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Comparative Analysis of Biogas and Methane Yields from Different Sizes of Groundnut Shell in a Batch Reactor at Mesophilic Temperature

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Authors' contributions

This research was carried out in collaboration among all authors. Author SOJ lead the design and supervision of the work. Authors AOA and OOO planned the experiment and guided when required. Author KOO managed the work and wrote the paper. All authors read and approved the final manuscript.

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ABSTRACT

Aim: To study the effects of different sizes of groundnut shell on biogas and methane yields using batch reactor at mesophilic temperature.
Place and Duration of Study: The laboratory experiment was carried out at the Laboratory of the Department of Agricultural Engineering, Ladoke Akintola University of Technology, Ogbomoso, Nigeria, between August and October, 2018.
Methodology: Batch experiment was set up for a period of 35 days with substrate reduced to 2, 4 and 6 mm sizes. The digesters were subjected to anaerobic digestion at mesophilic condition and the gas produced were collected with graduated gas sampling bottles dipped in measuring cylinders already filled with red liquid. The total gas produced was analyzed using gas analyzer to give the percentage composition of the gas components and Enwuff equation was used to calculate the biogas and methane yields of organic dry matter and fresh mass of the samples.
Results: The total gas volume of 482.5, 605.0 and 732.5 ml were recorded for the sizes 2, 4 and 6 mm respectively. The organic dry matter biogas yields were 357.1, 514.31 and 324.5 $l_N kg^{-1}$oDM for

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treatment 2, 4 and 6 mm respectively; while organic dry matter methane produced were 222.41, 298.41 and 211.31 $CH_4kg^{-1}oDM$ for 2, 4 and 6 mm, respectively. The fresh mass biogas yields were 147.6, 180.7 and 177.3 $l_Nkg^{-1}FM$ and fresh mass methane yield were 919, 104.8 and 115.4 l_NCH_4 $kg^{-1}FM$ for 2, 4 and 6 mm, respectively.

Conclusion: Considering the yields recorded, the experiment shows that size reduction had effect on biogas yields and it is an important factor to be considered in biogas production. Treatment with particle size 4 mm seems to be the ideal size when considered the yields in terms of organic dry matter and fresh mass basis.

Keywords: Biogas; pretreatment; groundnut shell; size reduction; mesophilic temperature; organic dry matter; fresh mass; methane.

1. INTRODUCTION

Anaerobic digestion (AD) is a series of suitably-arranged process where biomass/substrates are broken down and transformed to biogas (renewable energy) by the catalytic activities of microorganisms [1]. Biogas released from anaerobic digestion is majorly methane and carbon dioxide; and can be an alternative option to traditional energy [2]. In a distinctive manner, it holds 60-65% methane which is easily ignited (flammable). As a result of the improvement in technology of biogas usage, it is now one of the most accepted means of waste/residues to energy technologies [2]. Under normal conditions, energy crops, agricultural residues (fodder residues and manures), food remnants/kitchen wastes, municipal wastes and industrial wastes such as dairy waste are the available substrates for biogas production. Anaerobic digestions advantage over other processes like ethanol production is the ability to produce biogas from different wastes/residues. The general rule of substrate is the debasement of biodegradable substances (e.g. carbohydrates, protein and fats) in the absence of oxygen, where bacterial changed the biodegradable materials to methane, carbon dioxide, water and traces of some other gases. Nevertheless, degradation of some substrates can be very slow because they contain chemicals that disturb the microorganisms' activities and growth [1].

Biogas that is rich in methane from anaerobic digestion of biodegradable substances gives a wide variety of sustainable energy since methane can be employed to substitute for fossil fuels in either heat and power production, and in operating internal combustion engines thereby bringing about reduction in greenhouse gas emission and decrease the climate change rate. Methane has been appraised as one of the superlative energy-efficient and environmentally benign ways of producing vehicle bio-fuel [3]. With the present use of energy in our daily life style, biogas as a renewable energy as well as eco-friendly can be used to complement other forms of energy in use. According to [4] about 80% of the people in the South-Western part of Nigeria believed that they are paying exorbitant bills for the present poor electricity supply but are ready to spend more if uninterrupted electricity can be generated through the renewable energy.

