Predicting Rate of Biogas Production from Abattoir Waste using Empirical Models

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Abstract— Rate of biogas production using Zango-Zaria abattoir waste as substrate was monitored in a 10 litter laboratory scale batch reactor. 2.5 kg of the substrate with substrate to water ratio of 1:1 was used. The retention time was found to be 47 days. Analysis of the substrates gave an average COD of 19350 mg/L, average carbon-to-nitrogen ratio of 14.95, and concentrations of inhibitory substances below the minimum inhibitory values. AAS analysis of the biogas using NDIR Gas Analyzer, GASBOARD - 3100P indicated that its' methane and CO2 content were 67.76 % and 31.13 % respectively.Two empirical models based on the Gompertz and the Modified Logistic equations were used to fit the experimental data based on non-linear regression analysis using Solver tool in Microsoft Excel. Gompertz model gave a better goodness of fit than the Modified Logistic model with correlation coefficients of 0.998 and 0.996 for Gompertz and Modified Logistic models respectively.

Index Terms— Empirical model, Non-linear regression, biogas production, abattoir waste.

1 INTRODUCTION: Biogas is obtained by anaerobic decomposition of organic waste such as vegetables, plants, crop residues, human and animal wastes, and consists of methane as a major component with varying amount of impurities such as CO_2, N_2, H_2, and H_2S.

Abattoirs produce large amount of waste which could be used as substrate for biogas production, nevertheless this waste constitute a tremendous source of pollution in Nigeria as almost all abattoir solid waste is disposed of by open dumping and the liquid waste is channeled into streams and rivers or simply washed into open drains, untreated [1]. This practice will introduce enteric pathogens and excess nutrients into surface water and also the impurities may percolate into the underlying aquifers to contaminate wells that serve as sources of drinking water as well as for irrigation in the area.

Abattoir waste contamination can increase the level of nitrates in ground water, which causes methemoglobinemia or "blue baby syndrome" which means high nitrate ingestion by babies via contaminated drinking water, leading to short supply of oxygen to their brains and ultimately, death [2].

In most Nigerian abattoirs, the waste from the abattoir operations is a source of embarrassment, as conventional methods for the disposal of abattoir wastes, carcasses and manure, as well as other animal wastes are now proving inadequate. At Zango abattoir, in Zaria, the waste from the abattoir and dressing grounds are washed into open drainage untreated.

The abattoir waste treatment facility which consists of three underground septic tanks was designed to treat only the wastewater generated from the various processes, the solid waste was to be transported to an undesignated treatment plant. At present, none of the three septic tanks is functional and there is no provision for evacuation of the solid waste for treatment elsewhere hence all the waste generated is discharged into the environment. This resulted to a very serious land, water and air pollution. One of the proposed ways to reduce this environmental pollution is to use the waste for biogas production. To achieve this requires proper design, construction, and operation of an anaerobic biodigester.

Anaerobic biodigesters have received considerable attention in recent times because of the need to develop an alternative source of energy which is renewable in order to reduce the dependence on fossil fuels which are responsible for global warming. Extensive studies on the microbiology/biochemistry and operational characteristics of biodigesters have led to development of various types of biodigesters which include batch, sequencing batch, and continuous flow biodigesters. To develop a reliable design of an anaerobic biodigester and assess its performance, appropriate mathematical models describing the process is necessary. There are numerous mathematical models in literature such as; models for calculating biogas production based on stoichiometry and models based on reaction kinetics which also takes product inhibition, substrate limiting etc. into consideration. Gerber and Span [3] presented a comprehensive review on models available for biodigesters. However, the complexity of biodigesters (in terms of process variables), the presence of micro-colonies, the interaction between different microbial species, and the complex nature of substrates complicates such modeling. In fact, there is insufficient basic knowledge of the phenomena to guarantee development of a dependable mechanistic model. In this case, empirical models were formulated to elucidate basic mechanisms underlying this complex system and thus providing better guidance in biogas process design and control.

The empirical models parameters are established through non-linear regression methods. The most widely used empirical models used for predicting rate of biogas production are the Gompertz and Logistic equations [4].

In this study, experimental data from biodigester would be fitted into the two empirical models; Gompertz and Modified Logistic models for predicting the rate of biogas production.

2. ANAEROBIC BIODIGESTER MODELS

In modeling anaerobic biodigesters, two basic model classifications are common; Kinetic and Empirical models.

