

Effect of Varying pH on Biogas Generation using Cow Dung

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The effect of varying pH on biogas yield of cow dung was evaluated using three (3) different tin digesters maintained at pH of 4.52, 6.80 and 8.52 representing acidic, neutral and alkaline range respectively. The digesters were operated at mesophilic temperature conditions and hydraulic retention time of 21 days. For each set up, slurries were prepared using a ratio of 1:7 for cow dung and water respectively. The daily biogas yield (ml), weekly cumulative biogas yield and cumulative biogas yield of the different digesters were recorded. The results showed that daily biogas yield was higher in pH of 8.52 while acidic (pH 4.52) has the lowest biogas yield. Cumulative biogas yield (ml) revealed that alkaline pH has the highest biogas yield of 2850 ml while neutral and acidic pH has 2410 and 1300 ml of biogas respectively. The trend of biogas generation in the digester set up revealed that biogas generation starts 24 h after set up in alkaline

pH while delayed biogas production was recorded in acidic pH for 8 days. Overall, biogas generation in all the digester set up increase continuously with the last week (14-21 days) yielding the highest biogas yield in all the 3 pH ranges. The aim of this research is to determine the effects of varying pH on biogas generation using cow dung with a view to find out the optimum pH value that produce maximum biogas yield through Prepare different slurry, measure and vary the pH value of the slurry before and after digestion, determine the effects of different starting pH of slurry on daily yield of biogas generation using cow dung and determine the effects of different starting pH of slurry on cumulative yield of biogas generation using cow dung.

Keywords: Cow dung, hydraulic retention time, biogas yield, mesophilic temperature, alkaline pH

INTRODUCTION

The anaerobic digestion of biodegradable materials results to the production of biogas. It is composed of methane (45-65%), carbon dioxide (35-45%), nitrogen (0-3%), hydrogen (0-1%), and 0 - 1% hydrogen sulfide. Anaerobic digestion (AD) is a technology widely used for treatment of organic waste for biogas production. Biogas refers to a mixture of gases produced by anaerobic digestion of organic materials. Biogas is another source of renewable energy, it is produced when biomass is subjected to biological gasification and a methane-rich gas is produced from the anaerobic digestion of organic materials (Ofoefule *et al.*, 2010). It consists of varying percent of methane, carbon dioxide, nitrogen, hydrogen, ammonia, hydrogen sulphide and water vapour. Biogas can be utilized in all energy consuming applications designed for natural gas (Ross, 1966).

In Nigeria, as at 2001, the estimate of waste generated by cattle, poultry and piggery was put at 1.3, 6.4, and 5.2 million metric tons daily respectively. These have an estimated gas generation value of 3.27, 0.01, and 0.21

million cubic meters of biogas respectively (Itodo and Awulu, 1994). As at 2007, animal and agricultural wastes in Nigeria stood at 0.781 and 0.256 million tons per day respectively (Sambo, 2007). Dioha, (2009) posited that from animal waste alone, Nigeria can generate 4.75 x 10⁹ MJ per annum. This shows that large proportion of the country's energy can be sourced from biogas. It can be directly used for heating. A cubic meter of biogas with 60% methane content can substitute approximately 0.6 cubic meters of natural gas or 0.6 L of fuel oil during electricity generation in a combined heat and power (Kapdi, 2003). This type of energy generation is practically carbon-neutral as the greenhouse gases released during the combustion have been previously consumed by plants (especially when using Agro/animal wastes as the Substrate).

Biogas production is a complex biochemical reaction found to take place under the action of delicately pH sensitive microbes mainly bacteria in the presence of little or no oxygen. There are a number of bacteria that are