Therefore, how to improve biogas production and quality is an important area of interest in terms of technology, environment and economy [5]. To mitigate the problem associated with biogas production potential during anaerobic digestion, different technologies can be used to improve the yields of the biogas. Biogas yields (methane and carbon-dioxide) can be improved significantly with pressure increase which will reduce the pH values of the slurry [6]. Adebayo AO et al., Ogunkunle O et al. [7-10] reported that co-digestion of different substrates (animal waste and crop residue) results in improved biogas and methane yields. Increase in temperature had positive effect on biogas and methane yields [11]. To enrich the yield of biogas production various pretreatment processes can be used [12].

Lignin, cellulose and hemicellulose are the three major types of polymers present in lignocellulose and they are related to one another [13]. This lignin specifically creates an obstruction to enzymatic attack while the developed crystalline structure of cellulose is not soluble in water and the hemicellulose and lignin generate a protective cover around the cellulose. This manner of arrangement of lignocellulose therefore plays a tremendous function in inhibiting debasement of the hemicellulose and cellulose structure to monomeric sugars that is important for effective transformation of biomass into biogas. Pretreatment of lignocellulose is therefore fundamental for the conversion of lignocellulosic biomass to energies like biogas, methanol and bio-ethanol [14]. The pretreatment can enhance the bio-digestibility of the wastes for biogas production and increase accessibility of the enzymes to the materials. It results in enrichment of the difficult biodegradable materials, and improves the yields of biogas from the wastes [15]. Several researches have been carried out to compare biogas yields with pretreated and raw substrates, and also put forward the advantages and disadvantages of each pretreatment method. Pretreatments such as physical, biological, chemical, thermal and nanomaterials treatments were used to facilitate methane production by promoting the biodegradation of hemicelluloses and the lignin parts of the substrates [1].

Groundnut botanically belongs to *Arachis hypogea* of leguminous family. It is an herbaceous legume, annual and self-pollinated crop. Pod is a whole seed of groundnut and can have between one and five kermils that grows beneath the soil in the form of a needle referred to as peg that develop into the soil and then changed into pod [16]. Groundnut was grown on over 25 million hectares in the world in 2010 with a total production of about 37.64 million metric tons [17]. China, India, Nigeria, USA and Myanmar are the principal groundnut producing countries in the world (Table 1).

Groundnut shell (Fig. 1) is the covering layer of groundnut and it is between 25 to 35% of the pod while the remaining 65 to 75% accounts for the seed [16]. Nigeria is among the principal producers of groundnut in the world with about 2.699 and 1.55 million metric tonnes in the year 2002 and 2008 respectively [18]. In the developing countries of the world, groundnut shell has become a major solid waste over the years because there is little investigation on the strength of groundnut shell as useful engineering materials. The utilization of Groundnut shell will promote waste management at little cost, reduce pollution by these waste and increase the economic base of the farmers when such waste are sold thereby encouraging more production [19].

The main focus of this work was to pretreat groundnut shell with size reduction which is one of the mechanical pretreatment technologies and compare the yields of biogas and methane from different sizes of groundnut shell in batch digester at a constant temperature. The purposes of this pretreatment method are to make anaerobic digestion quicker, improve biogas yields, make use of new and locally

Table 1. The first 20 producers of groundnuts in the world

Rank	Countries	Production (Int $1000)	Production (MT)
1	China, mainland	7388368	16800000
2	India	2452413	4695000
3	United States of America	1334413	3057850
4	Nigeria	1308585	3071000
5	Myanmar	551522	1371500
6	United Republic of Tanzania	348380	810000
7	Indonesia	315292	1251000
8	Argentina	299808	685722
9	Senegal	285484	672803
10	Cameroon	242354	633799
11	Viet Nam	206349	470621
12	Ghana	201859	475056
13	Malawi	160885	268081
14	Chad	154426	371000
15	Brazil	148864	334224
16	Democratic Republic of the Congo	148186	371400
17	Mali	137111	230000
18	Guinea	130425	300000
19	Burkina Faso	127635	310759
20	Uganda	121691	295000

Source: [18]

Fig. 1. Groundnut shells

available biodegradable substances, and to reduce production difficulties like high electricity required for combining or the arrangement of floating layer.

