An Investigation into the Effect of Some Selected pH Control Chemicals {Ca(OH)$_2$, NaHCO$_3$ and CaCO$_3$} on Batch Digestion of Organic Fraction of Municipal Solid Waste: A Case Study of Jimeta Metropolis

Ojo Samuel[1*], Baba Mohammed[1] and Aaron K. Bakut[1]

[1]*Department of Chemical Engineering, Federal Polytechnic, P.M.B. 35 Mubi, Adamawa State, Nigeria.*

Authors' contributions

This study was carried out in collaboration between all authors. All the authors jointly designed the study, wrote the protocol and wrote the first draft of the manuscript and manage literature searches. Authors OS, BM and AKB managed the analyses of the study and literature searches. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

The large organic matter of solid waste such as agricultural and municipal solid waste offer great potential for biogas production. This work has been carried out to investigate the effect of some selected pH control chemicals on anaerobic digestion process which is expected to increase the yield of biogas from the digestion of organic fraction of municipal solid waste. The different pH control chemicals used in this work are NaHCO$_3$, CaCO$_3$ and Ca(OH)$_2$, which gave the following results (yield) 7350 cm^3/162.60 g V.S, 2500 cm^3/162.60 g V.S and 0 cm^3/162.60 g V.S of Biogas respectively in comparism with the controlled digester which yielded 600 cm^3/162.60 g V.S after digestion for a period of 30 days. The result obtained shows that NaHCO$_3$ is the most suitable to be used as a pH control chemical in comparism to the others and most effective in converting volatile solid contained in the organic fraction and equally served as the best buffer.

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Corresponding author: E-mail: femioctober22@gmail.com;

1. INTRODUCTION

In today's energy demanding lifestyle, the need for exploring and exploiting new sources of energy which are renewable as well as eco-friendly is a must. In the rural areas of developing countries, various cellulosic biomasses (cattle dung, agricultural residue, etc) are available in much quantity, which have a very good potential to cater for the energy need especially in the domestic sector [1].

This work focuses on municipal solid wastes (food wastes, agricultural wastes, treatment plant wastes special wastes etc) recycling by digestion using the anaerobic digestion process for resource recovery. It also focuses on the control of the pH level in the digestion process using some selected pH control chemicals.

Anaerobic digestion is the use of biological processes in the absence of oxygen for the breakdown of organic matter and the stabilization of these materials by conversion to methane (CH_4) and carbon dioxide (CO_2) gases and a nearly stable residue [2].

The control of pH is vital in that the acids produced during the digestion process tend to lower the pH of the digester liquor. However, ion bicarbonate equilibrium of the carbondioxide in the digester exerts substantial resistance to pH change. The resistance known as buffer capacity is quantified by the amount of strong acid or alkali added to the solution in other to bring about a change in pH. Thus, the presence of bicarbonate helps prevent adverse effects on microorganisms (methanogens) which could result from low pH caused by excessive production of fatty acids during digestion. Most organisms grow best under neutral pH conditions since other pH value may adversely affect metabolism by altering the chemical equilibrium or by actually destroying the enzymes [3].

Municipal Solid wastes (MSW) are wastes arising from human and animal activities that are normally solids and are discarded as un-usefull or unwanted [1]. It is a non-fluid type of wastes and this makes its handling and management relatively difficult, compared to the type of wastes that can flow from one location to the other, or even vaporize [4]. Thus municipal solid wastes can be describe as those wastes from human and animal activities including liquid wastes like paints, old medicines, spent oils etc.; and MSW contains large amounts of organic matter.

Anaerobic digestion is often considered to be a complex process, the digestion itself is based on a reduction process consisting of a number of biochemical reactions taking place under anoxic conditions [5]. Generally in an anaerobic digestion process, the rate limiting step can be defined as the step that causes process failure under imposed kinetic stress [5]. In other words, in a context of a continuous culture, kinetic stress is defined as the imposition of a constantly reducing value of the solids retention time until it is lower than the limiting value; hence it will result in a washout of the microorganism [6]. Most researchers report that the rate-limiting for complex organic substrate is the hydrolysis step [7] due to the formation of toxic byproducts (complex heterocyclic compounds) or non-desirable volatile fatty acids (VFA) formed during hydrolysis step whereas methanogenesis is the rate limiting step for easy biodegradable substrates [8].

