Evaluation of the Influence of Size Reduction on Methane Production of Orange Peel Waste samples at Ambient Temperature

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Abstract: Biogas production from four batch digesters containing varying mixture of cow dung and Sweet and bitter Orange peel waste was studied for a period of 21 days at ambient temperature. The maximum yield per Kg of dry solid was attained with the mixtures of cow dung and fruit waste. It was further observed that the highest biogas yield of 650 ml was recorded for sweet orange peel waste of small particle size and the difference in the production of biogas to a large extent depends on the nature of the substrate and other factors such as pH and C: N ratio etc. Throughout the entire anaerobic digestion process, the ambient temperature for digestion ranged from 26°C to 32°C and there was little temperature variation effect on biogas production once biogas production and refinement of the processes.

Keywords: sweet orange, bitter orange, volatile solids, particle size, carbon: nitrogen, storage days

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I. Background of The Study

Biofuel is a fuel that is produced through contemporary biological processes, such as agriculture and anaerobic digestion, rather than a fuel produced by geological processes such as those involved in the formation of fossil fuels, which include coal and petroleum, from prehistoric biological matter. Biofuel can be derived directly from plants, or indirectly from cultural, domestic, and/or industrial wastes. Renewable Biofuel generally involve contemporary carbon fixation, such as those that occur in plants or microalgae through the process of photosynthesis. Other renewable processes are made through the conversion of biomass (referring to recently living organisms, most often referring to plants or plant-derived materials). This biomass can be converted to convenient energy-containing substances in three different ways: thermal conversion, chemical conversion, and biochemical conversion. However, information is still inadequate about reliance and promising process for the treatment of organic solid waste. It is suggested that an economically viable anaerobic digestion require detailed feasibility study on the available substrate, local condition for the optimization of accurate process parameters which can improve production of biogas. The focus of interest today in the optimization of the volume of methane includes among others studies on substrate concentration, pH, pre-treatment factors that influence action of acidogenic and mesogenic bacteria etc.

II. Introduction

Due to its high biodegradability, the anaerobic digestion (AD) of organic waste could play a role as an unconventional non-renewable source of energy. A great deal of research has been conducted to study biogas production from different mixtures of organic waste (Bouallagui 2005; Berlian et al. 2013; Mizuki,1996; Angelidaki etal,2006), Past research has shown that on average 200-400 ml of biogas can be produced per gram of volatile organic solids (Kenneth 2001). The productivity of the biogas is affected by the pH of the reactor, the organic loading rate, the temperature of the waste, the type of organic waste used, and the mixture of the reactor and water content (Kaprajula and Rintala,2006; Persson etal 2006; Bouallagui et al. 2005). The biogas produced by the AD process contains 60% methane and 40% CO₂ as well as traces of other gases such as hydrogen sulfide, ammonia, nitrogen, and hydrogen. The anaerobic conversion of organic waste to biogas goes through four main steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis, with the latter responsible for methane gas production. Accordingly, the digestion time, called hydraulic retention time (HRT), is a crucial

parameter in maximizing the quantity of the biogas and its methane content. Accordingly, the methane composition of the biogas is expected to increase with time, reaching a maximum value at which it is recommended to withdraw the biogas for energy generation purposes. In their paper, the maximum concentration of methane gas in the biogas produced from potatoes, zucchini, orange peels, rice, and tomatoes was determined. The effect of mixing such vegetables with sludge and catties manure as well as the digestion temperature and the time at which the maximum is reached was also being investigated.

In view of several environmental factors responsible for the production of high volume of biogas, researchers are interested on way to reduce the time in biogas production using suitable substrates that contain the required nitrogen, carbon and fiber using appropriate treatment process with reactors that are appropriate. With that in view this work examines the aspect and particle size of fruit waste stored over a period of seven days so as understand the role of methagenic bacteria to utilize substrate of different C/N ratio and particles size. The changes in constituent of the peel stored under ambient condition with respect to biogas production potentially are assessed at one day, four and seven days of storage. Storage days are used as the blocking factor.