involved in the process of 405 anaerobic digestion including the hydrolytic bacteria group, acidogenic bacteria group, acetogenic bacteria group and the methanogenic archaea group, respectively (Schnurer and Jarvis, 2010). These organisms feed upon the initial feedstock, which undergoes a number of different processes converting it to intermediate molecules including sugars, hydrogen and acetic acid before finally being converted to biogas. Different species of bacteria are able to survive at different temperature ranges. The ones living between 25 - 40°C are called mesophiles and some of the bacteria that can survive at the hotter and more hostile conditions of 55 - 60°C are called thermophiles (Gerardi, 2003). Studies by (Igoni *et al.*, 2008; Ojolo *et al.*, 2008; Patil *et al.*, 2011; Li *et al.*, 2009; Budiyo *et al.*, 2010; Ofoefule *et al.*, 2010; Yusuf *et al.*, 2011) had shown that optimize biogas yield is possible in Anaerobic digestion. In anaerobic digestion process, microorganisms uses the organic matter available in the waste to produce a mixture of gases known as biogas (predominantly containing methane and carbon monoxide), which will result in the reduction of environmental pollution. The process is brought about by a consortium of interdependent and symbiotic populations of heterotrophic microorganisms which are capable of utilizing elements and compounds from a diverse spectrum of substrates for the synthesis of new cellular materials (Murphy and Keogh, 2004; Ghaly *et al.*, 2000). Anaerobic digestion process can be described by a four-stage scheme namely hydrolysis, acidogenesis, acetogenesis and methanogenesis (Demirbasa and Balat, 2009). First stage is hydrolysis, in which the complex organic structure of the substrate is broken down into simpler structure. In acidogenesis, the simple organic compounds formed at the end of first stage are converted into volatile organic acids (acetate, propionate, butyrate and valeric acid), carbon dioxide and hydrogen. Subsequently, acetate, hydrogen and carbon dioxide are synthesized from the organic acids during the acetogenesis. In methanogenesis, the products of third stage are converted into biogas which mainly consists of methane and carbon dioxide as its major composition (Yebo *et al.*, 2011; Chandra *et al.*, 2012; Gerardi., 2003). The pH-value is the measure of acidity/alkalinity of a solution (respectively of substrate mixture, in the case of Anaerobic Digestion) and is expressed in *parts per million* (ppm). The pH value of the anaerobic digestion substrate influences the growth of methanogenic microorganisms and affects the dissociation of some compounds of importance for the anaerobic digestion process (ammonia, sulphide, organic acids).

Researchers have shown that, one of the main environmental problems of today's society is the continuously increasing production of organic wastes. In many countries, sustainable waste management as well as waste prevention and reduction have become major political priorities, representing an important share of the

common efforts to reduce pollution and greenhouse gas emissions and to mitigate global climate changes. The increasing demand for energy, hikes in oil prices, depletion of fossil fuel resources and the increasing concern for environmental issues warrants researchers to look for new technological processes to obtain clean and sustainable energy from alternate energy sources (Chynoweth *et al.*, 2000; Gurung *et al.*, 2012). Rapid population growth and urbanization have led to an enormous increase of solid waste generation. Underdeveloped and developing countries have great challenges concerning appropriate solid waste management to minimize the risk to human health and pollution problems. These problems of energy and environment could be simultaneously handled by biogas production from waste. Biogas can be generated from a wide range of solid or liquid wastes (Weiland, 2010; Zamalloa *et al.*, 2012). As a renewable energy source, Biogas could be a relative means of solving the problems of grossly inadequate energy supply in Nigeria, rising energy prices, waste treatment/management and creating sustainable development. Moreover, the effluent of this process is a residue rich in essential inorganic elements like nitrogen and phosphorus needed for healthy plant growth known as bio-fertilizer which when applied to the soil, enriches it with no detrimental effects on the environment (Bhat *et al.*, 2001).

The production and collection of biogas from a biological process was documented for the first time in United Kingdom in 1895 (Metcalf and Eddy, 1991). Since then, the process was further developed and broadly applied for wastewater treatment and sludge stabilization. The energy crisis in the early '70s brought new awareness about the use of renewable fuels, including biogas from animal dung. The interest in biogas has further increased today due to global efforts of displacing the fossil fuels used for energy production and the necessity of finding environmentally sustainable solutions for the treatment and recycling of animal manure and organic wastes. In evaluating national development and the standard of living of any nation, the supply and consumption of energy are very important. Human energy consumption has been moderate before the industrial revolution in the 1890s. Man has mostly relied on the energy from brute animal's strength to do work. Recently, man acquired control over coal, electricity, crude oil, natural gas, etc. Sustainable resource management of waste and the development of alternative energy source are the present challenges due to economic growth. The aim of this research is to determine the effects of varying pH on biogas generation using cow dung with a view to find out the optimum pH value that produce maximum biogas yield. This was achieved through the following objectives:

- (i) Prepare different slurry, measure and vary the pH value of the slurry before and after digestion.