2. MATERIALS AND METHODS

2.1 Materials

Inoculum from previous biogas experiment of crop and animal residues was used for the experiment and it was collected from the laboratory of the Department of Agricultural Engineering, Ladoke Akintola University of Technology, Ogbomoso, Nigeria. Substrate which was the groundnut shell was collected from Aronpe village in Orire Local Government Area of Oyo State, Nigeria where groundnut production is one of the major crops produced. The physicochemical property of both the sample and the inoculum was carried out in the laboratory.

2.2 Methods

The quantity of substrate and inoculum measured in each of the reactor bottles were measured in line with German Standard Procedure, equation (1)

$$M_s = \frac{M_i C_i}{2 C_s} \quad (1)$$

Where:

M_s = Mass of substrate (g)
M_i = Mass of inoculum (g)
C_i = Concentration of Inoculum (%)
C_s = Concentration of substrate (%)

Inoculum required is 80% of the reactor [20].

The groundnut shell was milled with hammer mill using different screen sizes of 2, 4 and 6 mm, these sizes were selected for the experiment according to Barton, [21]. The substrate was grouped as shown in Table 2.

Table 2. Grouping for different sizes of treatments

Treatments	Sizes (mm)
A	2
B	4
C	6

One thousand (1,000) ml capacity reactors were loaded with 800 g of stabled inoculum and 9.37 g of the selected substrate sizes were added to the preloaded inoculum and labeled. The experiments were duplicated twice as stated by [22] and a set of the reactor were left with only the inoculum to serve as control experiment. The thermostatic cabinet was set at a predetermined mesophilic temperature of 37°C and this temperature was maintained throughout the experiment, the reactor bottles were carefully arranged in the thermostatic cabinet and all the openings were closed (Fig. 2a). Twenty-five litres of distilled water was boiled to a temperature of about 10°C and 900 g of NaCl was added to the water and stirred until it dissolved completely in the water. About 10 points of knife edge methyl orange was added to the solution while the pH was being measured intermittently to obtain between 4.5 - 5.5 pH level [20]. Calibrated measuring cylinders with calibrated glass sampling bottles inside were filled with red liquid until zero point of the calibrated glass sampling bottles were reached. Pipes were used to connect the reactor bottles with the corresponding calibrated gas sampling bottles dipped in the red liquid in measuring cylinders (Fig. 2b) and were used to collect and store the gas released, and the readings of the volume of the gas produced were taking from it on daily basis. In order to re-suspend the sediment and scum layers, the reactors were thoroughly shaken everyday throughout the experimental period [9] and Enwuff equation [20] were used to analyze the quantity and quality of biogas released.

The methane component of the gases produced were determined at interval depending on the gas volume with the use of gas analyzer ToxiRAE pro (Electrochemical sensors) model. The experiment was terminated at 35 days when it was observed that the daily quantity of gas produced was less than 1% of the cumulative quantity of gas release up to that time [20]. On daily basis, the following data were taking: date, time of the day when the readings were taken, volume of the gas (ml), gas temperature (°C) and air pressure (mbar) throughout the retention period. Standard temperature (°C) and standard pressure (1013 mbar) were employed to compute the biogas and methane yield. Gas factor was calculated and Enwuff equation was employed to calculate the fresh mass biogas and methane released; and the organic dry matter biogas and methane released were calculated daily throughout the retention period. Standard condition of 273.15 K and 1013.25 mbar was used to convert the volume of gas formed. Equation (2) was used to calculate the gas factor [20].

$$F = \frac{(P - P_{H_2o}) \, x \, T_o}{(t + 273.15) x \, P_o} \tag{2}$$

Where:

T_o = 273.15 °C (Normal Temperature)
t = Gas Temperature in °C
P_o = 1013.25 mbar (standard pressure)
P = Air pressure.

