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Biogas Production from Waste By-products of Ethanol Production: 3. Modeling of Gas Yield with Time

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Authors' contributions

This work was carried out in collaboration between all authors. The corresponding author AUO designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors AUO, UCO and ODO managed the analyses of the study. Author CNA carried out the regression analysis. All authors read and approved the final manuscript.

Research Article

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ABSTRACT

The modeling of gas yield with time for the biogas production from waste by-products of ethanol production process was studied. The wastes from the processing of four starch feedstock and from their fermentation wort were utilized for the biogas production studies. The wastes constituted: (i) process wastes from starch extraction (ET) and (ii) fermentation wort (ETP). The wastes were studied alone (ET-A) and (ETP-A) and in combination with some animal wastes (cow dung (CD) and swine dung (SD) and plant wastes (field grass (FG) and glycerol (GL) giving ET-CD, ET-SD, ET-FG and ET-FG-GL. The biogas production capabilities of the wastes were in terms of (i) biogas yields (ii) onset of gas flammability and (iii) effective retention time. This was carried out for a retention period of 45 days under ambient mesophilic temperature range of 23ºC–38ºC and slurry temperature of 38ºC to 48ºC using 1 liter micro-digesters under anaerobic conditions. The modeling and simulation of biogas yield with time was carried out using NLREG version 6.3 software. The results of

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the study showed that ET-SD had the highest co-efficient of multiple determinations (Ra^2) of 80% followed by the ET-A with Ra^2 of 70% and ET-CD, 51.5% while, ETP-FG-GL had the least Ra^2 value of 1.43%, ETP-A had 8.68%, and ETP-FG, 12.63%. General results showed that gas yield with time for these waste types can only be predicted for ET-A and its combinations (ET-SD and ET-CD).

Keywords: Biogas production; biogas yield; retention time; models; waste combination.

1. INTRODUCTION

The depletion of the world petroleum reserves and the increased environmental threat and security concerns has stimulated search for alternative sources to petroleum-based fuels. Biogas, a flammable gas (for cooking and lighting), obtained from biogenic sources is being viewed as one of the best alternatives to petroleum- based fuel. It can also be used in modern waste management facilities where it can be used to run any type of heat engine to generate either mechanical or electrical power. Biogas typically refers to a gas produced by the biological breakdown of organic matter in the absence of oxygen (anaerobic digestion). The organic waste materials include animal wastes, agricultural wastes, municipal wastes, industrial wastes, domestic wastes, human wastes, solid organic wastes etc [1]. The gas is composed of mainly methane (50–70%), carbondioxide (20–40%) and traces of other gases such as nitrogen, hydrogen, ammonia, hydrogen sulphide, and water vapour etc [2]. The gas is odourless and flammable and yields about 1,000 British thermal units (BTU) (1,055 kilojoules) of heat energy per cubic foot (0.028 cubic meters) when burned [3]. The other type of biogas is wood gas which is created by gasification of wood or other biomass. This type of biogas is comprised primarily of nitrogen, hydrogen and carbon monoxide with trace amounts of methane [4].

