EVALUATION OF BIO-METHANE POTENTIAL IN FRESH AND AGED COW DUNG THROUGH SOLID STATE ANAEROBIC DIGESTION METHOD

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ABSTRACT

Intensive agricultural activities have increased the volume of biodegradable agricultural wastes, resulting in environmental degradation, emission of greenhouse and other toxic gases. This study investigates the potential of different cow dung samples (based on age) through Solid State Anaerobic Digestion (SSAD) method, as feedstock for bio-methane production in order to reduce natural biodegradability of feedstock before utilization, as a measure to reduce greenhouse and other toxic gases emission to the atmosphere. A batch study to ascertain the suitability of fresh and aged cow dung at uncontrolled temperature and pH was carried out. Fresh cow dung obtained higher bio-methane yields of 0.7476 m^3/kg-VS and 0.540 m^3/kg-VS as theoretical and experimental values respectively than the exposed (sun dried) samples. The result also indicated that a longer retention time was required to allow for bacterial growth in the exposed (sun dried) samples. The data obtained establish that the use of fresh cow dung as feedstock enhances bio-methane yield at the given condition. However, future work should focus on conducting series of experiments at controlled temperature and pH through SSAD method.

Keywords: Cow dung, Solid state anaerobic digestion, Bio-methane potential, Cumulative bio-methane yield

1 INTRODUCTION

Climate related problems are among the serious global issues being experienced today which are devastating, such as rising sea levels that caused large scale dislocation of farms and human settlements, along with unreliable rainfall patterns, drought, flood, and heat waves, increased storm intensity [1]. Already some of these severe and unpredictable weather events are felt most strongly in both urban and rural communities of the world. The increased concentration of greenhouse gases is believed to be as a result of culpable human activities such as poor waste management represents one of the major causes of these problem. Recently in Nigeria, government support for intensive agricultural activities to address food insecurity has increased the volume of agricultural waste. Agriculture is said to be one of the sectors that produces high volume of waste in various forms [2]. While the disposal of these agricultural wastes particularly livestock waste on farmlands serves as nutrients for crops, when deposited in large quantities, result in environmental degradation, emission of greenhouse and other toxic gases [3]. On the other hand, accumulation of these livestock wastes particularly on large disposal site posed problem by releasing methane, carbon dioxide, carbon monoxide, ammonia, hydrogen sulphide etc., to the atmosphere, especially in summer, as a result of natural biodegradation. In addition, Livestock wastes contain high contents of organic substances, Nitrogen, Phosphorus, including pathogens, which cause environmental

pollution [4]. Aerobic and anaerobic digestion processes are mostly exploited for the management of livestock waste. While aerobic processes such as composting are of important because of its ability to produce stabilized materials as soil improvers, it is very energy-intensive [5]. On the other hand, anaerobic digestion results in two main outputs; a biogas stream consisting of mainly methane and carbondioxide gases and a more stabilized materials (digestate) as soil improvers [6]. Biogas generation from food and non-food biomass, using different digestion conditions and digesters by mostly anaerobic digestion method have been reported in quite a number of literatures including [7, 8, 9, 10, 11, 12, 13]. Presently, basically biomass of various organic wastes and domestic by-products which include animal dungs and remains of plants like leaves, stems, roots, vegetable wastes, etc., are being utilized for biogas production for a number of reasons including positively contributing to climate goals and rural livelihoods. Co-digestion of mixed organic materials are also reported in a number of literatures as it leads to higher biogas yields, due to improved stability of the system, neutralization of toxic compounds, encouragement of a multiple microbe society, and better nutrient balance, providing the needed amount of moisture for substrates, increasing the organic loading rates and improving the rate of organic degradation in the digester [14, 2, 13, 15, 16]. Implementation technology of biogas production from livestock waste and other wastes have also been carried out by many researchers to combat the negative effects of greenhouse gas emissions (GHG) on the environment [17, 18]. An earlier study by [19] revealed that cow dung is an effective feedstock for biogas production, achieving high cumulative biogas yield with stable performance in batch mode. However, in all of these studies, not much attention has been paid to the proper selection of feedstock for improved bio-methane yield. An assessment of the bio-methane yield of the feedstock (both theoretically and practically) is crucial to ascertain the economic viability of a biogas investment [20]. The aim of this study was to evaluate bio-methane potential in fresh and aged cow dung, using solid state anaerobic digestion (SSAD) method.

2 METHODOLOGY

2.1 Substrate preparation

Fresh cow dung used for this research was collected from Modibbo Adama University farm Yola, Adamawa State, Nigeria. A procedure by [4] was adopted for this study with slight modification on temperature and inoculum type. The fresh cow dung was then divided into five equal parts of 200g each, using Electronic precision balance (TL-600). One part was used immediately for the study while the remaining four parts were sundried for one, two, three and four weeks. 100g each of the fresh cow dung was added to each of the five samples as inoculum.