2.1 Kinetic Models

These models are based on rate of substrate utilization or rate of microbial growth. The microbial fermentation which is in four stages; hydrolysis, acidogenesis, acetogenesis and methanogenesis are represented here in a simplified single stage equation as follows;

$$\mathrm{S} + \mathrm{X} \rightarrow \mathrm{Biogas}\ (\mathrm{CH_4} + \mathrm{CO_2}) + \text{more microbes} \quad (2.1)$$

Where;

X = Microbes

S = Substrate

The kinetic of this reaction can be based on;

a) Rate of Microbial growth
b) Rate of substrate utilization
c) Rate of product(Biogas) formation

The microbial growth rate is based on exponential growth of microbes described by Malthus Law [5] & [6] which may be stated as;

$$\frac{dC_X}{dt} = \mu C_X \quad (2.2)$$

Where;

C_X = concentration of the microbes at time t (mg/L)

μ = specific microbial growth rate (s^{-1})

And the rate of substrate utilization is related to mi-

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crobial growth rate according to the following equation;

$$\frac{dC_X}{dt} = -Y\frac{dC_S}{dt} \Longrightarrow -\frac{dC_S}{dt} = \frac{1}{Y}\frac{dC_X}{dt} = \frac{\mu C_X}{Y} \qquad (2.3)$$

Where; Y = Microbial yield coefficient

C_S = concentration of the substrate at time t (mg/L)

There are different expressions for **μ** that are being used to describe microbial growth kinetics, among them is the Monod's equation [5] stated as;

$$\mu = \frac{\mu_m C_S}{(K_S + C_S)} \qquad (2.4)$$

Monod showed a hyperbolic relationship between the exponential microbial growth rate and substrate concentration. In this model, the raw kinetic parameters, namely, micro organisms' growth rate and half velocity constant are deterministic in nature, and these predict the conditions of timing of maximum biological activity and its cessation.

The Monod's model suffers from the drawback that one set of kinetic parameters are not sufficient to describe biological process both for short and long retention times and that kinetic parameters cannot be obtained from complex substrates. To alleviate limitations of the Monod model while retaining its advantages some other models have been developed which attempt to describe kinetics of substrate fermentation in terms of several parameters [3].

There are several models describing the rate of product (Biogas) formation, among the most commonly used is the two parameter model proposed by Luedeking & Piret in 1959 [5];

$$\frac{1}{C_x}\frac{dC_p}{dt} = \delta\mu + \varepsilon \qquad (2.5)$$

Where;

C_p= product concentration

The quantities δ and ε were found to be pH dependent.

Another model available in literature [5] for product that is produced at the same time as substrate is degraded such as biogas is;

$$\frac{dC_p}{dt} = \delta\mu C_x \qquad (2.6)$$

The work of Buswell and his colleagues in 1938 led to better understanding of the material balance between substrate composition and methane production. The work of Buswell was subsequently extended by Sykes in 2000 and can be used to estimate the amount of methane, carbon dioxide, ammonia and hydrogen sulfide that will be produced under anaerobic conditions if the substrate composition is known [6]. This stoichiometry model is time independent.

$$C_nH_aO_bN_cS_d + m_1H_2O \rightarrow m_2CH_4 + m_3CO_2 + cNH_3 + dH_2S \qquad (2.7)$$

Where;

$$m_1 = n - \frac{a}{4} - \frac{b}{2} + \frac{3c}{4} + \frac{d}{2}$$

$$m_2 = \frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3c}{8} - \frac{d}{4}$$

$$m_3 = \frac{n}{2} - \frac{a}{8} + \frac{b}{4} + \frac{3c}{8} + \frac{d}{4}$$

The gaseous ammonia formed will react with the carbon dioxide to form ammonium ion and bicarbonate according to the following reaction;

$$NH_3 + CO_2 + H_2O \longrightarrow NH_4^+ + HCO_3^- \qquad (2.8)$$

This reaction leads to formation of alkalinity under anaerobic conditions.

2.2 Empirical Models

Researchers on Biogas have attempted to use several models to fit empirical data, the most widely used model is the Gompertz model given by the following equation;

$$V = A\exp\left[\exp\left\{\frac{R_{max}\, e}{A}(\lambda - t) + 1\right\}\right] \qquad (2.9)$$

Where;

v = Cumulative volume of specific biogas production (ml/gVSS).

A = Biogas production potential (mL/gVSS).

R_{max} = Maximum biogas production rate (mL/gVSS.hr).

λ = Lag phase period (minimum time to produce biogas) (hr).

t = Cumulative time for biogas production (hr).

A, λ and R_{max} are constants to be determine by non-linear regression.