III. Materials and Method

3.1 Sample collection/preparation

Orange peel waste samples (sweet and bitter) from were dried at 1, 4 and 7 day intervals for the present study. Samples were collected from Girls'Hostel Dustbin and handpicked and utmost care was taken to ensure that just a particular type of orange was used.

3.2 Sample Analysis

Sample peels were analyzed at 1, 4 and 7 days intervals for total solid, volatile solid, moisture content, total organic carbon, and total nitrogen content was determined by kjeldahl method while the carbon fiber by AOAC (2005).

3.3Preparation of the Slurries

The mode of feeding used was discontinued feeding (batch feeding). This simply means the digester is loaded at once and maintaining a closed environment throughout the retention period. Twelve different digesters were prepared down for loading. The cow dung slurry was prepared by mixing with water in 1:5 proportions and sieved to remove coarse particles. The orange peel slurry was prepared by mixing the peels in 1:5 proportions. The cow dung and orange peel slurry were mixed in 1:1 proportion and the mixture was poured in the reactor. Three experimental set-ups were made each with 4 digesters containing 200g of orange peel waste of different particles size, 200g of cow dung and 600ml of water and mixed thoroughly. The procedures taken during feeding of the digester are as presented in next section.

3.4 Experimental Set-up (bioreactor set up)

A laboratory bioreactor was set up and experiment carried out in a 5 liter digester constructed using a plastic container with two openings. The opening was drilled and fixed with a value. First opening was used for inlet input materials and second for output digested material. The other opening is drilled to enable the biogas to flow from the digester. The opening was connected with 0.5 diameter bobber piping to a water container where biogas push the water by displacement which is the amount of gas produced. The digester is operated at around 26° C to 37° C at pH 6.8 with different amount of peels waste (500g to 1kg).

3.5 Reactor Operation

The peel waste slurry was fed into the reactor from the top by a one way funnel and equal quantity of the digestate is withdrawn for the physicochemical analysis. The cow dung slurry was prepared by mixing water in 1:5 proportions and sieved to remove coarse particles. The cow dung slurry and peel waste slurry are mixed in proportion and poured into the reactor. Nitrogen gas was purged through the reactor to remove oxygen toxicity and allow digestion of substrate. Biogas yield was determined at 37^{0} C at pH 6.8 while chemical analysis of total solid, volatile solid, moisture content, total nitrogen, pH value are measured at the beginning of the test and at intervals of 2,5,10,15,21 days). The volume of gas generated was determined every other day, and the reactor content was mixed by 100% recirculation from top to bottom shaking every other day.

3.6 Determination of Total Organic Carbon (TOC)

Total Organic Carbon (TOC) is the amount of carbon found in an organic compound and is often used as a non-specific indicator of water quality. TOC may also refer to the amount of organic carbon in sample. TOC was determined by the method of Schumacher (2002).

3.7 Determination of Moisture Content

The procedure of Christensen (2003) was adopted in determining the moisture content of the substrate.

3.8 Determination of Total Solid

The total solid present in the sample was obtained according to the method of Zhang (2007).

3.8 Determination of Volatile Solid

The volatile solid content of feed materials was determined as described in APHA Standard Methods (1995). The oven dried samples used for the determination of total solids content were further dried at 105°C for 3hrs in a muffle furnace and allowed to ignite completely. The dishes were then transferred to desiccators for final cooling. The weight of the cooled porcelain dishes with ash were taken by the electronic balance. The volatile solids content of the sample were calculated using the formulas:

 $VS = (Wd-Wa/Wd) \times 100$

Where, VS is the volatile solids in dry sample, Wd is the weight (g) of oven dried sample; Wa is the weight (g) of dry ash left after igniting the sample in a muffle furnace.

IV. Results and Discussion

4.1 Characterization of Dried Orange Peel Samples

The orange peel wastes were characterized for TS, VS, pH, C/N ratio and moisture content, the results obtained are given in Tables 1 and 2. When the moisture content was examined, there was sharp decrease from 62.14% to 15.51% for the sweet orange, and 49.21% to 9.9% for bitter over a period of 7days. The differences in water content is due to substrate chemical characteristic and biodegradation rate as observed by Kossmann,W etal (2013). The amount of water though significantly different for the dried materials, supports the observation that the water present in each sample upon drying makes possible the movement and growth of the bacteria facilitating the dissolution and transport of nutrient. In addition, the water reduces toughness of fibers which account for mass transfer of particulate substrate (Limuwoski et al, 2000).