2.2 Substrate Characterization

The five cow dung samples (substrate + inoculum) were first characterized before digestion, in terms of the key physiochemical characteristics and elemental composition related to these study such as moisture content (MC), total solid (TS) and volatile solids (VS) using the procedure below and percentage Carbon (%C), Hydrogen (%H), Oxygen (%O) and Nitrogen (%N) were determined using elemental analyzer (Euro EA 3000, Euro vector, Italy).

Moisture content (MC)

The moisture content was determined by taking approximately 100 g of solid sample (each substrate) and weighed into crucibles at room temperature, after which it was placed into the oven (Desktop constant temperature drying oven, WHL-25A) at 105 ℃ for 24 hours. Thereafter the heated samples were placed in desiccator to cool down. The silica gel inside the desiccators absorbs any moisture that remains. The cooled down sample is weighed again to obtain the mass of the dry sample.

$$\text{MC}\% = \left[\frac{mass\ of\ wet\ sample - mass\ of\ dry\ sample}{mass\ of\ wet\ sample}\right] x\ 100 \quad (1)$$

Total solids (TS)

Total solids (TS) is the measurement that represents the quantity of total solid residue that remains after the sample has been oven dried at 105℃ for 24 hours. The test was conducted in accordance to [21].

$$\text{TS\%} = \frac{mass\ of\ dry\ sample}{mass\ of\ total\ sample}\ x\ 100 \quad (2)$$

Volatile solids (VS)

The residue from the TS test is placed in the furnace (Muffle furnace, Veicster LP3), which was fired / ignited at 550 ℃ for 2 hours to calculate the VS. Before placing the residue in the furnace, it was pre-heated to 550 ℃. The total VS test was used to determine the quantity of organic matter in the sample [21].

$$\text{TVS\%} = \left[\frac{mass\ of\ dry\ sample - mass\ of\ sample\ fired\ in\ furnace}{mass\ of\ total\ sample}\right] x\ 100 \quad (3)$$

2.3 Mathematical models for determination of theoretical methane production

The elemental composition of a substrate was used to estimate the maximum theoretical methane yield using Buswell's equation (4). The Biochemical Methane Potential or Ultimate Methane Potential (BMP) of a substrate are mostly based on the assumption that the substrate will completely degrade and that the microorganisms in the substrate does not use energy [22].

The general molecular formula can be presented to be of the form $C_aH_bO_cN_d$.

$$C_aH_bO_cN_d + \left(a - \frac{b}{4} - \frac{c}{2} + \frac{3d}{4}\right)H_2O \rightarrow \left(\frac{4a+b-2c-3d}{8}\right)CH_4 + \left(\frac{4a-b+2c+3d}{8}\right)CO2 + dNH3 \quad (4)$$

Equation 4 above represents the degradation of carbon in the substrate under consideration. The coefficients a, b, c and d are dimensionless coefficients and can be evaluated from the approximated ratio of each component number of moles to the minimum number of moles among all the components [23], equations 5-8 respectively.

$$a = \frac{\%C}{molar\ massC/l} \quad (5)$$

$$b = \frac{\%H}{molar\ massH/l} \quad (6)$$

$$c = \frac{\%O}{molar\ massO/l} \quad (7)$$

$$d = \frac{\%N}{molar\ massN/l} \quad (8)$$

$$L = \frac{\%M}{molar\ massM} \quad (9)$$

%C, %H, %O and %N represent the composition of C, H, O and N in the organic substrate respectively. M represents the element with the minimum number of moles in a given sample, and in most cases, M is usually nitrogen, such that the value of d is almost always equal to1. Molar Mass C is the molar mass of carbon, and the same applies for hydrogen (H), oxygen (O) and nitrogen (N).

The maximum theoretical bio-methane production (M_{tm}) can be estimated from Equation 10.

$$\text{Mtm}\left(\frac{\text{mL}}{\text{gvs}}\right) = \frac{22.415\left(\frac{4a+b-2c-3d}{8}\right)}{12a+b+16c+14d} \quad (10)$$

