and 5 respectively. It can be established from figure 6 that with an increase in fermentation time (retention days) the rate of production in biogas increase linearly. The biogas rate of production would decrease linearly after reaching a maximum point to zero as the maximum fermentation time (days) is achieved.

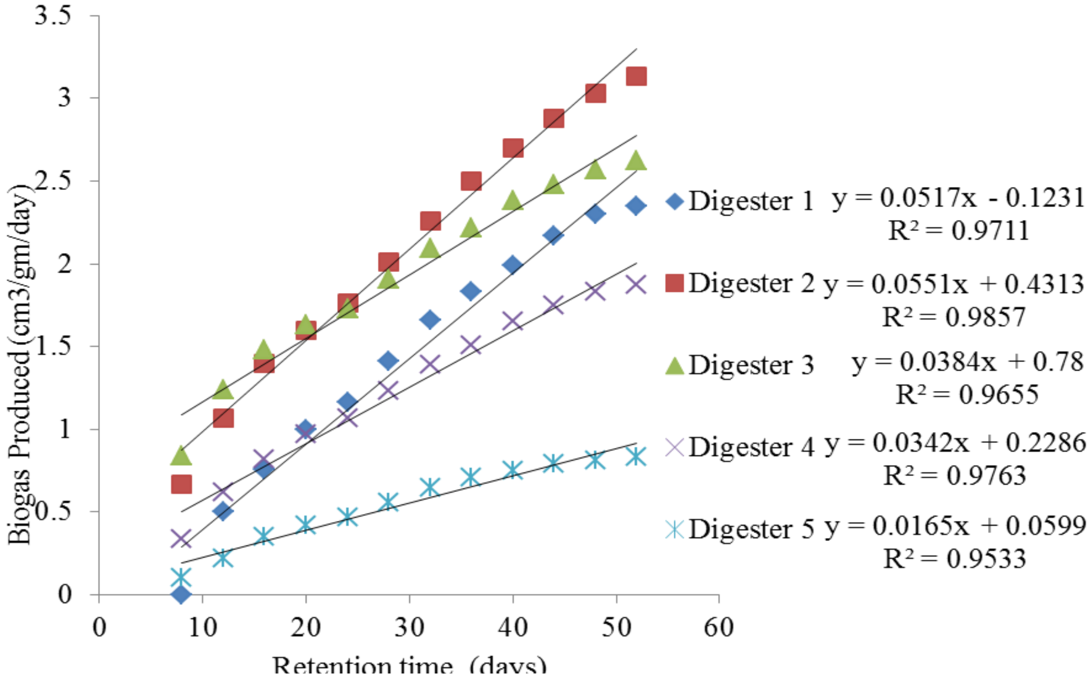

Figure 6. Linear model for the produced biogas

Table 5: Composition of the Biogas Produced in Digester 2 using Gas Chromatography

Element	CH_4	CO_2	NH_3	H_2S	O_2	N_2	H_2O
Compositions (wt. %)	66.60	20.75	1.30	1.00	0.6	8.8	0.95

Table 5 depicts the composition of biogas produced in digester 2 that had maximum biogas. 66.60 wt.% of methane gas was generated. This methane yield obtained in this work is similar to that reported by Eze and Ojike, [40]. Biogas produced can be used as a source of heat in cooking since it is combustible with the methane (CH_4) concentration that is above 50 wt.%. The mixture of the gases is combustible if the methane content is more than 50% in concentration as reported by [10,41].

4. CONCLUSIONS

Biogas production from anaerobic co-digestion of corn cob, poultry, and pig droppings, was carried out in this work. The co-digestion of poultry dropping (50 wt. %), pig dropping (50 wt. %), and corn cob gave a higher cumulative biogas yield of 313 cm3. The CH4 content of 66.60 wt. % was obtained in digester 2 that had the maximum cumulative biogas. The presence of methyl group, alkanes, and alkenes groups in corn cob, poultry, and pig droppings as revealed by the FTIR enables these materials to be good substrates for production of biogas. The linear kinetic model fitted well to the experimental data obtained. The net performance of the digesters were; digester 2 > digester 3 > digester 1 > digester 4 > digester 5. The GC analysis on the biogas produced in digester 2 for biogas production showed 66.60 wt.%, 20.75 wt.%, 1.30 wt.%, 1.0 wt. %, 0.6 wt. %, 8.8 wt.%, and 0.95 wt. % for methane (CH4), carbon dioxide (CO2), NH3, H2S, O2, N2, and H2O respectively. Low values of C/N and volatile solid (VS) present in poultry dropping enables it to perform better in biogas production compared to pig dropping. The growth of methanogens which subsequently influence the biogas production yield is enhanced more by the presence of ions like; silica, iron, zinc, sodium, magnesium, potassium cations, molybdate and phosphate anions, and calcium in these substrates as seen in the X – ray fluorescence analysis.

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