 Table 1 %Nitrogen and Organic Carbon content of dried Orange Peel Waste before digestion.

S/No.	Days	Total Organic Carbon		Nitrogen content		C : N	
		Sweet Peel	Bitter Peel	Sweet Peel	Bitter Peel	Sweet Peel	Bitter Peel
1	1	33.66	31.44	0.89	0.87	34:1	31:1
2	4	31.60	27.67	0.84	0.85	32:1	28:1
3	7	30.68	26.62	0.76	0.79	31:1	27:1

S/No	Days	Total solid		Volatile solid		pH		Moisture content	
		Sweet	Bitter	Sweet	Bitter	Sweet	Bitter	Sweet	Bitter
1	1	43.01	40.50	48.77	38.68	5.15	5.05	62.14	49.21
2	4	40.49	30.54	38.75	28.63	5.09	4.99	40.99	28.44
3	7	31.21	28.14	29.38	26.23	4.94	5.08	15.51	9.90

Where the total solid was examined to determine how decrease in water content affect level of microbial activity. From the results there was no sharp decrease in PTS with drying time to suggest the slurries are acidic and would therefore not affect the increase of volume of biogas.

However, when the pH of the substrate was examined at interval of 1, 4, and 7 days, the results in Table 4 indicated that the material is acidic and below the optimum required for biogas production. The highest recorded pH for both bitter and sweet peels was 5.15 and 5.05 respectively.

Where the carbon and nitrogen contents were examined for the two types of orange peel, the % carbon was significantly high and fall as drying continued. However the amount of nitrogen was insignificant and the highest recorded value was 0.89% (sweet orange) to suggest that C: N ratio was overall to be compared to other vegetables materials. Studies of methanogenic bacteria from the report of Schriftenreihe (2010) showed that the C: N ratio of substrates is significant in optimization of biogas and when it is high the addition of co-digestion support is needed to produce high volume of biogas.

4.2 Optimization of Biogas

Biogas production from cellulose biomass can be enhanced using various pre-treatment processes such as grinding, drying, use of nutrients, co-digestion with other substrates etc. When the cellulose is dried and grinded, the process increases partial disintegration of plant cell wall to allow hydrolysis of the feedstock. The breakdown of cell wall as a result of impact could also improve anaerobic digestion. Although no increase may substantially be observed there is always early onset of biogas production. Studies revealed that the generation of biogas from the orange peel depends on the physical state of substrates which allows early onset of gas production. This is consistent with the report of Schumacher (2002).

When daily production of biogas was monitored for 21 days at room temperature for the orange peel waste of different particles size (2mm and 5mm) and different C: N ratio, the results in Figs 1-3 were obtained. The average volume of biogas generated by orange peel was highest for Sweet (2mm, 189.05ml, 1 day) while bitter had 113.81ml, (2mm, 4 days). However in terms of the amount generated per day, peels of small particles size produced more gas on the average.



Fig 1.Production of biogas from peel waste dried 1day.



Fig 2.Production of biogas from peel waste dried 4days.



Fig 3.Production of biogas from peel waste dried 7days.

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It is further observed that there is general trend in the variation of gas production by two types of peels irrespective of particles size. At first stage, the biogas productions increase because hydrolysis and acidogenesis reactions are very fast as bacteria utilize the waste more rapidly. After a few days the gas productions fall as acid increase in the digestate. At this stage the methanogenic bacteria utilize the fatty acids to produce the biogas is deactivated due to high acid condition of slurries. The gas yield starts to fall until there was no yield. What was significant about the study was that the slurries remain acidic throughout the bio digestion time and the bacteria was still active to produce more gas without adjusting the pH to the required level to power the methanogens for methane production. The inability to produce biogas after 15 days for all samples of different particles sizes or drying periods suggests that high volume of C: N ratio has a negative effect in the production of biogas. Since the nitrogen was consumed rapidly by methanogens to meet their protein requirement and no longer react on the left over carbon content of the material, the result is low gas production. Based on the study of Markel (2010), the metabolic ability of methanogenic bacteria is possible to be optimized at C: N 8:20 depending on the substrate or in the case of vegetable conversion to methane, the reported C: N is 25:30. In this study, the average C: N ratio for the samples was 32:1 (sweet) and 28:1 (bitter) and is far inadequate for the production of large volume of biogas.