- (ii) Determine the effects of different starting pH of slurry on daily yield of biogas generation using cow dung.
- (iii) Determine the effects of different starting pH of slurry on cumulative yield of biogas generation using cow dung.

MATERIALS AND METHODS

The materials used in this research work were: cow dung as the sample/substrate. Empty tins (400 g capacity each) sparked as the digesters, while 1000 cm³ measuring cylinder served as the gas holder. The following are the apparatus/equipment employed in the research includes; pH meter, weighing balance, measuring cylinders, empty tins and rubber horse.

Sample collection

Fresh cow dung was collected from cow market Sokoto (Kasuwan Kara), Sokoto metropolis. A clean container with cover was used for the collection of the sample. The cow dung was dried under the sun for four days and then crushed to powder using mortar and pestle. The crushed dung's were sieved and dried again for a day.

Slurry preparation

One hundred (100) grams of dried cow dung was weighed into six different empty tins which serve as the digester and then 700 ml of water was added to each tin to give a ratio of 1:7, the mixtures were stirred thoroughly with a glass rod to obtain homogeneity; the slurries were obtained when a saturated solution was formed.

Dilution ratio and pH determination

The prepared slurries were grouped into 3 and labelled as A1/A2, A3/A4 and A5/A6. Sodium chloride (NaCl) was added to the first group of the digester in order to make it acidic while the second group was kept neutral and then the last group was made alkaline by adding calcium carbonate (CaCO₃) in order to vary their pH.

Digester setup

The digesters containing the slurries were sealed using candle wax to ensure anaerobic conditions and then labelled as (digester A1/A2, A3/A4 and A5/A6) respectively. A hose was then connected from the top of the measuring cylinder of 1000 cm³ capacity to each digester which served as a gas holder filled with water and placed in an inverted position held firmly by a retort stand in a basin filled with water (water displacement

method). The gas produced from the digesters will pass through the hose pipe and then to the measuring cylinder which displaces the water downward. The volume of gas produced was measured by the amount of water being displaced from the measuring cylinder and it was recorded at 12:00 noon throughout the retention period.

Data analysis

The results were presented as means of the 2 replicate and mean yield of the biogas produced from each pH range will be analyzed using simple descriptive statistics of bar chart and line graph in order to show the trend of the relationship between varying pH and yield of biogas produced.

RESULTS

The results on the effects of varying pH on biogas generation using cow dung are shown in (Figures 1-3 and Tables 1-2). The starting pH of the slurries revealed that samples added with sodium chloride (NaCl) falls within the acidic range with pH values of 4.28 while samples added with calcium carbonate showed an alkaline pH range of 8.52 which is slightly alkaline. However, the neutral pH sample which is the control has a pH value of 6.8 which is very close to neutral pH (7.0).

Daily yield of biogas generation (ml)

The results of the 21 days anaerobic digestion as influenced by three different pH range (acidic, neutral and alkaline) revealed that in alkaline medium, biogas production starts 24 h after setting up the digester while in neutral medium, generation of biogas start 48 h after setting up the digester. Acidic medium showed delayed onset of biogas generation by 8 days after setting up the digesters (Table 2). The daily yield of biogas for the three different pH range increased with increasing retention time (days). The alkaline treatment has the maximum daily biogas yield of 175 ml at day 19 and 20 retention time while acidic treatment has the lowest daily biogas yield of 75 ml at days 11, 12 and 17 retention time (Figure 2). Overall, the alkaline treatment set up revealed maximum daily biogas yield among all the treatments (acidic and neutral) and started yielding biogas just after 24 h of digester set up.

Cumulative yield of biogas generation (ml)

The cumulative biogas generations for acidic, neutral and alkaline pH ranges were 1300, 2410 and 2850 ml respectively. Alkaline and neutral pH ranges have higher