Biogas from anaerobic digestion has a density of 1.2 kg/l at atmospheric pressure which makes it denser than air [5]. Methane can be combusted or oxidized with oxygen. This energy release allows biogas to be used as a fuel. Biogas is a renewable fuel, so it qualifies for renewable energy subsidies in some parts of the world [4]. The chemistry of the digestion process leading to biogas involving hydrolysis, acidogenesis/acetogenesis and methanogenesis has been well documented [6-8]. The production of biogas via anaerobic digestion of large quantities of various agricultural residues, municipal wastes and industrial wastes would go a long way in solving the problem of indiscriminate waste disposal and hence environmental pollution. Biogas technology amongst other processes (including thermal, pyrolysis, combustion and gasification) has in recent times also been viewed as a very good source of sustainable waste treatment / management, as disposal of wastes has become a major problem especially to the third world countries [9]. The effluent of this process is a residue rich in essential inorganic elements like nitrogen and phosphorus needed for healthy plant growth known as biofertilizer which when applied to the soil enriches it with no detrimental effects on the environment [10]. Co-production of bioethanol and biogas would allow all the components of both plant biomass and animal manure to be used in industries where provisions for cellulosic ethanol facilities are not incorporated. An earlier study on the biogas production from the pure wastes from bioethanol process which constituted the waste from starch processing and that from fermentation wort showed that their biogas production profile needed optimization, even though the biogas production of the variant from starch processing was better in terms of cumulative and average yield, onset of gas flammability and microbial load [11]. A follow-up study investigated the effect of batch co-digestion of the pure waste with some plant and animal wastes including swine waste and cow dung (for animal wastes) and field grass and glycerol (for plant wastes). The results showed that the variant with swine wastes gave the best biogas production in terms of gas yield, onset of gas flammability and retention time [12]. This study was undertaken to investigate the predictability of the gas yield with time of the pure wastes and their combinations through modeling. They were studied alone (ET-A) and (ETP-A) and in combination with some animal wastes [cow dung (CD) and swine dung (SD)] and plant wastes [field grass (FG) and glycerol (GL)]. The combinations were done in a 1:1 ratio thus giving ET–CD, ET–SD, ETP–FG, and ETP– FG-GL.

2. MATERIALS AND METHODS

2.1 Materials

The wastes were studied alone (ET-A, from starch processing) and (ETP-A, from fermentation wort) and in combination with some animal wastes [cow dung (CD) and swine dung (SD)] and plant wastes [field grass (FG) and glycerol (GL)]. The combinations were done in a 1:1 ratio thus giving ET–CD, ET–SD, ETP–FG, and ETP– FG-GL.

Other materials used for the digestion studies include; 1 liter Buckner flask which formed the micro-digesters. These were fitted with metal beehive at the bottom and connected to 2 liter measuring cylinders for measurement of the daily biogas production. The micro-digesters were fitted at the top with corks, slightly perforated for insertion of thermometers to measure the influx temperature. Additional materials used were hose pipes, water trough, clamps and stands to hold the measuring cylinders in place, biogas burner fabricated locally for checking gas flammability.

2.2 Digestion Studies

2.2.1. Waste sample preparations

The ET-A was allowed to degrade for two months. After that, it was soaked in water for four (4) days to allow for partial decomposition of the waste by aerobic microbes, which has been reported to aid faster digestion of the waste by anaerobic microbes [13-14]. It was then strained from the water using large size mesh screens while the water was also used for the charging of the wastes. The ETP – A was also allowed to degrade for the same period as the ET-A. This was done to also allow for partial decomposition of the waste by aerobic microbes. Consequent upon the sterilization by autoclave which the substrate was subjected to before and during fermentation, this was necessary to aid faster digestion of the wastes by aerobic microorganisms. The field grass (FG) was cut from the surrounding environment and allowed to degrade for a period of one month. It was then chopped into small sizes of 2″ (two inches) to reduce the particle sizes, to aid intimate contact between the waste and microorganisms and also to aid ease of stirring. After chopping the grass, it was soaked in a small bowl for one week, to allow for partial decomposition of the wastes by aerobic microorganisms and reduction of acidity [15]. At the end of 7 days, the waste was strained using large mesh screens while the water was kept and utilized for the charging of the waste. The cow dung, swine dung and glycerol were used as obtained without modification of their structure.

2.2.2 Experimental set-up

For ET-A, ET–CD, ET–SD, ETP–FG and ETP–FG–GL, the wastes and water were mixed in the ratio of 1:2 while for the ETP-A, the waste was mixed with water in the ratio of 1:1.25. The constitution of the wastes determined the waste to water ratio. The mixtures were stirred thoroughly and stoppered with the cork.

They were all charged up to ¾ of the micro-digesters while leaving ¼ head space for gas collection. All the micro- digesters were stirred thoroughly on a daily basis to ensure intimate contact of the wastes with microorganisms responsible for converting the wastes to biogas. Daily biogas production was measured by downward displacement of the water in the trough by the gas produced and recorded as the difference between the initial reading at the beginning of each day and the final reading at the end of that same day. pH of the waste slurries were monitored daily for a period of five days to ensure stability of the waste slurries. Gas flammability was monitored daily from 24 h of charging the micro-digesters till the onset of gas flammability (lag period). Microbial load of the waste slurries were carried out four times during the retention period; at the point of charging the micro- digesters, at the onset of gas flammability, at the peak of gas production and at the end of the retention period. Ambient and slurry temperatures were monitored daily throughout the retention period. Fig. 1 shows the experimental set up of the micro digesters for the biogas production.

