The Effect of pH, Volatile, and Total Solid in Cumulative Yield of Methane

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ABSTRACT

This work studied the effect of pH, volatile solid, and total solid concentration on the cumulative yield of methane gas. The experiment was performed November 5th-20th, 2016. The inoculum used was digested cow dung slurry gotten from Animal Science Department University of Nigeria, Nsukka. The 50 liter capacity metallic prototype biogas plant constructed at the National Center for Energy Research and Development, University of Nigeria, Nsukka was used to investigate the anaerobic digestion in generating biogas from cow dung. The experiment was batch operated and daily gas yield from the plant was monitored for 20 days.

Samples were taken every two days to determine the total and volatile solid concentration. The ambient and slurry temperature, pH, and pressure were also monitored and presented. The digester was charged with this waste in the ratio of 1:2 of waste to water, respectively. The total solid concentration varied from 20% to 8.4%. Also the volatile solid concentration decreased from 35 – 73% while the pH range was 6.1 - 8.4. The ambient temperatures range attained within the testing period were 25 - 34°C and a slurry temperature range of 27 - 39 °C.

(Keywords: biogas, cow dung, anaerobic digestion, slurry temperature, ambient temperature)

INTRODUCTION

Anaerobic digestion is a process that converts organic matter into a gaseous mixture mainly composed of methane and carbon dioxide through the concerted action of a close-knit community of bacteria [1]. It has been traditionally used for waste treatment but there is also considerable interest in plant-biomass-fed digesters, since the produced methane is a useful source of energy. The production of biogas from covered anaerobic digesters is of growing interest to many developed and developing countries, as fossil-fuel resources decline [2]. Biogas is a renewable and sustainable energy, which is compatible with coal seam gas (CSG) and/or energy from crops, such as algae.

Anaerobic digestion has been considered as a waste-to-energy technology, and is widely used in the treatment of different organic wastes, for example: organic fraction of municipal solid waste, sewage sludge, food waste, animal manure, etc. [3]. Anaerobic treatment comprises of decomposition of organic material in the absence of free oxygen and production of methane, carbon dioxide, ammonia and traces of other gases and organic acids of low molecular weight [4].

Recently, large volumes of cow dung generated from feedstock farming increases annually, most of which are disposed into landfills or are applied to the land without treatment. Anaerobic digestion provides an alternative option for energy recovery and waste treatment [5].

In this paper, cow dung was assessed for the use of anaerobic digestion with the objectives of treating the dung waste to decrease disposal costs and to generate biogas. The biogas produced contains mainly methane and carbon dioxide, and can be used as a source of renewable energy. The aim of this paper was to investigate the effect of pH, volatile, and total solid in cumulative yield of methane.

In evaluating national development and the standard of living of any nation, the supply and consumption of energy are very important [6]. 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 history of waste utilization shows independent developments in various developing and industrialized countries. Anaerobic digestion can convert energy stored in organic matter present in manure into biogas. Energy supplied from fossil fuels is not easily recycled and takes a long time to form, hence is exhaustible and not renewable.

Renewable energy has remained one of the best alternatives for sustainable energy development since the grid electricity has become too expensive. Sources of renewable energy are wind, hydro, ocean waves, geothermal energy resources and solar energy, which can be applied as solar thermal and solar electricity (photovoltaic).

Heat-based technologies developed for the utilization of heat energy from the sun (solar thermals).They are applied in water heaters, drying, chick-brooding, cooking, manure dryers, biogas and thermal refrigerators. With the advent of industrialization and energy based intensive agriculture, chemical pathways for raw materials conversion became predominant with extensive use of petrochemical based feedstock.

The damaging long term environmental impacts and resource depletion indicate unsustainability of the current methods. [7]. 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. Achieving solutions to possible shortage in fossil fuels and environmental problems that the world is facing today requires long-term potential actions for sustainable development. In this regard, renewable energy resources appear to be one of the most efficient and effective solutions [8].