The anaerobic digestion process proceeds in the absence of oxygen and presence of anaerobic microorganisms. The process occurs in three stages.

Hydrolytic and fermentative stage: This is the first step in anaerobic digestion process, it involves the enzyme-mediated transformation of insoluble organic materials and higher molecular mass compounds such as lipids, polyssacharides, proteins, fats, nucleic acid etc. into soluble organic materials i.e. to compounds suitable for the use as source of energy and cell carbon such as monosaccharides, amino acids and other simple organic compounds. This step is carried out by strict anaerobes such as bacterides, clostridia and facultative bacteria such as streptococci etc. [9]. It is commonly found that hydrolysis particularly of complex polysaccharides is the rate limiting step [10].

Acetogenic or Acid forming stage: In the second stage, acetogenic bacteria also known as acid formers, convert the products of the first phase to simple organic acids, carbondioxide and hydrogen. The principal acids produced are the acetic acid (CH_3COOH), propionic acid ($CH_3CHCOOH$), butyric acid ($CH_3CH_2CH_2COOH$), and ethanol (C_2H_5OH). It is important that the organisms which carry out the

anaerobic oxidation reactions collaborate with the next group, the methane forming microorganisms; this collaboration depends on the partial pressure of the hydrogen present in the system. Under anaerobic oxidation, protons are used as the final electron acceptors which lead to the production of H_2. However these oxidation reactions can only occur if the partial pressure of hydrogen is low, which explains why the collaboration with the methanogens is very important since they will continuously consume the H_2, to produce methane. Hence during this symbiotic relationship inter-species hydrogen transfer occurs [11]. This stage likewise takes place in about a day. The product formed during the acetogenesis are due to a number of different microbes such as *SyntrophobacterWolinii*, a propionate decoposer and *Sytrophomonos Wolfei, a* butyrate decomposer. Other acid formers are *Clostridium Spp, Peptococcusanaerobes, lactobacillus and actinomyces* [2]. An acetogenic reaction is shown below:

$$C_6H_{12}O_6 \text{ ----------------------- } 2C_2H_5OH + 2CO_2$$

Methanogenic or methane forming stage: In the methanogenic phase, the production of methane and carbon dioxide from intermediate products is carried out by methanogenic bacterial under strict anaerobic conditions. Methanogenesis is a critical step in the entire anaerobic digestion process as it is the slowest biochemical reaction of the process [7].

The methane forming bacteria slowly in about 14 days at 35ºC to 40ºC complete the digestion to CH_4 and CO_2 with some traces of H_2 and perhaps H_2S. The metanogenic bacteria include *methanobacterium, methanobaciiius, methanocuccus and methanosarcina*. The methanogenesis reaction can be expressed as follows:

$$CH_3COOH \text{ ------------}CH_4 + CO_2$$
(Acetic acid)   (Methane) (Carbondioxide)
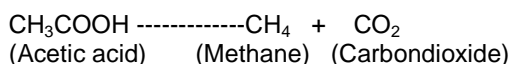
Temperature is also an important factor in anaerobic digestion process. Most of the acid forming microorganisms grows under mesophilic conditions [12].

There are basically three temperature ranges that provides optimum digestion conditions for the production of methane, which are psycophillic, mesopillic and thermophillic temperature ranges, but the mesophilic temperature range which is used in this work is believed to be more effective in converting volatile solids into methane and carbondioxide [3]. This temperature range is between a moderate temperature range of 30ºC to 40ºC and the optimum temperature is considered to be 30ºC to 35ºC. At this temperature, organisms known as mesophiles with growth optima around 20ºC to 45ºC and temperature minimum of 15^0C to 20ºC acts on the waste and as a result degredate the organic fraction of the waste.