Table 1. Daily and cumulative biogas yield of different pH ranges of slurries

RT (Days)	Daily Biogas Yield (ml)			Cumulative Biogas Yield (ml)			T (°C)
	Acidic	Neutral	Alkaline	Acidic	Neutral	Alkaline	
1	0.0	0.0	0.0	0.0	0.0	0.0	34.60
2	0.0	0.0	115.0	0.0	0.0	115.0	33.60
3	0.0	100.0	105.0	0.0	100.0	220.0	32.20
4	0.0	100.0	110.0	0.0	200.0	330.0	34.10
5	0.0	105.0	115.0	0.0	305.0	445.0	35.90
6	0.0	105.0	135.0	0.0	410.0	580.0	33.80
7	0.0	115.0	135.0	0.0	525.0	715.0	34.00
8	0.0	135.0	135.0	0.0	660.0	850.0	31.30
9	105.0	135.0	150.0	105.0	795.0	1000.0	32.20
10	90.0	150.0	155.0	195.0	945.0	1155.0	35.60
11	75.0	135.0	160.0	270.0	1080.0	1315.0	33.10
12	75.0	125.0	155.0	345.0	1205.0	1470.0	34.20
13	115.0	120.0	145.0	460.0	1325.0	1615.0	33.90
14	90.0	115.0	140.0	550.0	1440.0	1755.0	32.90
15	90.0	110.0	145.0	640.0	1550.0	1900.0	32.80
16	75.0	145.0	130.0	715.0	1695.0	2030.0	32.60
17	105.0	140.0	160.0	820.0	1835.0	2190.0	32.60
18	115.0	130.0	150.0	935.0	1965.0	2340.0	32.40
19	125.0	145.0	175.0	1060.0	2110.0	2515.0	32.10
20	140.0	150.0	175.0	1200.0	2260.0	2690.0	31.90
21	100.0	150.0	160.0	1300.0	2410.0	2850.0	31.80

Table 2. Weekly cumulative biogas yield of different pH ranges of slurries.

pH Range of Slurries	Weekly Cumulative Yield of Biogas (ml)		
	Week 1 (1-7 Days)	Week 2 (8-14 Days)	Week 3 (15-21 Days)
Acidic	0.00	550.00	750.00
Neutral	525.00	915.00	970.00
Alkaline	715.00	1040.00	1095

cumulative biogas yield more than acidic pH range (Figure 3). On weekly cumulative biogas yield, alkaline treatment has the maximum weekly biogas yield of 1095 ml at week 3 while acidic treatment has no biogas yield at week 1 (1-7 days). In all the treatments that is, acidic, neutral and alkaline pH and the cumulative biogas yield of each is higher at week 3 than in week 1 and 2 (Table 2).

DISCUSSION

The results on varying pH on biogas yield of cow dung revealed alkaline (pH 8.52) has better yield than other samples (acidic and neutral). Previous studies by Ukpai and Nnabuchi, (2012) revealed that neutral pH of 7 has better biogas compared to acidic and alkaline in both cow dung and cassava peels. Similarly, Jayara *et al.* (2014) reported that pH 7 has the highest biogas yield compared to others and that pH 8 produced better biogas yield than 6, 9 and 5. In our findings, the alkaline group (8.52) has better yield than neutral pH (6.80) which may be due to the fact that our neutral pH fall within slightly acidic group and thus affect the activity of the methanogen bacteria.

The pH of 8.52 which is slightly alkaline produced better due to the fact that even previous report has suggested that slightly alkaline condition is next to neutral conditions in terms of biogas yield and hence in the absence of neutral (7) it produced the best yield. The reduced yield of biogas recorded in acidic medium is however in agreements with many reports on cow dung (Ukpai and Nnabuchi, 2012; Budiyo *et al.*, 2010) and food waste (Jayara *et al.*, 2014). Augenstein *et al.* (1976) suggested that during anaerobic fermentation, micro-organisms require a natural or mildly alkaline environment for efficient gas production. An optimum biogas production is achieved when the pH value of input mixture in the digester is between 6.25 and 7.50 (Mahanta *et al.*, 2004; Wise, 1987). The pH value in a biogas digester is also a function of the retention time.