Biomass is the biological organic materials that are renewable and can be recycled to produce biogas [9]. A huge amount of wastes is generated daily from the various processing industries in Nigeria. The wastes that are usually disposed off either into the sea, river, or on the land as a solid amendment materials, which causes support for breeding of flies, and constitute health hazards to people living around the area are converted into biogas by anaerobic fermentation [10].

What was considered as waste many years ago have in recent time become useful that it can be inferred that in life, nothing is a 'waste'. They are only waste when they lack the useful technology for their transformation and application. The biomass wastes are held in a digester or reactor. The gas is produced from a three-phase process namely, hydrolysis, acid-forming and methane-forming phases. It is a biological engineering process in which a complex set of environmentally sensitive micro-organisms are involved.

The gas is typically composed of 50-70% Methane, 30-40% Carbon dioxide, 1-10% Hydrogen, 1-3% Nitrogen, 0.1% Oxygen and Carbon monoxide and trace of Hydrogen sulphide [11]. Biogas is also a waste management technique because the anaerobic treatment process eliminates the harmful micro-organisms. It is a cheap source of energy due to the feed stock is usually waste materials. The technology ensures energy independence as a unit can meet the need of a family or community.

The digester slurry is a good fertilizer. It is claimed that its value as fertilizer could double crop yield. Biogas when further refined burns as well as liquefied gas, but does not add to global warming like liquefied natural gas [12].Cow dung has high nitrogen content and due to pre-fermentation in the stomach of ruminant, and has been observed to be most suitable material for high yield of biogas through the study made over the years [13].

Thermal decomposition of the ligand and synthesized complexes were studied by thermogravimetric analyses (TG) in order to evaluate their thermal stability and thermal decomposition pathway. Plant materials such as crop residues are more difficult to digest than animal wastes (manures) because of the difficulty in achieving hydrolysis of cellulosic and lignin constituents with attendant acidity in the biogas systems leading to reduction and sometimes cessation of gas flammability/gas production [14], etc. Flammable gas which helps in reducing forestation and desert encroachment is produced through the conversion of this organic matter such as animal and plant wastes into biogas [15].

MATERIALS AND METHODS

Methods

The samples taken were analyzed for total solids (TS), volatile solids (VS), and chemical oxygen demand (COD) using the Standard Method [16].
Total solid is made up of the digestible and non-digestible material in the waste. The Meynell (1982) method was used. 3g of the raw waste was dried in an oven at 105^oC for 5 hours. The dried sample was cooled in a desiccator and then weighed. The weight obtained after all moisture loss is the total solid.

$$\% \text{ T.S} = \frac{B-C}{g} x \frac{100}{1}$$

T.S = Total solid
B = Weight of crucible + dry residue
C = Weight of crucible
g = Original weight of sample.

The volatile solid is the true organic matter available for bacterial action during digestion. The method of Meynell (1982) was used. The solid residue from the total solid determination was heated in a muffle furnace at 600^oC for 2 hours. The heated residue was cooled in a desiccator and weighed.

$$\text{Volatile solid (VS)} = \frac{B-C}{g} x \frac{100}{1}$$

B = Weight of dried residue from total solid determination
C = Weight of residue after further heating at 600^oC
g = Original weight of sample.

Experimental Procedure

17 kg of cow dung was charged into the digester with 34 kg of water in the ratio of 1:2 of waste to water and the slurry was properly stirred [17]. The mixing ratio was determined by the moisture content of the waste. The daily ambient and slurry temperatures were measured using thermometer (-10 to 110^{0}C).

The pH Values were monitored on 3 days interval to determine the action of methanogens, which utilize the acids, carbon dioxide and hydrogen produced by non-methane producing bacterial using a digital pH meter (PHS-3c pH meter).

The volume biogas produced was measured by a downward displacement method using a transparent 13 L calibrated plastic bucket as used by [18]. The composition of the flammable biogas produced from each of the waste was determined through the use of Orsat apparatus. In checking the flammability of the gas, a locally fabricated biogas burner was used.

