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EFFECT OF THE NUTRITIONAL COMPOSITION OF FRUIT WASTES ON METHANE GAS PRODUCTION AND ENERGY POTENTIAL

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Abstract

Nutrients have been considered the main factor affecting microorganisms responsible for methane gas production during anaerobic digestion processes. In this study, the nutritional composition of some fruit wastes; mango (M), watermelon (W), pawpaw (P), their effects on methane gas production, and resulting energy values were assessed. Substrate samples for anaerobic digestion where prepared into various slurry treatments; M, W, P, WM, PW, MP, MWP and CONTROL. Proximate compositions of the substrates were determined using standard methods of the Association of Official Analytical Chemists, while the mineral element composition were assayed using Perkin Elmer atomic absorption spectrophotometer (Model 306). Qualification of methane gas yields were by Exibd I Portable Multi-Gas Analyzer (Model 160204001). The energy values of the methane gas were determined using standard equations. The nutritional analysis revealed that the substrates had high amounts of nutritive contents suitable for methane gas production, however, pawpaw substrate contained a higher level of cellulose compared to the other two fruit wastes. At the end of the process the total methane gas yields from the different fruit waste treatments and the positive CONTROL (Cow dung) treatment were respectively 86.8cm^3, 232.8 cm^3, 0.0 cm^3, 309.4 cm^3, 103.2 cm^3, 56.2 cm^3, 263.2 cm^3 and 252.2 cm^3 from M, W, P, WM, PW, MP, MWP and CONTROL, each having energy value estimations of 62600 kJ/m^3, 209600 kJ/m^3, 0 kJ/m^3, 274400 kJ/m^3, 211200 kJ/m^3, 69400 kJ/m^3, 284400 kJ/m^3, and 97200 kJ/m^3. The energy potential of the methane gas produced from Watermelon treatment and other treatments made especially with watermelon waste were appreciably higher, if harnessed, can contribute immensely to the development of renewable energy in Nigeria.

Keywords: anaerobic digestion; energy values; fruit wastes; methane gas; renewable energy

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1. Introduction

Organic wastes such as plant and animal based materials make up a huge portion of the total wastes generated globally. Moreover, the traditional methods (such as incinerating or dumping) employed in the maintenance of organic wastes are not cost effective nor sustainable (Elhaggar and Omar, 2017). In addition, global concerns about climate change has triggered the search for new natural materials that will be amenable to processing, to substitute fossil fuel. Production of methane gas from organic wastes, is an effective two-pronged method of generating alternative energy and managing organic wastes in the environment.

Furthermore, Nigeria as a developing country is recently confronted by a staggering demand for energy with supplies that may not meet future demands, especially if a major supplier "interrupts" service. Such an interruption by the Nigerian National Petroleum Corporation (NNPC) in May/June 2016 led to an energy rush and subsequent supply problems that brought about a rise in the prices of fuels, endless queues at the fuel stations, hike in transport fare,

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untold hardship and poverty. This situation calls for rapid measures to be taken in order to provide alternative energy sources to the Nigerian populace and methane gas could serve as one of such alternatives since it happens to be a renewable and sustainable energy source.

When digestible wastes get disposed of in garbage dumps, they would ultimately undergo microbial degradation and oftentimes in the absence of molecular oxygen, resulting in a landfill gas generation. In this case, the gas will in the long run, integrate into the aerosphere and contribute to local smog, thus, adding to worldwide environmental problems (Vazoller et al., 200l). Rather than permitting the dumpsite gas to escape into the aerosphere it can be trapped, transformed and utilized as a vital source of energy.

In order to manage organic wastes in the environment like fruit residues which have high water contentefficiently, anaerobic digestion is the best technology to be employed (Asquer et al., 2013). The generation of methane gas when anaerobic degradation of biological material takes place, is dependent on the nature of raw material added to the anaerobic digesters (Bouallagui et al., 2003) as methane-forming microorganisms have several enzyme systems which require trace mineral elements that are different from those of other bacteria (Gerardi, 2003).