In this study, we observed early onset of biogas production in the alkaline sample within 24 h of set up while delayed production of biogas was observed in acidic sample (almost 8 days after set up). This trend is in accordance with so many reports on cow dung that showed delayed production of biogas in acidic pH and early production in neutral (Budiyo *et al.*, 2010; Jayara *et al.*, 2014). Though, varying pH ranges were studied in

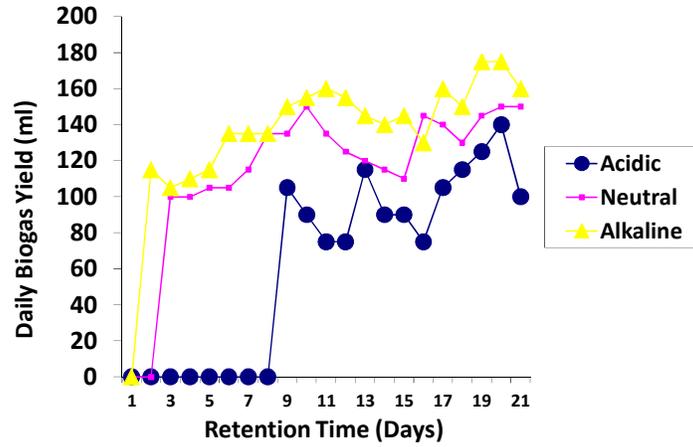


Figure 1. Effects of varying pH on daily biogas yield of slurries using cow dung.

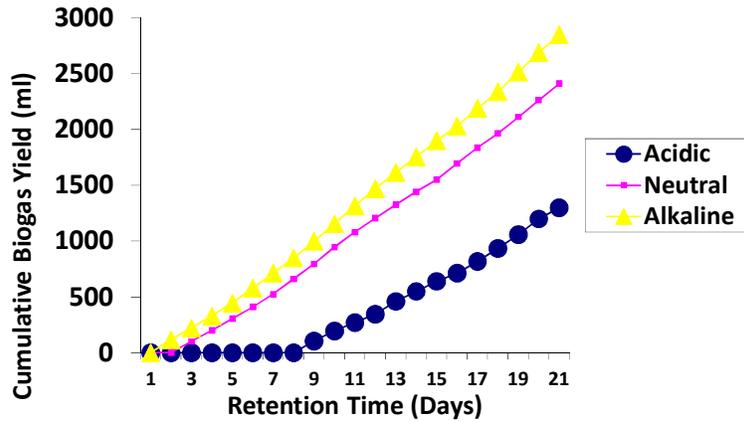


Figure 2. Effects of varying pH on cumulative biogas yield of slurries using cow dung.

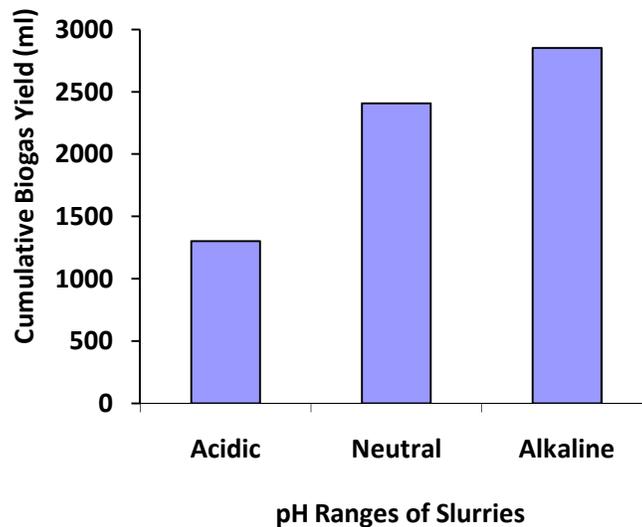


Figure 3. Cumulative biogas yield of different pH ranges of slurries.

this research, it is evident that other factors influenced biogas generation such as temperature and loading rate. The results obtained may also be influenced by temperature of the digester as methanogenic bacteria may work efficiently under certain specific range of temperature. Methanogenic bacteria is very sensitive to pH value and do not thrive below a value of 6.5. Later, as the digestion process continues, concentration of NH_3 increases due to the digestion of N, which can increase the pH value to above 8. When the methane production level is stabilized, the pH range remains between 7.2 and 8.2. According to studies in China, during the period when ambient temperature varies between 22 and 26°C, it takes approximately 6 days for pH value to acquire a stable value (SPOBD, 1979).

Conclusion

The results of this research revealed that cow dung has the potentials to generate biogas using anaerobic digestion process and pH range play a vital role in the yield of biogas produce. In general, alkaline pH favored higher biogas yield than other pH values.

Recommendations

(a) Proper management of organic waste should be encouraged so as to promote their use in biogas production there by contributing to energy needs of the nation.

(b) More research should be carried out on other factors affecting biogas generation so as to correlate the optimum range required by each factor in biogas generation.

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