A top loading balance (50 kg capacity, “Five Goats” model no Z051599) was used in the measurement of the water and waste volumes [19]. The plant consists of the fermentation chamber, the inlet and outlet pipe, the gas pipe and the stirrer. The digester was charged and its performance monitored for 20 days. The organic wastes were allowed to stabilize, anaerobic fermentation involving the degrading of the wastes by the action of various microbes of different sizes and functions, leading to the production of biogas in the absence of oxygen.

RESULT AND DISCUSIONS

The cumulative yield of methane from the experiment was zero from 1-4 days of the experiment. This indicated that there was no biogas yield from the first 4 days of the experimental set up. The day 5 recorded 0.2 liters of cumulative methane yield which still not sufficient enough indicating poor startup of methane yield. On day 6 the cumulative yield increased to 0.7 liters. There was progressive slow increased of the methane yield up to day 12. The day 13, 14, 15, 16, witnessed rapid cumulative methane yield of 11.3 liters, 14.5 liters, 18.7 and 23.5 liters, respectively. The rapid cumulative yield increased up to day 20.

This is predicted because biogas production rate in batch condition is directly equal to specific growth of methanogenic bacteria [20]. Also during the first 4 days of observation, there was no daily methane production and mainly due to the lag phase of microbial growth. Whereas, in the range of 4 to 6 days of observation; methane production was less substantially due to slow growth of methanogens. Highest daily methane production rate of 7.8 L was measured on day 20.

On the commencement of semi-continuous digestion, biogas production was observed to decrease considerably and, this is probably due to unregulated pH region employed, which concurrently leads to increase in concentration of ammonia nitrogen that might be assumed to inhibit the process. It was reported by Chen Ye, et al. [21] that high concentration of ammonia nitrogen is toxic to anaerobes, which will decrease the efficiency of the digestion and upset the process.

Besides, the fluctuations in the daily biogas production found during the semi-continuous, it could also be attributed to the varying input of VS load. At the end of the observation, cumulative biogas yield of 50.4L was achieved. This yield seems particularly similar to that reported by [22] during the anaerobic digestion of beef manure in mixed and unmixed reactors.

Table 1: Volume of Biogas yield (liters).

Days	Control
1	0.0
2	0.0
3	0.0
4	0.0
5	0.2
6	0.5
7	0.7
8	0.9
9	1.0
10	1.3
11	1.8
12	2.5
13	2.8
14	3.2
15	4.2
16	4.8
17	5.6
18	6.4
19	7.1
20	7.8

It is clear that cow dung is an effective feedstock for anaerobic digestion and could significantly enhance the cumulative biogas production. It therefore shows that considerable amount of anaerobic bacteria in the cow dung functions effectively to degrade the organic fraction from cattle manure even though pH was unregulated. The methane content of the biogas generated during the entire operation was on average 47%. This result implies that all the processes are most likely in balanced and stable operation.

Table 2: Cumulative Volume of Biogas yield (liters).

Days	Control
1	0
2	0
3	0
4	0
5	0.2
6	0.7
7	1.6
8	2.6
9	2.9
10	4.2
11	6.0
12	8.5
13	11.3
14	14.5
15	18.7
16	23.5
17	29.1
18	35.5
19	42.6
20	50.4

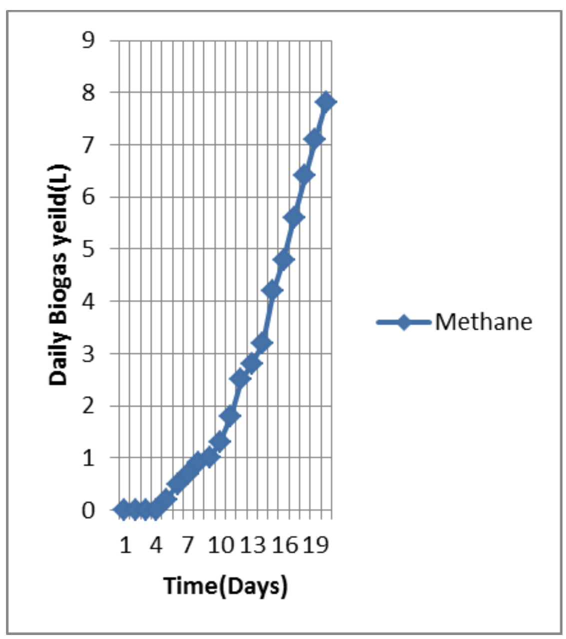

Figure 1: Daily Methane Yield versus Time (Days).