Water vapour pressure (P_{H_2O}) depends on the gas temperature and amounts to 23.4 mbar for 20°C. Equation 3 describes the water vapour pressure as a function of temperature and depicts the range between 15 and 30°C.

$$P_{H2O} = y_0 + a.e^{b.t} \tag{3}$$

Fig. 2a. **Fig. 2b.**

Fig. 2. Batch experiment set-up

Where:

y_o = -4.3905;
a = 9.762 and b = 0.0521

The normalised biogas volume is given as

$$\text{Biogas [Nml]} = \text{Biogas [ml]} \times F \qquad (4)$$

Normalised by the quantity of biogas released, the total gas that took off the control batch is as follows:

$$\text{Biogas [Nml]} = (\text{Biogas [Nml]} - \text{Control [Nml]}) \quad (5)$$

On weight basis, mass of biogas released in standard litres/kg FM fresh mass can be calculated as follows:

1 standard ml/g FM = 1 standard litres/kg FM = 1m^3/t FM

$$\textit{Mass of Biogas Yield} = \sum \frac{\textit{Biogas}\,[\textit{Nml}]}{\textit{Mass}\,[g]} \qquad (6)$$

oDM biogas produced was as a result of the percentage of volatile solid (VS) that was available in the substrate. Therefore,

$$\textit{oDM biogas yield} = \sum \frac{\textit{Biogas}\,[\textit{Nml}]}{\textit{Mass}\,[g]} \qquad (7)$$

$$CH_{4\,corr.} = \frac{CH4\,[vol]x\;100}{(Mass\,[g] + CO2\,[vol\,\%])} \qquad (8)$$

$$\text{Fresh mass Methane yield} = \frac{\textit{Fresh mass biogas yield x}\ \text{CH4corr.}}{100} \qquad (9)$$

$$\text{oDM Methane Yield} = \frac{\textit{oDM biogas yield x}\ \text{CH4corr.}}{100} \qquad (10)$$

3. RESULTS AND DISCUSSION

3.1 Physicochemical Properties of the Substrate and Inoculum

Table 3 shows physicochemical properties of the substrate and inoculum used for the experiment. The experiment was carried-out with substrate that had organic dry matter of 92.26% (Table 3); this implies that there is high buffering capacity of the substrate for micro-organisms degradation. The average dry matter content of the substrate was 92.58%, dry matter content is one of the principal parameters that regulate anaerobic digestion. Dry matter contents between 25 – 30% leads to creation and discharge of outflowing which can lead to further mass losses [23]. The dry matter of the substrate was higher than the required standard which is 30%, [20], and calculated amount of water was added to the substrate to reduce the dry matter to the specified percentages. The C/N ratio presents the relationships between the quantity of carbon and nitrogen available in organic materials and is a crucial indicator that control biological treatment. The C/N ratio of substrate in anaerobic digestion greatly regulates biogas release [24]. Higher quantity of carbon furnishes with more carbon for methane production, and lower ratio of nitrogen content reduces microbial activeness because microbes required a relatively higher amount of nitrogen to assert growth and this can slow down the process. The optimal C/N ratio range of 20 to 30 is the ideal value for anaerobic digestion [25]. The physicochemical properties of the substrate used in this experiment has C/N ratio of 26.23% (Table 3). The C/N was significantly high and this encouraged the methane production in the gas produced.

3.2 Effects of Size Reduction on Biogas Yields

From the experiment performed in the laboratory, anaerobic digestion of groundnut shell from treatment A, B and C at mesophilic temperature with retention period of 35 days produced the total gas volume of 482.5, 605.0 and 732.5 ml, respectively at average ambient temperature of 32.8°C and average ambient pressure of 776.8 mmHg. The set of results obtained contains biogas and methane in both fresh mass and organic dry matter forms for the three different treatments. The plot of gas yield against time (days) for various sizes of the substrate for the experiments are shown graphically in the Fig. 3 - 6 and it was observed that cumulative gas yields increases with number of days.

3.2.1 Effect of size reduction on fresh mass biogas yield

At the end of the 35 days retention period, treatment B has the highest yield of fresh mass biogas yield (180.7 l_N/kgFM), followed by treatment C (177.3 l_N/kgFM) and lastly treatment A with 147.6 l_N/kgFM (Fig. 3). The yields of treatment B and C are in line with what [26] discovered in their research when groundnut shell was pretreated with size reduction. It was reported that treated groundnut shell yielded 200 ml biogas while untreated groundnut shell yielded 180 ml. [27] also performed experiment on the consequence of particle size on biogas