Watermelon, mango and pawpaw are among the many fruits native to the Nigerian society. Watermelon in particular contains 68% palatable pulp laced with 2% small-sized seeds and about 30% rind (Abu-Hiamed, 2017). Although, mango also has an edible pulp, it has, however, a stony seed kernel that form a fairly large proportion of the fruit (9-23%) with an outer fibrous skin (Elgind, 2017). Pawpaw on the other hand, is composed of a smooth skin (12%) that is yellow at maturity but green while young, 79.5% sweet pulp and 8.5% seeds (FAO, 2003). In addition, the rind of an unripe pawpaw is very rich in latex and papain (Kumar, 2004).

In the worldwide market, fruits are amongst the most essential trading goods (Wikandari et al., 2014). As the production of fruits increases every year, so does the generation of fruit wastes. Besides, the poor storage culture and lack of adequate preservation facilities in Nigeria increases the vulnerability of fruits to spoilage and deterioration. The accumulation of fruits wastes creates serious environmental problems such as foul odors, dumpsite gas generation, as well as attracting flies and rats.

This study was aimed at detemining the nutritional composition of some fruit wastes; mango (M), watermelon (W), pawpaw (P), their effects on methane gas production, and resulting energy values. In addition, co-digestion of the fruit wastes were carried out in other to assess the synergetic effect of combined treatments; (WM, PW, MP, MWP) on methane yields.

2. Material and methods

2.1. Determination of nutritional composition of substrates

Proximate and mineral compositions of the substrates were determined using standard methods as described by AOAC (2007). The tests were conducted in triplicates and the mean values reported.

2.2. Estimation of proximate composition

The proximate composition considered include carbohydrate, fibre, fat, protein, nitrogen (N), carbon (C), ash content, volatile solid (VS), moisture content, total solid (TS), lignin and cellulose.

2.3. Estimation of mineral elements

A Perkin Elmer atomic absorption spectrophotometer (Model 306) with a digital readout was used to determine the elemental compositions of the fruit wastes in this study as described in the instruction manual of the instrument. The elements determined with their respective wavelength and lamp current include; 766 nM, 0.7 mA (Potassium), 550.0 nM, 0.2 mA (Sodium), 422.6 nM, 0.7 mA (Calcium), 285.2 nM, 0.7 nM (Magnesium), 240.8 nM, 0.2 mA (Iron), 213.9 nM, 0.7 mA (Zinc), 324.7 nM, 0.7 mA (Copper), 279.5 nM, 0.7 mA, (Manganese) and 660.0 nM, 0.7 mA (Phosphorus). The process involved the preparation of an acidic solution of inorganic elements in the samples after removal of organic matter by wet oxidation, with 2.0 g of samples digested with a mixture of concentrated Nitric acid and Per-chloric acid. The digest got was sprayed into the flame of the atomic absorption spectrophotometer and we measured the absorption of each of the elements at their specific wavelengths using the elemental lamps and filter that match the different elements.

2.4. Preparation of slurries for anaerobic digestion

Substrate samples for anaerobic digestion were prepared into various slurry treatments; mango (M), watermelon (W), pawpaw (P), watermelon + mango (WM), pawpaw + watermelon (PW), mango + pawpaw (MP), mango + watermelon + pawpaw (MWP) and CONTROL (cow dung) as described previously (Anika et al., 2019). The anaerobic digestion was held at a 45 days retention.

2.5. Percentage methane yield

Percentage methane from the gas yields of the various treatments were analyzed using Exibd I Portable Multi-Gas Analyzer (Model 160204001) connected by a pipe to the gas outlet tap and the gasflowed into the analyzer which analyzed the quantity of methane and carbon dioxide, produced in percentage, while the quantities of hydrogen sulfide, carbon monoxide and hydrogen where given in ppm as describe by Zhang et al. (2015).

2.6. Energy value estimation

The heat production rate and the energy content of the gas generated were determined using the methods described by Ulbig and Hoburg (2002) where a specific volume of the gas 5×10^{-5} m^3 (50 cm^3) was ignited and used to raise the temperature of 5 mL of distilled water in a test tube containing mercury-in-glass thermometer (for recording the initial and final temperatures) at room temperature (26 °C) with respect to time recorded by a stop watch. The volume of the gas combusted, temperature change, and the time taken to raise the temperature were used to calculate the combustion rate and energy yield of the resulting gas using the following Eqs. (1-2):

$$Q = \frac{mC\rho\Delta\theta}{t}(kJ/Sec) \tag{1}$$

where: Q = combustion rate of the gas with respect to time m = mass of the distilled water heated; $C\rho$ = specific heat capacity of the distilled water heated (4.19 kJ/kg); $\Delta\theta$ = change in temperature; t = time; Cv = calorific value.

$$Cv = \frac{Q}{M}(kJ/m^3) \tag{2}$$

M = volume of combusted gas in m^3

2.7. Statistical analysis

Replicates readings from this study were subjected to analysis of variance (ANOVA test at 5% significance level. This was done using the trail version of the NCSS statistical software.