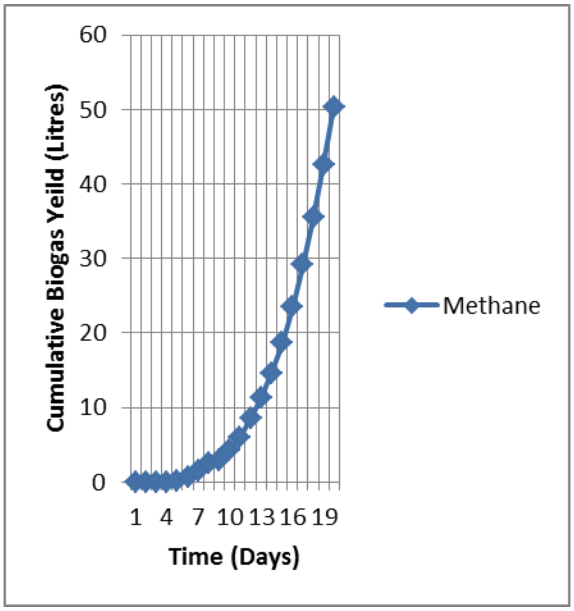

Figure 2: Cumulative Methane Yield versus Time (Days).

Effect on pH and Ammonia-Nitrogen Concentration

The pH of the anaerobic digestion was not stable. There was gradual reduction of pH value during the test period. This shows proper bacterial activity during the anaerobic digestion process. The pattern of pH and ammonia nitrogen demonstrated by all experimental mixing ratios was typical of a digester operating under stable condition (Figure-3).

A decrease in the process pH was observed in the first few days of the digestion and this is due to high volatile fatty acid (VFA) formation [23]. However, the pH increased to its normal operating value after VFAs metabolism. Ammonia nitrogen concentration and pH was observed to increase substantially with little variation on the commencement of the semi-continuous operation, leading to lower biogas yield Bujoczek *et al*., [24] have reported that, the efficiency of converting the organic matter in cattle manure to methane decreased as the organic loading increased.

It was earlier seen from the mixing ratio of 0.5:5 tested data not shown, that the variation of NH_3-N concentration had no obvious variation and maintained below 500 mg/l. At the end of the experiment, NH_3-N was reduced to 87% which is 20% higher than that at mixing ratio 1:5 and 1.5:5 [25]. This showed that higher reduction in efficiency of NH_3-N was achieved and this is likely caused by the availability of microbial population, which aids the anaerobic bioconversion (Angelidaki). It was reported by Angelidaki and Ahring [26] that process stability due to NH_3 resulted in VFA accumulation and lowering of pH, thus decreasing the concentration of free NH_3 in the reactor. This explains the observed ability of the operation to stabilize even with high ammonia concentration and with lower, but stable biogas production.

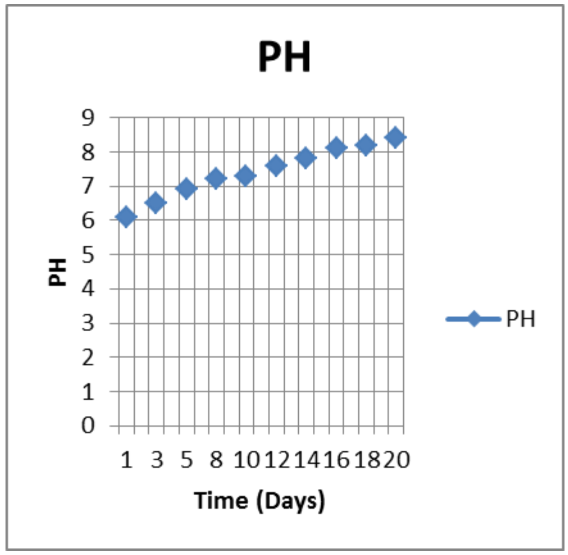

Figure 3: pH versus Time Days.