2.4 Bio-methane potential experiment

Two 2L (0.002m^2) flat bottom flask were used in this study. The first 2L flask equipped with a manual stirrer at the center, acts as an anaerobic solid state bio-digester. The working volume of the bio-

digester estimated to be between 1.2-1.5L (Samples with pores in the solid bulk) and run under uncontrolled pH and temperature, which means without acid or base addition and at ambient temperature. The moisture content of each of the samples B, C, D and E were made up to 82.15%, as in sample A before the digestion process. The second 2L flask contains 1.5L of solution of 2N NaoH in water. The biogas produced in the first flask was bubbled through the solution in the second flask for CO_2 capture. The two flasks were plugged with rubber to avoid leakages and the plug fitted with delivery tubes for gas transport. The delivery tube from the second flask was connected to a measuring cylinder for bio-methane measurement by water displacement method. The anaerobic digester was flushed with nitrogen gas before starting the runs and stirring was carried out twice daily (6.00 am and 6.00 pm) each day during the tests. The individual contributions of the substrate and the inoculum to bio-methane production was never evaluated in the Biochemical methane Potential (BMP) test conducted. The test was conducted for 45 days as recommended by [4, 24] for SSADs and cumulative bio-methane measurement taken every 2 days [25].

3 RESULTS AND DISCUSSION

3.1 Sample characteristics

Cow dung samples at different ages were evaluated for the purpose of obtaining their bio-methane potentials, under uncontrolled temperature and pH. Table 1 shows the results of proximate and ultimate analysis of all the five samples (substrate + inoculum) for the SSAD. The results show some significant variation in moisture and Oxygen contents of the samples, with good CN ratios for all the samples which falls within the range 20-30, for optimum anaerobic reactor performance [26, 27] reveal an optimal CN ratio of 25 to be the best if significant amount of bio-methane is to be generated. However, variation in bio-methane yield of the samples was observed. [28] reported that operating conditions such as temperature may affect the depletion of carbon and nitrogen, creating inhibitory condition for bio-methane production.

Table 1. Sample characterization

Sample	Composition (%)			Elemental composition (wt%)				
	MC	TS	VS	H	O	C	N	C/N
A	82.15	19.80	72.30	3.50	11.45	40.80	1.65	24.73
B	62.32	21.30	71.60	3.33	20.10	39.40	1.52	25.92
C	48.31	22.20	71.40	3.41	21.62	39.00	1.66	23.49
D	35.82	22.60	69.40	3.42	25.20	38.10	1.60	23.81
E	28.58	23.30	69.00	3.41	31.65	38.10	1.47	25.92

A: Fresh cow dung; B, C, D and E: Sun dried cow dung for 1, 2, 3 and 4 week(s) respectively

3.2 Theoretical methane production potential from sample's elemental composition

Elemental analysis is used to calculate the cumulative methane yield of the five cow dung samples in order to investigate the bio-methane potential of each sample. Equation (5) was used to estimate the cumulative methane yield of the samples. The results obtained are shown in Table 2. It can be noted that bio-methane yield of the sample A (fresh cow dung) was higher (0.7476 m^3/kg-VS) than the other samples with the lowest being 0.4445m^3/kg-VS obtained from sample E (4 week's sundried cow dung) which is in agreement with a statement in the literature as cited by [29], indicating that if cow dung is not used quick enough, it loses both water and energy contents.

Table 2. Mathematical ultimate methane yield of the five cow dung samples using elemental analysis

Sample	Elemental analysis (wt%)				C, H, O, N coefficients				Molecular	M_{tm}
	H	O	C	N	a	b	c	d	formula	(m^3/kg-VS)
A	3.50	11.45	40.80	1.65	28.85	29.70	6.07	1	$C_{29}H_{30}O_6N$	0.7476
B	3.33	20.10	39.40	1.52	30.24	30.67	11.57	1	$C_{30}H_{31}O_{12}N$	0.5933
C	3.41	21.62	39.00	1.66	27.41	28.76	11.4	1	$C_{27}H_{29}O_{11}N$	0.5695
D	3.42	25.20	38.10	1.60	27.78	29.93	13.78	1	$C_{28}H_{30}O_{14}N$	0.5179
E	3.41	31.65	38.10	1.47	30.24	32.48	18.84	1	$C_{30}H_{32}O_{19}N$	0.4445

A: Fresh cow dung; B, C, D and E: Sun dried cow dung for 1, 2, 3 and 4 week(s) respectively