Table 3. Physicochemical properties of the substrate and inoculums

Parameter (%)	Substrate	Inoculum
Dry matter	92.58	67.15
Organic Dry matter	92.26	95.51
C/N ratio	26.23	8.45
Ash content	1.72	2.49
Crude fibre	9.46	0.45
Crude lipid	0.63	6.15
Moisture content	7.42	32.85
Protein	20.05	4.26

produced from sisal fibre waste and their results confirmed that size reduction had positive effects on biogas yield. However, [28] reported that excessive reduction of particle size of the substrate leads to Volatile Fatty Acid (VFA) aggregation which leads to reduction in solubilization of the anaerobic digestion process and decreased methane production. Therefore, the results shows that smaller sizes can significantly increase fresh mass biogas yield, but there is a limit below which the reduction in size would not have positive effect on fresh mass biogas yield of the groundnut shell as demonstrated by treatment A in this experiment.

3.2.2 Effect of size reduction on organic dry matter biogas yield

After terminating the experiment at 35 days retention period, treatment B produced the highest yield of organic dry matter biogas with 514.30 $l_N$kgoDM, followed by treatment A 357.10 $l_N$kgoDM and lastly treatment C with 324.50 $l_N$kgoDM (Fig. 4). The yield from treatment B and C is in agreement with what [29] reported in their experiment that groundnut shell pretreated with sonication released 469.36 ml biogas while the untreated substrate released 185.4 ml and [30, 31] also reported that size reduction had positive effect on biogas yield. [32,33] reported that size reduction of pomace and maize fibre reduced to 0.4 mm particles size had faint effect on the gas produced and pace of their enzymatic hydrolysis. It can be deduced from this research that treatment A had lower organic dry matter biogas yield when compared with treatment B as a result of weak enzymatic hydrolysis rate. This shows that the highest organic dry matter of biogas yield is between treatment A and B.

3.2.3 Effect of size reduction on fresh mass methane yield

The yield recorded after 35 days period shows that treatment C yielded the highest fresh mass methane of 115.4 l_NCH_4FM, followed by treatment B with a total yield of 104.80 l_NCH_4FM,