Fig. 1. Digester set-up for biogas production of the wastes.

2.3 Analyses of Wastes

2.3.1 Physicochemical analyses

Ash, moisture, fibre and Energy contents were determined using AOAC method [16]. Fat, crude nitrogen and protein contents were determined using Soxhlet extraction and micro-Kjedhal methods described in Pearson [17]. Carbon content was determined using Walkey and Black method [18], while Total and Volatile solids (TS) and (VS) were determined using Bhatia method [19].

2.3.2 Microbial analysis

Total viable counts (TVC) of the microbes for the treated wastes slurries were carried out to determine the microbial load of the blends using the modified Miles and Misra method described in Okore [20]. This was carried out at four different periods during the digestion; at the point of charging the micro-digesters, at the point of flammability, at the peak of production and at the end of the retention period.

2.3.3 Data analysis

Statistical analysis was carried out on the data generated using “Completely Randomized design (CRD)”; a one way analysis of variance (ANOVA). It was carried out using a combination of SPSS 17.0 version and Genstat 3. For the modeling and simulation of the biogas yield with time for the biogas production, NLREG version 6.3 software; a specialized computer program designed for non-linear regression analysis was used [21].

3. RESULTS AND DISCUSSION

The result of the daily biogas production for all the variants (ET- A, ET-CD, ET-SD, ETP-A, ETP-FG and ETP-FG-GL) are graphically presented in Fig. 2. Gas production for ET-A, ET-CD, ET-SD and ETP-A commenced within 24 h of charging the micro-digesters. However, ETP-FG-GL started biogas production from 48 h while ETP-FG commenced gas production from the 7th day. The experiment was carried out under ambient temperature range of 23ºC–36ºC and slurry temperature range of 28ºC–48ºC (All within the mesophilic and thermophilic temperature ranges). Gas flammability took place at different lag periods (which is from the point of charging the digester to the onset of gas flammability) as shown in Table 1. However, the ETP- A and ETP- FG did not combust throughout the retention period and both systems had the least biogas yields. Biogas that will serve the basic need of cooking and lighting must be flammable. If it burns, it means that the methane content is at least 45%. If it does not burn, it means that the methane content is less than 45% and contains mainly CO_2 and other gases [22].

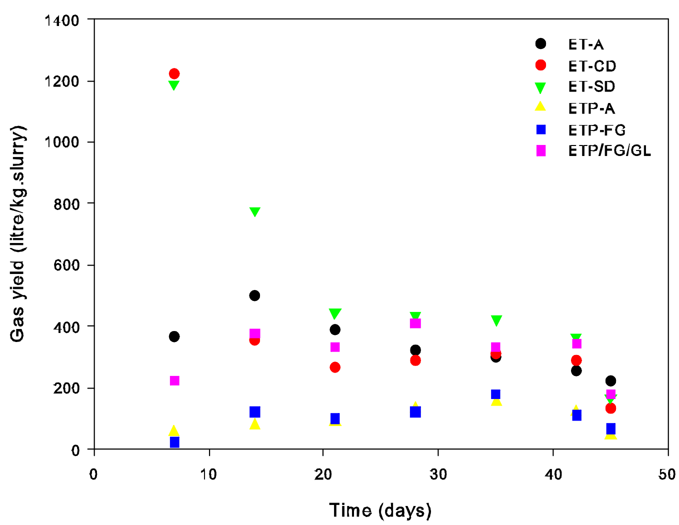

Fig. 2. Biogas production for the different wastes.