3.3 Experimental Biochemical methane potential

The bio-methane potential of the samples estimated theoretically was thereafter investigated through experimental process. The cumulative bio-methane volume was monitored and measured for 45 days [24]. The plots in Figure I depicts a sigmoidal growth path. Bio-methane yield was measured according to the total bio-methane volume produced per gram volatile solid [30]. The cumulative bio-methane production for the 45 days' study period revealed that accept sample A, all the samples experienced delay in bio-methane production till 4-5 days of digestion (lag phase) and increased slowly at the beginning and the end periods of the observation for all the samples. This is predicted as bio-methane production rate is directly proportional to the specific growth of methanogenic bacteria in the batch bio-digester [19]. Bio-methane production significantly increased between 5-16 days as a result of exponential growth in the methanogens and then slowly to 36 days for all the samples. After 36 days, bio-methane production tends to decrease for sample A, due to stationary phase of microbial growth. The high initial volume of bio-methane noticed in sample A during the digestion process could be attributed to the fact that, if cow dung is not used immediately, it loses its water and energy contents which are both essential parameters in bio-methane generation. Among the five samples, Sample A produced the highest bio-methane yield than the other four sample (B, C, D and E), this may be as a result of increased oxygen contents of the samples as they are being dried. Oxygen is toxic to most anaerobic microorganisms. However, the fairly reasonable bio-methane yields in these samples may have been possible where facultative anaerobes metabolize the dissolved oxygen before toxic effects are noticeable [31]. In sample (B, C, D and E) values of the bio-methane yield suggested that longer retention time was required for microbial growth as the constant yield was not achieved after 45 days.

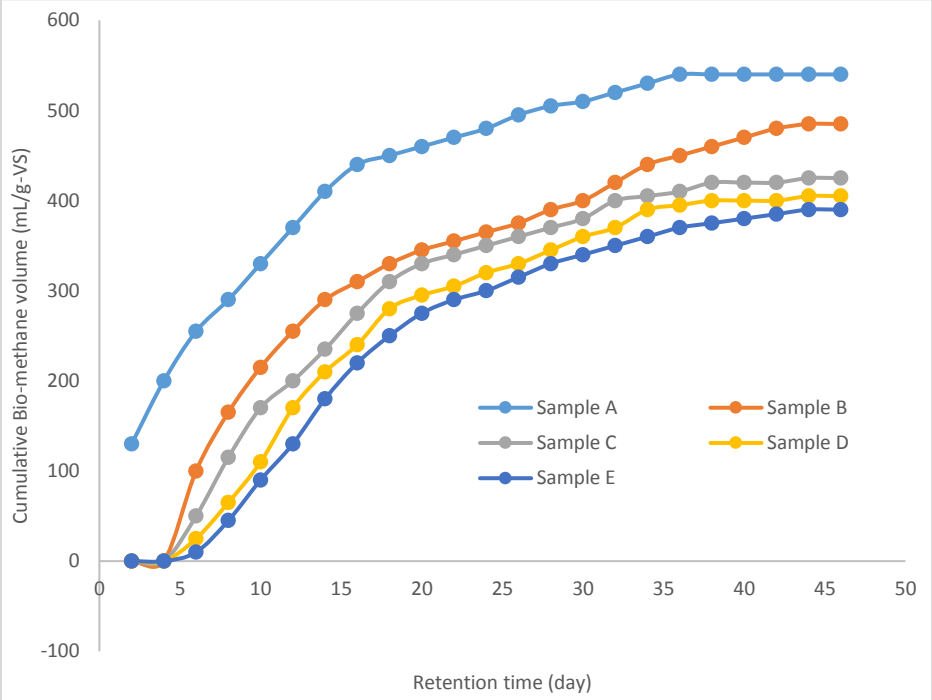

Figure 1. Cumulative bio-methane production of varying cow dung samples

3.4 Comparison between theoretical and experiment bio-methane yields

The difference between the theoretical and experimental bio-methane yields as indicated in Table 3, was obviously as a result of an earlier assumption by [22] in the theoretical bio-methane yield computation, that the substrate will completely degrade and that utilization of energy produced by the microorganisms in negligible.

Table 3. Comparison between theoretical and experiment bio-methane yields

Sample	Theoretical Bio-methane Yield (m^3/kg-VS)	Experimental Bio-methane Yield (mL/g-VS)	(m3/kg-VS)	Difference (m^3/kg-VS)
A	0.7476	540	0.540	0.2076
B	0.5933	485	0.485	0.1083
C	0.5695	425	0.425	0.1445
D	0.5179	405	0.405	0.1129
E	0.4445	390	0.390	0.0548

A: Fresh cow dung; B, C, D and E: Sun dried cow dung for 1, 2, 3 and 4 week(s) respectively

4 CONCLUSIONS

Solid state anaerobic digestion was employed to determine the bio-methane potentials of five cow dung samples. The results indicated that bio-methane yield decreases with increase age of the feedstock samples using both theoretical and experiment values. The most important finding from this work is that sample A (fresh cow dung) exhibit higher bio-methane yield than the exposed (sun dried) samples. Therefore, it can be concluded that fresh cow dung is the most suitable feedstock for bio-methane production using Solid State anaerobic digestion method at uncontrolled temperature and pH.

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