Total Solid content of a given waste is the percentage of the total solid remaining after the sample has been dried to about 103ºC to 105ºC for one hour [13]. Low Solids (LS) about 10% Total Solids (TS). Medium Solids (MS) about 15% - 20% and High Solids (HS) processes range from 22% - 40%.

Total Solids (TS) = Weight remaining after drying at 105ºC for 1 hour [13].

The waste treated by anaerobic digestion may comprise of a biodegradable organic fraction a combustible and an inert fraction called the volatile solid. The biodegradable organic fraction includes kitchen scraps, food residue, grasses and tree cuttings etc. The combustible fraction includes slowly degrading lingnocellulosic organic matter containing coarser wood, paper and cardboard.

The Volatile solids (VS) = Total Solid – Ash content. (After ashing at 450ºC for 4 hours) [13].

Acetate and fatty acids produced during digestion tend to lower the pH of digester liquor. However, the ion bicarbonate equilibrium of the carbondioxide in the digester exerts substantial resistance to pH changes. An advantage of chemical addition is that the pH can be stabilized immediately and the unbalanced population allowed to correct themselves more quickly.

2. MATERIALS AND METHODS

2.1 Materials

2.1.1 Source of waste

The sample of the wastes was collected at different locations within Jimeta metropolis in Yola, Adamawa states Nigeria. The sample of the wastes was then sorted to remove non-biodegradable materials such as stones, metals, glass etc. the wastes was then mixed thoroughly

to obtain an homogenous uniform mixture of the organic wastes.

2.2 Methods

2.2.1 Determination of Total Solids (TS)

50 g of the prepared sample was collected and put into the crucible and then into the oven set at a temperature of 105ºC. The sample was left inside the oven to dried at 105ºC for one hour then removed. The dried sample at this temperature was weighed and this gave the total solid content of the waste.

2.2.2 Determination of Volatile Solids (VS)

The sample obtained after drying at 105ºC was put back into the oven now set at 450ºC. The sample was then left inside the oven to be ashed at 450ºC, for four hours after which it was removed and weighed. The difference in the weight of the dried sample at 105ºCand the weight at 450ºC gave the total volatile content of the waste. The sample after drying at 450ºC became ash.

2.3 Experimental Set-up

Four digesters were charged with 300 g of the waste each (prepared waste) after taking the pH value of the waste.9.80 g each of $Ca(OH)_2$, $NaHCO_3$ and $CaCO_3$ were put into three different digesters and closed under air tight condition. The fourth digester was left to serve as the controlled digester in which no chemical was added. The digesters were left under mesophilic temperature range to undergo the degradation process for a period of thirty (30) days.

The volume of biogas produce was measured daily from the digesters for thirty (30) days. The total accumulated volumes of the biogas produced was calculated and recorded at the end of the digestion process for each of the digesters. The relationship between the daily production of biogas and the retention time was plotted which was also used to conclude on the best pH control chemical among the selected pH control chemicals.

3. RESULTS AND DISCUSSION

From the result obtained, it was seen that the digester containing $NaHCO_3$ produced the highest volume of biogas followed by the digester containing $CaCO_3$ then the control digester. The digester containing $Ca(OH)_2$ could not produce any gas.

The production of biogas from the digester containing $NaHCO_3$ started on the first day of digestion, which shows that the application of pH chemicals enhances the fermentative stage of anaerobic digestion resulting into shorter digestion time and provide higher methane yield.

For the digester containing $CaCO_3$ and the control biogas production started on the 3rd and 10th day respectively. The total accumulated volume of biogas produced from digesters containing $NaHCO_3$,$Ca(OH)_2$,$CaCO_3$ and the controlled were 7350 cm^3, 0 cm^3, 2500 cm^3 and 610 cm^3 respectively and the yield per day shown in Table 3.