Table 1. Lag period, cumulative and mean volume of gas production

Parameters	ET-A	ET-CD	ET-SD	ETP-A	ETP-FG	ETP-FG-GL
Lag period (days)	8	5	5	0	0	13
Mean vol. (ml/kg. slurry)	52.34 ±24.23	63.70 ±56.67	84.44 ±58.67	15.06 ±6.76	16.05 ±9.34	48.89 ±19.59
Cumulative vol. (ml/kg. slurry)	2,355.49	2,866.62	3800.01	677.71	722.15	2199.94

The ET–SD had the highest cumulative biogas yield followed by the ET-CD, while the ETP-A had the least biogas yield followed by the ETP-FG.

There was significant difference (P<0.05%) between the biogas yields of ET-SD and the rest. There was no significant difference (P>0.05%) between the biogas yield of ET-A, ET-CD and ETP-FG-GL and there was also no significant difference between the biogas yield of ETP-A and ETP-FG.

In view of the fact that anaerobic digestion of substrates is generally a function of time, this relationship was quantified using regression analysis. Cumulative weekly biogas yield (Table 2) was modeled with time to determine how the gas yield of this waste type can be predicted with time.

Table 2. Biogas yield with time for the waste variants (weekly cumulative)

Time (days)	ET–A (ml/kg slurry)	ET – CD	ET – SD	ETP – A	ETP – FG	ETP-FG/GL
7	366.66	1,222.21	1188.89	55.55	22.22	222.20
14	500.00	355.55	777.77	777.77	122.21	377.78
21	388.89	266.67	444.44	88.88	99.99	333.33
28	322.20	288.87	433.33	133.32	122.21	411.12
35	299.98	311.09	422.23	155.54	177.76	333.31
42	255.54	288.90	366.68	122.21	111.10	344.43
45	222.22	133.33	166.67	44.44	66.66	177.77

The model gave the equation represented below;

GV = P0 + P1 x t

Where;

GV = Gas volume (l/kg slurry)

t = Time (days)

P0, P1 = Constants (Table 3)

A good model is determined by the R^2 and Ra^2 values. These represent the proportion of variance and coefficient of multiple determinations respectively. The amount of variants explained by the model (R^2) also shows the level to which other variants can be predicted by the model. (A very good model is expected to have R^2 values in the range of 0.90 – 0.99). From equation 1, the analysis indicated that gas yield for these waste types can be predicted as a function of time but with some limitations. The regression parameters for the equation (Table 3) indicates that the equation can only be reliably applied to some extent for the prediction of gas yield for ET–A and ET–SD (Ra^2 = 70% and 80% respectively).

Table 3. Regression parameters for gas volume vs time

Waste Type	P0	P1	Ra^2 (%)	R^2 (%)	Prob(t)
ET – A	485.67	-5.44	67.00	70.0	0.00017
ET – CD	913.51	-18.38	41.80	51.50	0.01311
ET – SD	1125.49	-21.24	76.76	80.63	0.00051
ETP – A	73.33	0.86	-9.58	8.68	0.11050
ETP – FG	69.77	1.22	-4.85	12.63	0.17015
ETP-FG-GL	333.41	-0.70	-18.29	1.43	0.00852

The co-efficient of multiple determinations Ra^2 is also shown for each of the six wastes studied. Adequate physicochemical properties are known to promote biogas production. The results of the physicochemical properties of the wastes are shown in Table 4.

The physicochemical properties of ETP and its blends in terms of calorific value, volatile solids, nutrient content (fat and protein), and carbon to nitrogen (C/N) ratio were quite poor. Those of ET-A though better than ETP, were lower when compared with its blends (ET-SD and ET-CD). Co-digesting the ET–A with cow dung (CD) and swine dung (SD) improved the physicochemical properties and consequently the gas production profile of the waste with concomitant positive effect on the Ra^2 values of the animal wastes combinations. Animal wastes have been reported to be good biogas production enhancers and starters [21]. The ET–SD had the highest cumulative biogas yield, calorific value, volatile solids, nutrient content (fat and protein), and carbon to nitrogen (C/N) ratio (which has been given to optimum in the range of 20-30:1). This is because the microbes that convert wastes to biogas take up carbon 30 times faster than nitrogen [23]. Their volatile solid (which is the biodegradable portion of the waste) was also the highest. This indicates that adequate physicochemical properties may also enhance the predictability of gas yield with time for these waste types.