3. Results and discussion

The results of the study are presented in the figures and table below. Fig. 1 shows the proximate composition of the fruit wastes (Mango, Pawpaw and watermelon) studied. Cellulose was highest in pawpaw (4.60 mg/100 g dry matter) and least in mango waste though comparable with that obtained in watermelon. The ligin content of the three fruit wastes was minimal and comparable. Watermelon (W) fruit waste had the highest moisture content of 90.57% dry matter followed by pawpaw (P) with 83.50 mg/100 g dry matter and then mango (M) with 78.50%. The ash content of watermelon fruit waste was significantly ($P<0.05$) higher than that of the other two wastes screened. Watermelon fruit waste was richer in protein content than mango and pawpaw with a value of 12.64% dry matter when compared with 10.28% dry matter and 6.41% dry matter found in mango and pawpaw respectively. The fat (57.9%) content of watermelon was significantly ($P<0.05$) higher than the quantity (0.63 and 0.48% dry matter) obtained in mango and pawpaw, respectively. Fiber and carbohydrate were found in significantly ($P<0.05$) higher amounts in watermelon fruit wastes than in the other two fruit wastes studied. Values amounting to 7.39% and 13.01% dry matter of fiber and carbohydrate, respectively, were found in watermelon fruit wastes as compared with 3.52% and 1.47% in pawpaw and 2.95 and 4.12% dry matter in mango.

The results of the elemental compositions of the different fruit wastes are presented in Fig. 2. The potassium content was the highest (14.3-17.6 mg/100 g), followed by calcium (7.3-15.8 mg/100 g), phosphorus (7.4-13.4 mg/100 g) and the magnesium (8.5-10.3 mg/100 g). Furthermore, sodium and iron were present in minimal concentrations between 0.42-0.7 mg/100 g and 0.2-0.4 mg/100 g respectively, whereas zinc, copper and manganese were in trace amounts.

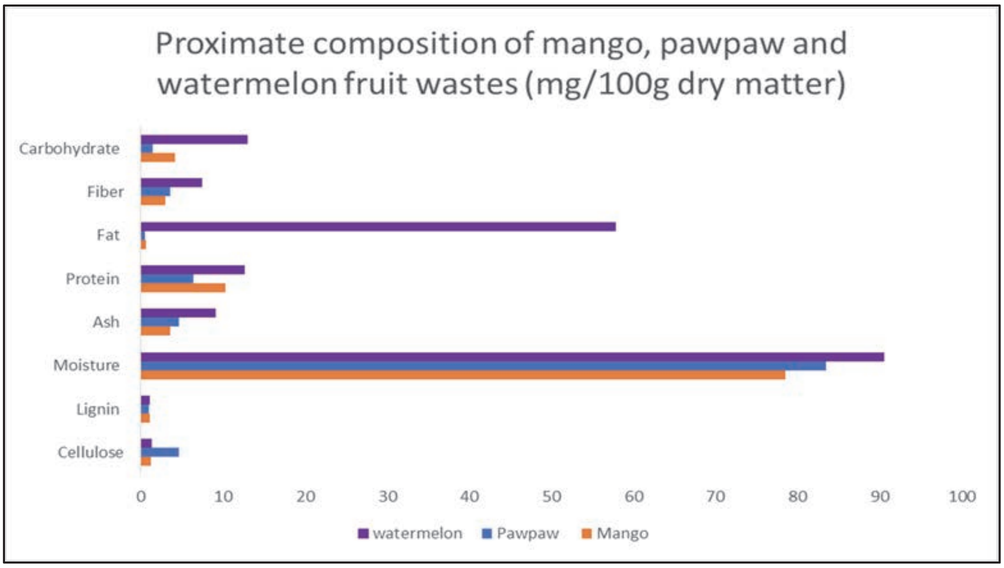

Fig. 1. Proximate composition of the organic and inorganic nutrients of the fruit wastes (%)