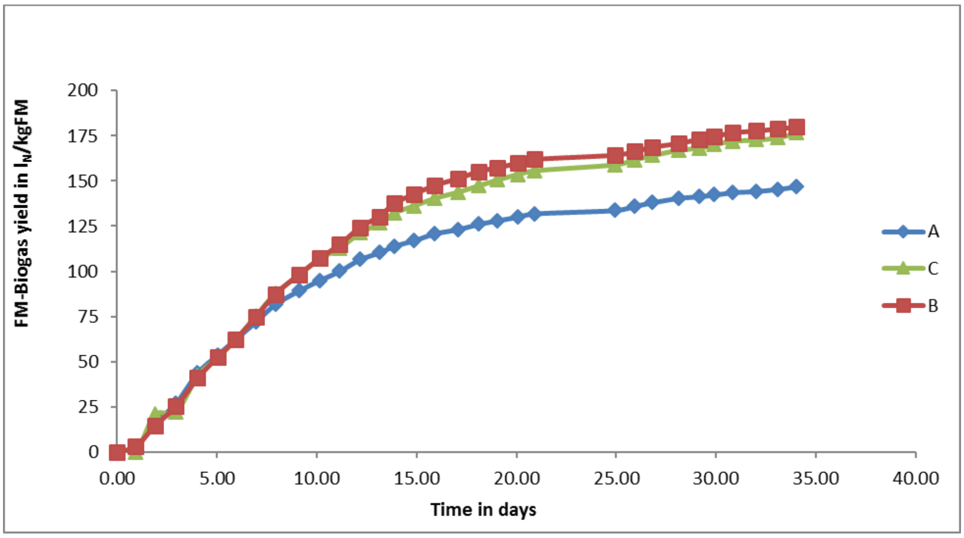

Fig. 3. The fresh mass biogas yield

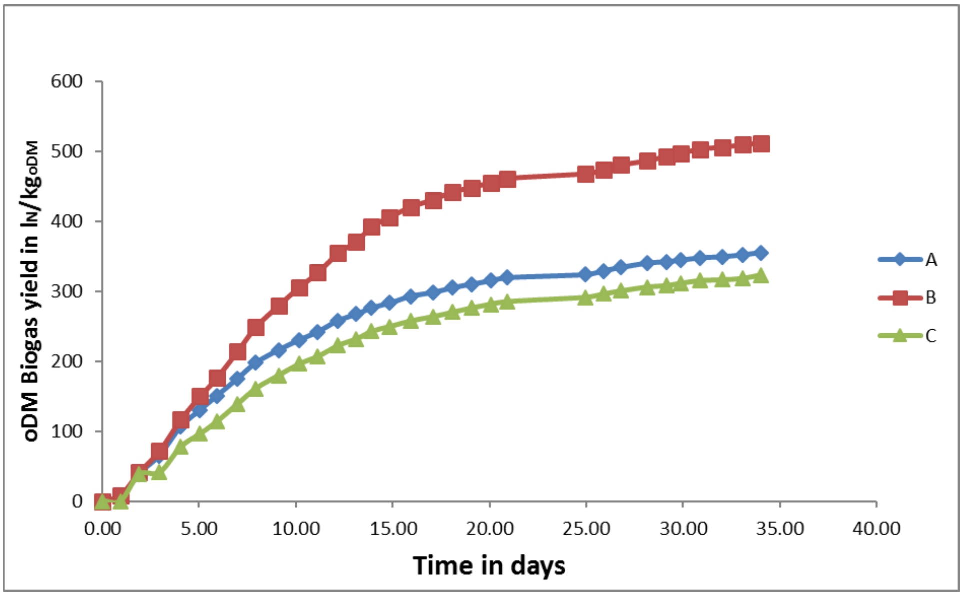

Fig. 4. Organic dry matter biogas yield

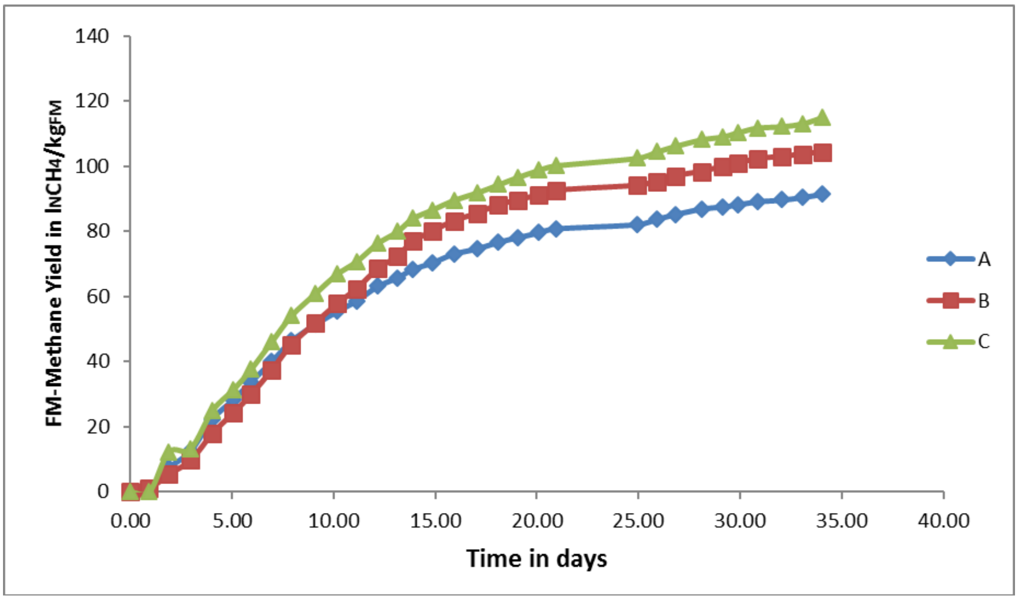

Fig. 5. Fresh mass methane yield

while treatment A was the least with the yield of 91.90 l_NCH_4FM (Fig. 5). [34] earlier reported that for some substrate such as barley and wheat straw, mechanical pretreatment improved methane produced while for some substrate likemaize stalk and rice straw mechanical pretreatment did not have positive impact on methane yield. From this research it can be deduced that size reduction did not have effect on the fresh mass methane yield from groundnut shell. As a result of this, groundnut shell can be said to be in the same category with maize stalk and rice straw that mechanical pretreatment did not had positive effect on their methane yield since size reduction is one of the mechanical pretreatment methods.