This shows that the digester containing $NaHCO_3$ improved the yield of biogas over the period of 30 days. This result agreed with the work of [14] in which it was found that the addition of buffer ($NaHCO3$) based on total solids contents increased the biodegradability of organic fraction of solid waste. It increased the cumulative volume of biogas production and percentage volatile solids reduction in substrate. This research work also shows that Food Waste (FW), Green Waste (GW) and anaerobic sludge seed in the ratio 2:2:1 produced the highest biogas production of 5750 cc/Gvs and volatile solids destruction with the best pH (6.2) stability when compared with the performances of the other non-chemically buffered cultures studied. Also little buffering effect is indicated in the case of Food Waste and anaerobic sludge seed in the ratio 4:1 which produced the highest volume of biogas of 6700 cc/gVS but with very poor pH stability this is due to Acetogenesis which lead to accumulation of large amounts of organic acids resulting in low pH value which can inhibit the production of biogas [14].

Table 1. Result for experimental analysis for 50 g of sample

Mass of sample after drying at 105ºC for one hour	Mass of sample after ashing at 450ºC for four hours	Total slid	Volatile solid	Moisture content (MC)
28.30 g	1.20 g	1.20 g	1.20 g	1.20 g

The significant increase in the volume of gas produced by both $NaHCO_3$ and $CaCO_3$ additive is as a result of the buffering capacity of the additives which maintained the digester pH at almost neutral pH value.

After analyzing the gas, the percentage of CH_4 and CO_2 for the $NaHCO_3$ was found to be 75% and 25% respectively, for $CaCO_3$ was found to be 65% and 35% respectively and that of the control was also found to be 65% and 35% respectively which shows that more Methane gas was produced in all cases.

At the end of the process, the masses of the various residual wastes was weighed and the result for digester with $NaHCO_3$ decreased to 160 g from 300 g, the digester with $CaCO_3$ decreased to 220 g from 300g, the controlled digester decreased to 260 g from 300 g while the digester with $Ca(OH)_2$ decreased to 280g from 300 g.

Table 2. Result for 300 g of sample

Volatile solid	Total solid	Amount of each of the control chemical used
162.60 g	169.80 g	9.80 g

The differential in the time for the production of the gases was mainly as a result of the buffering capacity of the additives as a result of amount of alkalinity present in the system. The bicarbonate ion (HCO_3-) is the main source of buffering capacity to maintain the system's pH in the range of 6.5 – 7.6.

The graphs for the relationship between the yield of biogas against the retention time for each of the control chemical digesters are as shown in Fig. 1 for $NaHCO_3$, $CaCO_3$ and the controlled digester.

Table 3. Yield of biogas per day

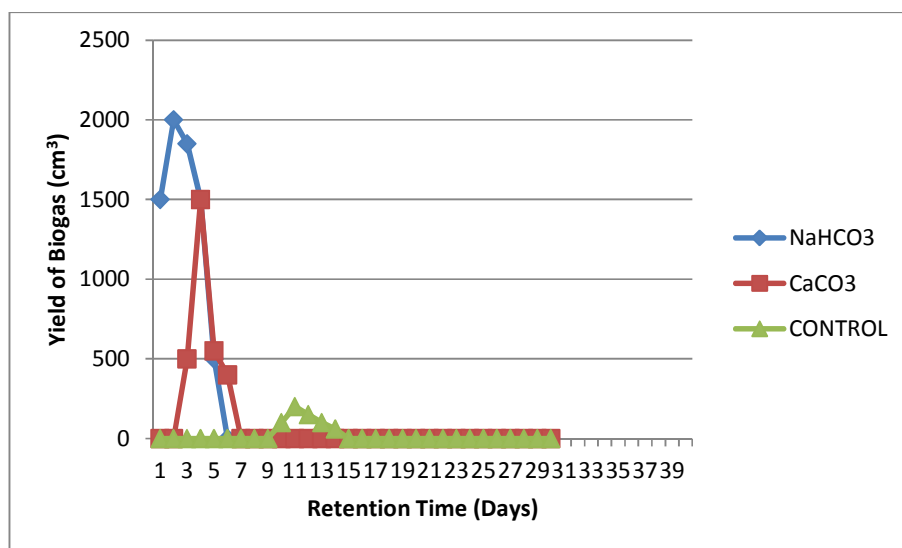| Retention time	Volume of biogas produced (cm^3)			
Day	NaHCO$_3$	CaCO$_3$	Ca(OH)$_2$	Control
1	1500	-	-	-
2	2000	-	-	-
3	1850	500	-	-
4	1500	1500	-	-
5	500	550	-	-
6	-	400	-	-
7	-	-	-	-
8	-	-	-	-
9	-	-	-	-
10	-	-	-	100
11	-	-	-	200
12	-	-	-	150
13	-	-	-	100
14	-	-	-	60
15	-	-	-	-
16	-	-	-	-
17	-	-	-	-
18	-	-	-	-
19	-	-	-	-
20	-	-	-	-
21	-	-	-	-
22	-	-	-	-
23	-	-	-	-
24	-	-	-	-
26	-	-	-	-
27	-	-	-	-
28	-	-	-	-
29	-	-	-	-
30	-	-	-	-
Total volume of biogas produced	7,350 cm^3	2,500 cm^3	0 cm^3	610 cm^3