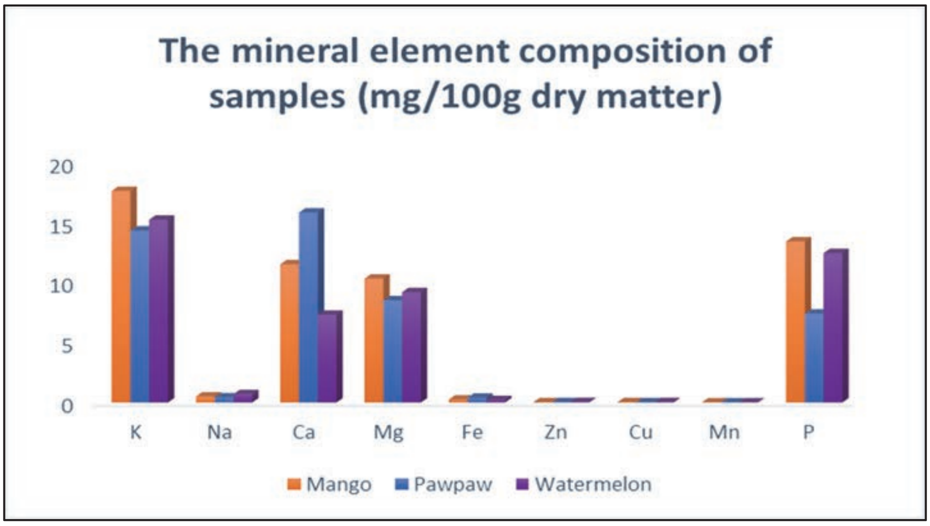

Fig. 2. The mineral elements composition of fruit waste samples (mg/100g dry matter)

Table 1 shows the summary of the chemical properties of the fruit wastes. The total solid (TS) content was 9.5, 16.5 and 21.5 in W, P and M substrates, respectively, while the volatile solid (VS) recorded were 90.94, 95.4 and 96.48 in W, P and M substrates respectively. The carbon to nitrogen (C: N) ratio of the watermelon substrate ranged between 25.8:1, on the other hand the substrate, P, had a high C: N ratio of 51.5:1, while the substrate M had a ratio of 32.7:1. Meanwhile the calorific value of the substrate was highest in W (623.23 kcal/100 g) followed by 62.6 kcal/100 g in M and 34.94 kcal/100 g in P.

Fig. 3. presents the results of the percentage methane yield in the anaerobic digestion of the fruit wastes is presented in Fig. 3. There was no methane yield at the early days of the anaerobic digestion process. However, from the tenth day, two of the anaerobic digestion treatments began to liberate some quantity of methane gas. The treatment MWP produced 6.20% and 9.20% while the treatment WM generated 1.40% and 12.40% after the 10th and 15th days of digestion respectively. However, watermelon fruit waste and the control samples gave yields of 4.0% and 13.60%, respectively, after 15 days and increased as the anaerobic digestion progressed. But, pawpaw fruit waste did not yield any methane gas throughout the digestion. The watermelon waste treatment produced the highest methane gas compared with the other single treatments studied, whilst the combined treatment (MWP) gave the highest methane gas yield overall though comparable with that obtained in the WM treatment. Fig. 4. presents the cumulative methane yields over the 45 days retention time, which was highest in the double substrate treatment WM (309.4). The value 263.2 gotten for the MWP treatment was comparable with those of the single watermelon treatment (232.8) and the control (252.2).

Fig. 5 shows the methane production rate over the 45 days retention time of the anaerobic digestion of the fruit wastes. There was a steady increase in methane production rate with slight fluctuations for the treatments MWP, WM and the control from the 5^{th} to 25^{th} days of the anaerobic digestion process. The production rate for the other treatments fluctuated throughout the process, although the production rate for MP was slightly constant. There was, however, a rapid increase in the production rate for the watermelon treatment between the 25^{th} to 30^{th} days.