Table 4. Physicochemical properties of the wastes

Parameters	ET-A	ET-CD	ET-SD	ETP-A	ETP-FG	ETP-FG-GL
Moisture (%)	21.50	45.90	55.15	83.30	58.70	74.90
Ash (%)	1.60	7.00	8.25	0.25	6.30	1.65
Crude fibre (%)	3.90	3.28	2.86	1.90	2.15	2.13
Crude fat (%)	0.43	0.27	0.44	0.25	0.24	0.49
Crude protein (%)	4.20	2.98	3.30	2.01	3.06	2.54
Crude nitrogen (%)	0.67	0.48	0.53	0.32	0.49	0.41
Total solids (%)	78.50	54.10	44.85	16.70	41.30	25.10
Volatile solids (%)	36.60	47.10	56.90	16.45	23.45	35.00
Carbon (%)	16.35	9.81	14.23	3.92	15.86	11.12
C/N ratio	24.40	20.44	26.84	12.26	32.37	27.12
Carbohydrate (%)	68.37	40.58	27.00	12.29	27.42	18.29
Calorific value(kcal/g)	125.20	176.65	294.14	59.47	87.70	125.26
Initial pH	7.59	8.09	8.11	7.98	6.14	6.29
pH at charging	7.51	7.80	7.85	7.42	6.97	7.21

The biogas production profile of ETP–A and ETP–FG in terms of biogas daily/cumulative yield and onset of gas flammability was very poor. The moisture content of ETP-A was quite high showing that the waste was mainly watery with little nutrients. Most of the nutrients may have been taken up during the fermentation to ethanol production. According to Brigas et al.

[24], spent brewery waste is normally thrown out as a waste after the sparging operation in the brewery process. This gives rise to the death of most of the microbes that should be inherent in the waste after operation. As a result, spent wastes obtained in this way are normally attacked by moulds which inhibit the growth of the bacteria in the waste. Therefore, for the spent waste to produce flammable biogas, it has to be pre-decayed and co-digested with the good starter wastes in order to improve on the microbial load of the waste. A look at the microbial total variable count (Table 5) shows that the ETP–A had very low microbial load when compared with the other variants. This corroborates the report by Uzodinma *et al*., [25] on the poor biogas production of brewery spent grain when used alone. Again, the process of fermentation wort preparation (sterilization, pH control with acids and bases etc), may have contributed to the poor production performance of ETP– A and hence the poor models obtained from it and its blends.

Table 5. Microbial total viable count (TVC)

Parameters	ET-A	ET-CD	ET-SD	ETP-A	ETP-FG	ETP-FG-GL
At charging	$2.89x10^7$	$4.51x10^7$	$5.08x10^7$	$1.72x10^7$	$1.41x10^7$	$5.00x10^5$
At flammability	$2.21x10^7$	$3.05x10^7$	$4.52x10^7$	-	-	$9.01x10^6$
At peak of production	$3.21x10^7$	$5.28x10^7$	$5.52x10^7$	$3.82x10^6$	$6.31x10^6$	$9.01x10^6$
At end of digestion	$9.50x10^6$	$2.71x10^7$	$3.23x10^7$	$2.92x10^6$	$5.00x10^6$	$6.43x10^6$

The obtained models especially ET-CD, ETP-A, ETP-FG and ETP-FG-GL does not adequately describe the dependence of gas volume on time for these wastes. This study was carried out between January and February - the hottest seasons/months in the year with high ambient temperatures. Thus, the wastes were expected to give a better pattern of biogas production. This indicates that during the wet/cold seasons, the gas production would be highly unpredictable. Even though the models generated were poor, however, they give a fair idea of the pattern of the biogas production over time for these waste types under the prevailing environmental conditions.

4. CONCLUSION

The study looked at the modeling of gas yield with time. The results have shown that the gas volume of this waste type cannot be adequately predicted with time especially for the ETP-A and its blends even during the periods of hot season with high ambient temperatures. Even though the models generated were poor, however, a pattern of biogas production was clearly shown from them. The models for the ET-A and its blends gave better models which underscores the better performance of biogas production obtained from them.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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