4.3 Factors Affecting Biogas Production

4.3.1 Carbon: Nitrogen Ratio

Carbon and Nitrogen ratio is very significant factor that affect biogas production. The results obtained for both dried peels waste samples have high C/N ratio and small amount of gas was produced within 12days which supports the observation of Alan et al (2009) and Alistair et al(2008), that substrates with high C:N ratio tend to produce little gas and can be co-digested with another low price materials or vice versa to bring C:N to the optimum range of 25-30. The variation of TOC and TON content during digestion of peel waste samples are given in Figs 4 and 5.



Fig4.Variation of % total organic carbon (TOC) during digestion of peel waste.





4.3.2 Particle Size

Production of biogas with respect to particles size was investigated and the results obtained are given in Figs 1-3. The volume of gas generated increased with decrease in particle size of peel because, large surface area is exposed to the hydrolyzing enzymes resulting too many intermediates that cannot be utilized by the slow methanogens but acetonogens which results in to acidic situation to commence biogas process. This finding agrees with the observation made by Palmwoski and Muller (2000) who studied the influence of anaerobic digestion by size of substrates.

4.3.3 PH

When the pH of the digestate was analyzed, the results in Fig 6 were obtained and pH decreased as digestion continued. Since the slurries remained acidic from the contribution of hydrolytic effect and the substrate, fast hydrolysis and acidogenesis reaction make the organisms utilize the waste more rapidly to produce gas but in small quantity. In the present study, the high acid condition does not favor the slow growing methanogens which are sensitive to pH range 6-6.8. The resultant effects is that no gas was produced after 15 days. This agree with the report of NallathambiGunaseelan, V(2004)who obtained the best optimized condition for biogas generation for methane bacteria best at pH 6-7.



Fig 6. Variation of pH during digestion of peel waste.

4.3.4 Total Solid

The relationship between the volume of biogas produced and percentage total solid was analyzed and the results are given in Fig 7. The relationship shows that a marginal increase in the %TS results is a geometric increase in the volume of biogas produced suggesting that a continual increase in the PTS at some point becomes immaterial to the increasing volume of biogas produced. This is possible because when %TS increases, the amount of water decreases, thus reducing the level of microbial action which then affects the amount of biogas particularly at higher values of %TS. When the sample was further analyzed, the %TS of slurries at 1, 4,7,11 days interval gave high %TS values and are acidic to suggest more reason why the volume of biogas produced could not significantly increase.





4.3.5 Volatile Solid

The volatile fatty acids are substrates for methanogenic bacteria and include acetate, propionate, butyrate etc produced in the acidogenic and acetogenic stages. However the accumulation of those acids leads to decrease in pH and methanogenic bacteria are not active in very high acid conditions and therefore reduce volume of gas generated. From the results in Fig 8, the condition of digester is acidic and as the reaction progress the pH decreased to 3.83 which requires stabilization with buffer in term of carbonate to raise pH to optimum value but and was not done and that slowed production of gas which eventually ceased after the 15th day.



Fig 8. Variation of % volatile solid (VS) during digestion of feel waste.

V. Conclusion

The study revealed that Biogas generation depends on the characteristics of the substrate as well as the pre-treatment process that allows fast hydrolysis and early generation of biogas. The present study revealed that the average volume of gas generated was influenced by both C: N ratio as well as the pH of the slurries. As the digestate became more acidic without addition of alkali, the methanogenic bacteria were less active and no gas was produced. From the outcome of investigation, it is suggested that orange peel waste can be co-digested with other substrate in order to improve on the nitrogen content and adjusting acidity to the desired pH of 6-7 that allow full utilization of cellulosic material.

Compliance With Ethics Requirement

This paper does not contain studies with human and animals

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Declaration of Interest

No conflict of interest

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