Fig. 1. Plot of Biogas Yield against Retention time

In comparing the yield of biogas in each of the digesters with respect to the controlled digester shows that:

$$\text{For digester with NaHCO}_3 = \frac{\text{volume of biogas with NaHCO}_3}{\text{volume of biogas from control}}$$

$$= \frac{7350 \text{ cm}^3}{610 \text{ cm}^3} = 12{:}1$$

$$\text{For digester with CaCO}_3 = \frac{\text{volume of biogas with CaCO}_3}{\text{volume of biogas from control}}$$

$$= \frac{2500 \text{ cm}^3}{610 \text{ cm}^3} = 4{:}1$$

4. CONCLUSION

This work has to a large extent shown that various pH control chemicals have varying effects on the conditions inside the digester and the yield of biogas from the digestion process. Based on the different pH control chemicals used and results obtained, it can be concluded that NaHCO$_3$ improved the yield of biogas and has proved to be the best pH control chemical in comparism with the other control chemicals.

It also show the application of pH control chemicals in digesters can enhance the early production of biogas while maintaining the pH condition of the digester at a nearly neutral pH. The NaHCO$_3$ used has also shown a good buffering capacity which could be used in maintaining the digester pH at optimal level. The yield of biogas using the various pH control chemicals in comparism with the controlled digester are in the ratio of 12:1, 4:1and 0 for NaHCO$_3$, CaCO$_3$ and Ca(OH)$_2$ respectively.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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APPENDIX-A

Let
A = weight of dish
B = weight of dish + sample
C = weight of dish + sample after dying at 105ºC
D = weight of dish + sample after ashing at 450ºC
Weight of dish = 10.2g
Mass of sample (waste) used for Total Solid and Volatile Solid analysis = 50 g
Mass of sample after drying at 105ºC for 1 hour = 28.30 g
Mass of sample after ashing at 450ºC for 4 hours = 1.20 g
Mass of Total Solid in the sample = 28.30 g
Mass of Volatile Solid in the sample = C − D = 38.50 − 11.40 = 27.10 g
pH of sample before digestion = 6.02
Amount of pH control chemical used = 60 g/1000 g V.S, = 0.06 g/g V.S
Amount of sample digested in each of the digesters = 300 g

Calculations:

For the 300 g sample,

Since 50 g = 27.10g Volatile Solid (V.S)

Therefore, 300 g sample = Xg Volatile Solid (V.S)

Therefore, Xg (Volatile Solid) $= \dfrac{300 \times 27.10}{50} = 162.60$ g

Therefore 300 g of sample of the waste gives 162.60 g Volatile Solid (V.S)

Amount of Chemical Used:

0.06 g/g (V.S) was used = 60 g of chemical = 1000 g (V.S)

Therefore, 162.60 g Volatile Solid (V.S) = Xg chemical

Xg chemical $= \dfrac{60 \times 162.60}{1000} = 9.80$ g

Therefore amount of chemical used for each of the 300 g of waste digested = 9.80 g

Moisture Content (M.C) = B − C = 60.20 − 38.50 = 21.70 g

Percentage (%) Moisture Content (M.C) $= \dfrac{B - C}{B} \times 100$

$$= \dfrac{60.20 - 38.50}{60.20} \times 100 = 36\%$$

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