Fig. 6 illustrates the effect of the calorific value of the fruit wastes on the cumulative yield of methane. Watermelon wastes had a calorific value of 623.23 kcal/100g and produced a high cumulative methane yield of 232.8 cm^3. Mango waste generated a moderate quantity (86.8 cm^3) of cumulative methane with a calorific value of 62.6 kcal/100g. We recorded no methane yield, however, for pawpaw waste, which had a calorific value of 34.96 kcal/100g. Fig. 7 shows the combustion rate and calorific value of the biogas generated at the peak of the methane gas (30^{th} day) production during the anaerobic digestion process. Of the single digestion, watermelon treatment compared to the control treatment (cow dung) had a higher calorific value of 209600 kJ/m^3, followed by mango treatment (62600kJ/m^3). However, no calorific value was measured for pawpaw treatment because we did not record methane yield for pawpaw waste treatment.

Table 1. Chemical properties of fruit wastes used

Sample	*TS%*	*VS%*	*TN%*	*TC%*	*C:N*	*pH*	*Calorific value (kcal/100g)*
Mango	21.5	96.48	1.64	53.6	32.7:1	5	62.6
Pawpaw	16.5	95.4	1.03	53	51.5:1	5.6	34.96
Watermelon	9.5	90.94	2.02	52.19	25.8:1	7.2	623.23

Values are means of triplicates readings. KEY: VS = Volatile solid, TS = Total solid, TC = Total carbon, TN = Total nitrogen, C: N = Carbon/Nitrogen ratio

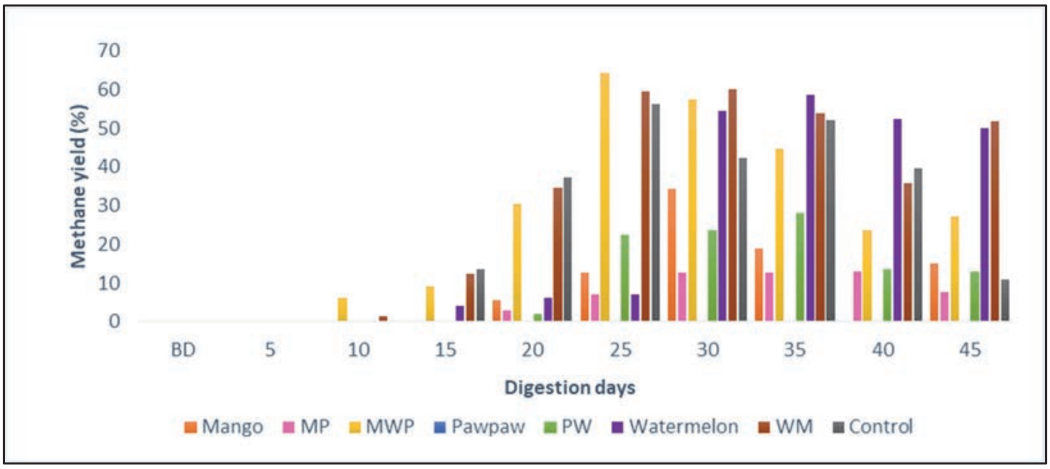

Fig. 3. Percentage methane yield of all treatments (*Key: MP= Mango waste + Pawpaw waste, MWP = Mango waste + Watermelon waste+ Pawpaw waste, WM = Watermelon waste + Mango waste, PW = Pawpaw waste + Watermelon waste*, BD = Before digestion)