3.2.4 Effect of size reduction on organic dry matter methane yield

In terms of organic dry matter methane yield, cumulatively at the end of the 35 days, treatment B produced the highest yield with the yield of 298.4 l_NCH_4, followed by treatment A 222.4 l_NCH_4 while treatment C has the least yield 211.3 l_NCH_4 (Fig. 6). Treatment B and C aligned

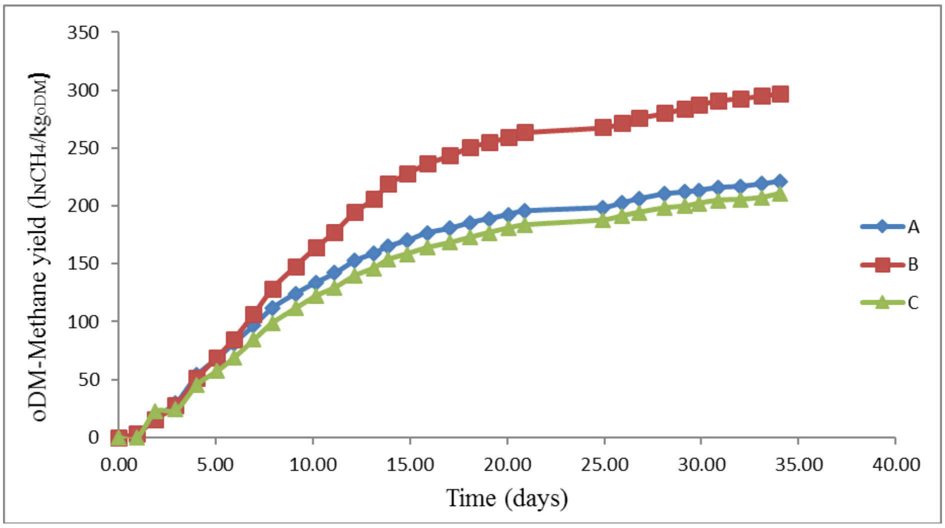

Fig. 6. Organic matter methane yield (ODMMY)

Table 4. Composition of biogas generated by percentage volume

Parameters	**CH_4 (%)**	**CO_2 (%)**
Samples		
A	64.25	35.75
B	65.05	34.95
C	66.60	33.40

with what [26] reported in their research. They reported that treated groundnut shell produced 64% methane while the untreated groundnut shell released 60% methane. [28,32] reported that there is a particular size limit whereby size reduction may not have substantial effect on the organic matter methane yield. Comparing the organic dry matter methane yield from the treatment A, B and C; treatment B can be said to be the best size for anaerobic digestion in order to have maximum yield of organic dry matter methane.

3.3 Quality of Biogas Produced

Some samples of the gas produced from each of the three treatments were analyzed and the mean values of the composition of biogas were given in Table 4. It can be seen clearly that all the treatments have a very good methane content going by the values obtained. This shows that the experiment was very tight and oxygen was unable to react with the system. Treatment C has the highest methane content. The size actually improved methane yield during biogas production process. This may be due to the fact that it still holds some of its carbon/nitrogen content and the high organic dry matter since it is a bit far from powdery form. Also, treatment B has a high quality methane content of 65.05%. This also was as a result of having high carbon/nitrogen content and high organic dry matter that were still holds together in the substrate during the experiment. As the treatment is moving towards the powdery form, the percentages of methane gas contents were reducing. Treatment A that was the smallest among all gave the least percentage of methane content 64.25%. This indicates that as the substrate tends to powdery form, the carbon/nitrogen ratio and organic dry matter were reducing. The methane percentage recorded for both treatments from this research are in the same range with what [26,29] recorded for treated groundnut shell and higher when compared with [5] 55 - 75% methane and [35] who recorded 55 - 65% methane. It shows that all the three sizes (2, 4 and 6 mm) produced good methane content and can be used when selecting substrate size for anaerobic digestion in terms of methane yield.

4. CONCLUSIONS

From this experiment, it can be concluded that size reduction had effect on biogas and methane yield of groundnut shell, but there is a limit to which size reduction will not have positive effects on organic dry matter biogas yield, fresh mass biogas yield and organic mass methane yield and there is another set limit for fresh mass methane yield.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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