Total Solids and Volatile Solids in Digester

Total solid is made up of the digestible and non-digestible material in the waste and the volatile solid is the true organic matter available for bacterial action during digestion.

Figures 4 and 5 show the TS and VS profiles of the digester content during the experiment. TS and VS destruction is a vital aspect in evaluating anaerobic digestion performance. The most effective performance in terms of VS degradation was observed during batch digestion, probably through efficient hydrolysis in the acid phase. However, on Day1-Day 2 when the system was operating under batch mode, a slight removal of VS was observed with large fluctuations probably due to sampling difficulties. Although there is still tendency for further TS and VS reduction with low or non-biogas production, it presumably because of the inherent hardly biodegradable constituents, consequently higher ammonia concentration contribute to process inhibition.

According Nielsen and Angelidaki [11], animal manure such as cattle manure used in this study contain lignocellulosic rich materials; hence makes anaerobic digestion quite un-optimum. The TS and VS reduction of 49% and 47%, respectively was stably achieved during the operation.

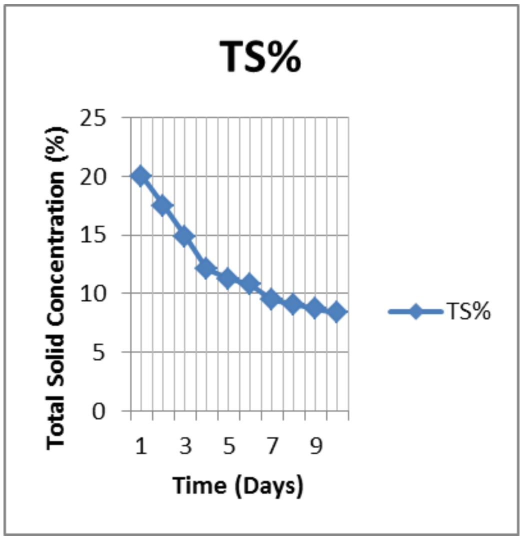

Figure 4: Total Solid Concentration versus Time (Days).

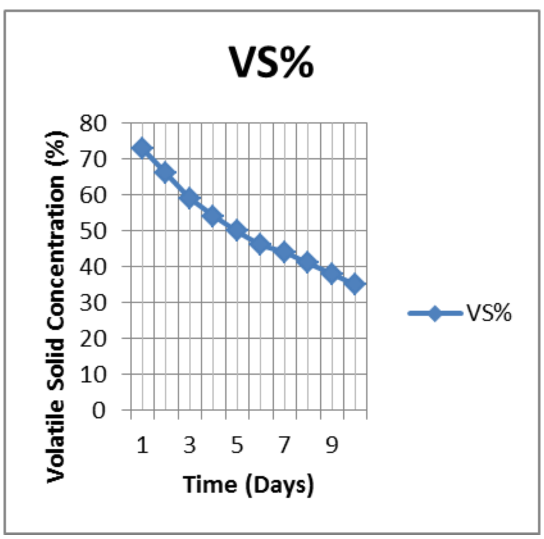

Figure 5: Volatile Solid Concentration (%) versus Time (Days).

CONCLUSION

The result of this research on the effect of pH, total solid, and volatile solid on the cumulative yield of methane. The work also reviewed that cow dung has shown that flammable biogas can be produced from these wastes through anaerobic digestion for biogas generation. These wastes are always available in our environment and can be used as a source of fuel if managed properly.

The study revealed further that cow dung as animal waste has great potentials for generation of biogas and its use should be encourage due to its early retention time and high volume of biogas yields. Also in this study, it has been found that temperature variation, pH and concentration of total solids etc, are some of the factors that affected the volume yield of biogas production.

The highest cumulative methane yield from the experiment was 50.4 liters. The pH was measured every two day during the experiment and varied from 6.1 - 8.4. The maximum daily methane yield was 7.8 liters.

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