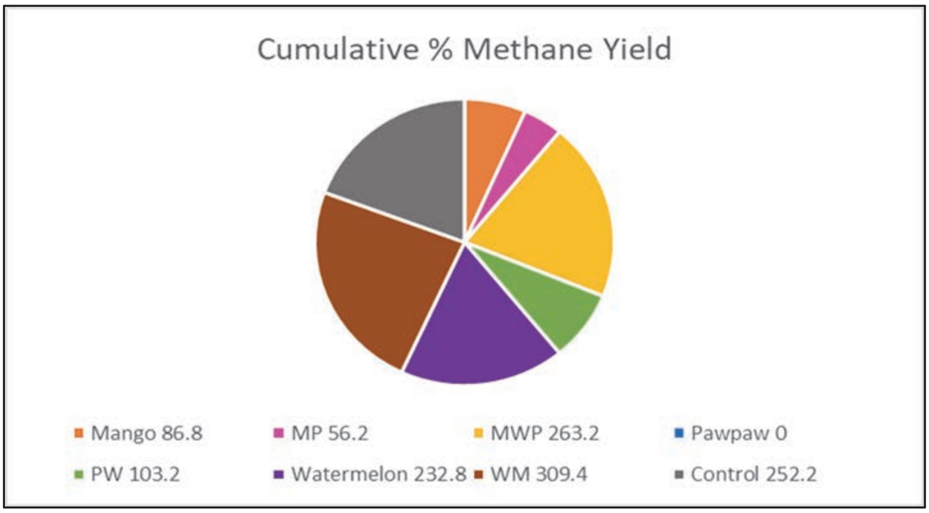

Fig. 4. Cummulative percentage methane yield of all treatments (*Key: MP= Mango waste + Pawpaw waste, MWP = Mango waste + Watermelon waste+ Pawpaw waste, WM = Watermelon waste + Mango waste, PW = Pawpaw waste + Watermelon waste*

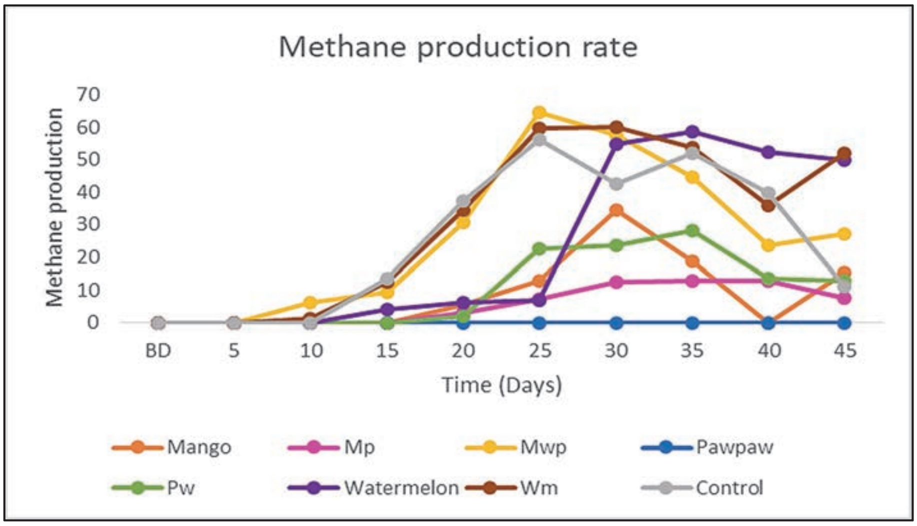

Fig. 5. Methane production rate in 45 days *(Key: MP= Mango waste + Pawpaw waste, MWP = Mango waste + Watermelon waste+ Pawpaw waste, WM = Watermelon waste + Mango waste, PW = Pawpaw waste + Watermelon waste)*

According to the ASM (2011), nutrients are essential to any biological process. Nutrients play a significant role in influencing the performance of microorganisms involved in the breakdown of organic matter into useful energy. The proximate composition of the fruit wastes presented in Fig. 1 showed that the wastes contained adequate organic matter that are convertible into energy, but in varying proportions with watermelon having the most balanced nutritional content while pawpaw waste contained the highest value of the compound cellulose which according to Boontian (2014) degrades slowly and incompletely. In addition, hydrolysis of hardly decomposable polymers like cellulose, are regarded as one of the conditions that places a limit on an anaerobic bio-degradation rate (Zieminski and Frac, 2012). This could be one of the underlying causes of the poor performance recorded in the digester fed with only pawpaw substrate.

Mineral elements in trace amounts are essential for methane-forming microorganisms as they have several enzyme systems which require it, however, at high concentrations they may produce toxic effects on the microbial population. In this study, the measured concentrations (Fig. 2) of the mineral elements present in the various substrate were not above the thresholds that can inhibit methane gas formation and is in conformity with that measured by other researchers (Bozym et al., 2015; Matheri et al., 2016).

The TS contents of the fruit wastes on Table 1 and their percentages in VS shows the fraction of the organic components in them that are convertible into methane gas by microorganisms. Total solid (TS) content values of 9.5, 16.5 and 21.5 respectively, were measured in W, P M substrates and according to the work of Orhorhoro et al. (2017) on the impact of substrate properties on biogas yield, the substrate with 10.16% TS gave the most yield, no wonder watermelon substrate in this study gave a high yield compare to the other two single treatments studied. Volatile solid (VS) values of 90.94, 95.4 and 96.48 respectively, were estimated in W, P M substrates, and were also within the range reported by Orhorhoro et al. (2017).

We observed that the C:N ratio of pawpaw waste (51.5:1) was higher than the optimum range (25-30:1) required for successful methane gas formation, meanwhile, watermelon and mango substrates fall within this standard range of 25.8:1 and 32.7:1 respectively. In an earlier study by Wang (2014) on the effects of temperature and carbon-nitrogen (C:N) ratio on the performance of anaerobic co-digestion of dairy manure, chicken manure and rice straw, a maximum methane gas yield was achieved when the C/N ratio was at 25 and 30.

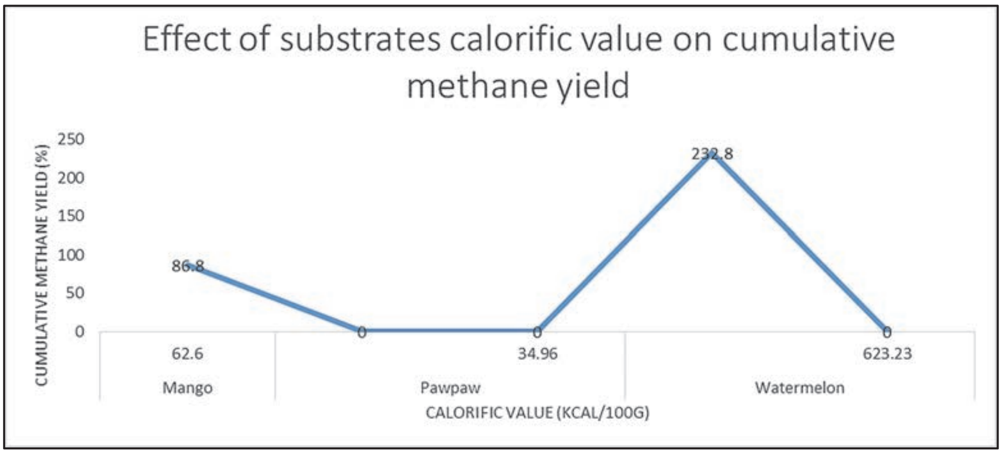

Fig. 6. Effect of calorific value of substrates on cumulative methane yield

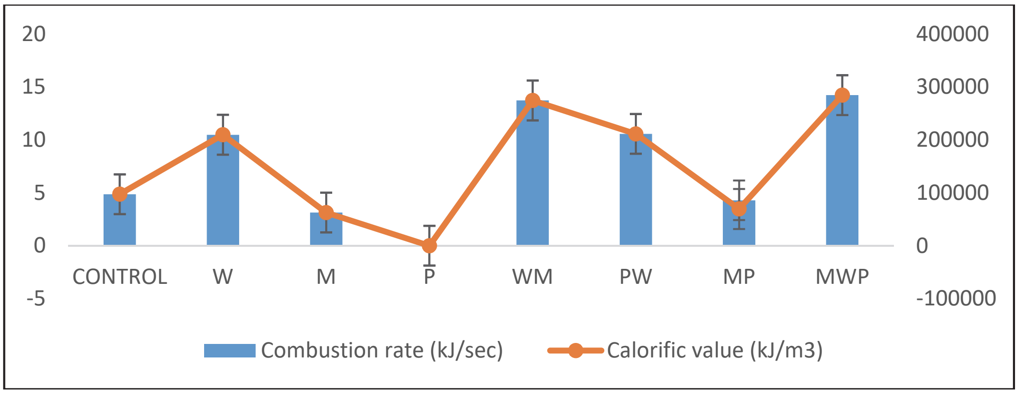

Fig. 7. The combustion rate and calorific values of the resulting gas (Key: W = Watermelon waste, M = Mango waste, P = Pawpaw waste, WM = Watermelon waste + Mango waste, PW = Pawpaw waste + Watermelon waste, MP= Mango waste + Pawpaw waste, MWP = Mango waste + Watermelon waste+ Pawpaw waste)

The high C:N value of the pawpaw substrate is indicative of a very low concentration of Nitrogen that is an essential growth component for the methane-formers. This could account for the failure if methane generation in the pawpaw single substrate treatment.

From the results shown on Fig. 3, we observed that of the three fruit wastes studied, watermelon waste gave the highest percentage methane yield (58.6%), the reason may be because watermelon waste displayed a balanced nutritional content compared to the other two fruit wastes investigated (Fig. 1 and Table 1). Also, the co-digestion of watermelon waste with other wastes studied produce better yields compared to other co-digestion mixes.

Watermelon cumulatively produced the highest methane gas (232.8%) for the single treatments, but increased by 76.6% when co-digested with Mango and by only 30.4% when co-digested with both pawpaw and mango (Fig. 4). In an earlier study, enhanced methane production was achieved using anaerobic co-digestion of with combined fruit waste, they observed that there was a significant increase by 31% in the volume of cumulative methane generated. They concluded that co-digestion provide better nutrient balance for microbial communities involved in anaerobic digestion process (Hallaji et al., 2019).

In our study, during the early days of digestion the production rate was slow but later increased rapidly in the combined substrates WM and MWP after the 15th day and continued to the 25th day, production rates however, remain fluctuated at other points. Speda et al. (2017) enhanced bio-methane production rate of anaerobic digestion of lignocellulolytic wastes with enzymes. In their study, they showed that biomethane production was rate was faster in the treatment co-digested with enzyme than that without enzymes. In addition, the almost steady rise in methane production rates displayed by the combined treatments WM and MWP in Fig. 5 when compared with the fluctuations observed the other treatments suggests that the nutrients in them were balanced and readily biodegradable.

Fig. 6 shows that watermelon waste has a very high stored energy (623.23 kcal/100g) compared to mango (kcal/100g) and pawpaw (kcal/100g). This proves that a high substrate calorific content level does support a level high methane yield. Kozłowski et al. (2019) reported maize straw with a calorific value of 55,567 Jg^{-1} to generate 207.75 m^3 Mg^{-1} cumulated methane.

Watermelon substrate which had a very high calorific value (623.23 kcal/100g) produced methane gas of a corresponding high energy value (209600 kJ/m^3) as seen in Fig. 7. Zieminski and Franc (2012) inferred that 1 m^3 of biogas with an energy values of approximately 25.9 MJ/m^3 may supplant 0.77 m^3 flammable gases of roughly 40 MJ calorific value, 1.1 kg hard coal of 24.4 MJ calorific value or 2 kg firewood of 13.3 MJ energy value. In addition, Wang et al. (2014) revealed that to achieve the C: N ratio that is most favorable for an anaerobic digestion, the raw organic substrate having high C: N ratio are mixed with substrates of low C: N. This we carried out in our study and may account for the success recorded when we digested pawpaw substrate in combination with other substrates especially watermelon waste.

In an earlier study, on the estimation of the electrical energy potential of methane gas from anaerobic digestion of canteen food waste samples, 47.38 m^3 and 30.72 m^3 of methane respectively gave an energy yield of 0.034 MJ and 0.029 MJ per day (Suhartini et al., 2019). Compared with our findings, the heat energy estimated per second, from 5×10^{-5} m^3 volume of the methane generated from the anaerobic digestion of the fruit wastes were 209,600 kJ and 62,600 kJ respectively, for the single treatments watermelon and mango, while, we estimated 274,400 kJ, 211,200 kJ, 69,400 kJ and 284,400 kJ respectively, from the combine treatments WM, PW, MP and MWP. The finding in this study, shows that methane gas from mango and especially watermelon fruit wastes have great potential as heat energy sources when anaerobically digested singly or in combination.

4. Conclusions

The study aimed to determine the impact of the nutritional composition of some fruit wastes and their combination on methane gas production and the results presented in this study show that the nutritional composition of each fruit waste material affected the resulting methane yield. Therefore, to achieve a high methane yield from any organic waste processing, the substrate used must have balanced nutritional properties. The finding in this study, shows that methane gas from mango and especially watermelon fruit wastes have great potential as heat energy sources when anaerobically digested singly or in combination. In addition, since the co-digestion of watermelon waste with other wastes studied produced an appreciable quantity of methane gas characterized by a high energy value, watermelon wastes would be useful in achieving high methane yields during anaerobic digestion processing.

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