And the modified Gompertz equation also called Gompertz-T equation given as;

$$V = (\delta t + A)\exp\left[\exp\left\{\frac{R_{max}\, e}{(\delta t + A)}(\lambda - t) + 1\right\}\right] \quad (2.10)$$

Where;

δt = Slope correction factor in the terminal phase (mL/hr)

In differential form, the Gompertz equation can be written as[7];

$$\frac{dV}{dt} = -\alpha V \ln\frac{V}{R_{max}} \quad (2.11)$$

$$R_{max} = V_o e^{\beta/\alpha} \quad (2.12)$$

Where;

V_o = Initial volume of biogas during the exponential growth phase (mL)

α = retardation rate (s^{-1})

β = Initial growth rate (s^{-1})

Modified Logistic model [8] can be presented as follows;

$$V = \frac{A}{1+\exp\left(\frac{4R_{max}\,(\lambda - t)}{A}+2\right)} \quad (2.13)$$

Apart from the Gompertz and Logistic models, there are numerous other empirical models used for predicting rate of biogas production, out of which three are shown in Table 1.

The Gompertz equation and the modified Logistic models have been used with experimental data from anaerobic digesters [9].

Table 1: Other empirical models for predicting rate of biogas production

Model Name	Mathematical Expression
Von Bertalanffy [10]	$V = a\{1 - b\exp(-ct)\}^3$
Brody [11]	$V = a\{1 - b\exp(-ct)\}$
Transference [8]	$V = A\left\{1 - \exp\left[-\frac{R_m(t-\lambda)}{A}\right]\right\}$

3. MATERIALS AND METHODS

3.1 Characterization of the substrate;

Samples of the abattoir waste (paunch and intestinal content) were collected on a weekly basis over a period of one month and analyzed for the following parameters; COD, TSS, VSS, Carbon to Nitrogen ratio using standard methods (ASTM) as shown in Tables 2 & 3. The samples were also analyzed for methanogenic bacteria inhibitory substances.

3.2 Inoculation; A mixture of fresh rumen obtained from the abattoir and sludge taken from a waste dump at Shika was used as inoculum.

3.3 Substrate preparation and digestion; The abattoir waste was collected from Zango-Zaria, mixed with water in the ratio 1:1 [4] to form slurry which was then inoculated with the inoculums at 100 ml/liter. 2.5 kg of the waste was used to form 5.7 liters of slurry which was loaded into a 10-liter locally fabricated Biodigester shown in Figure 1. The biogas produced was monitored through a pressure gauge and the temperature through a thermometer over a period of forty-

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seven days.

The pressure was converted to volume at normal conditions using ideal gas equation and data fitted into Gompertz and modified Logistic models using Non-linear regression analysis with Solver tool in Microsoft Excel. The biogas produced was analyzed at National Research Institute for Chemical Technology NARICT using NDIR Gas Analyzer, GASBOARD - 3100P.

Fig. 1 10-Liter Locally fabricated laboratory scale biodigester

4. RESULTS

The results for the characterization of the abattoir solid waste is shown in Tables 2, 3a & 3b, while Table 4 shows the result for the analysis of the biogas produced.

Table 2: Characteristics of the abattoir solid waste

Sample	COD (mg/L)	TSS (mg/L)	VSS (mg/L)	Carbon %	Total N_2 %	C : N Ratio
wk1	19600	1230	745	33.7	2.10	16.0
wk2	19000	2160	1335	32.1	1.93	16.6
wk3	19000	1570	776	19.1	1.75	10.9
wk4	19800	1980	915	21.1	1.30	16.2
Ave.	**19350**	**1735**	**942.7**	**26.5**	**1.77**	**14.9**
Test Method	ASTM D1252	ASTM D5907	ASTM D1868	ASTM D4839-03	ASTM D3590-89	-

Note: wk1 means sample taken in week 1from the date of substrate charge into the Biodigester.

Table 3a: Concentration of inhibitory substances in the abattoir solid waste

Sample	NH_3 (mg/L)	Zn (mg/L)	Mn (mg/L)
wk1	2.00	1.27	0.175
wk2	0.30	1.27	0.263
wk3	5.60	1.20	0.31
wk4	0.10	1.27	0.14
wk5	0.52	1.30	0.35
Ave.	**1.70**	**1.26**	**0.25**
Test Method	**ASTM D1426**	**ASTM D1691-12**	**ASTM D858-12**

Table 3b: Concentration of inhibitory substances in the abattoir solid waste

Sample	Cu (mg/L)	Cr (mg/L)	Ni (mg/L)
wk1	0.061	ND	0
wk2	0.061	ND	0
wk3	0.148	ND	0
wk4	0.200	ND	0
wk5	0.148	ND	0
Ave.	**0.12**	**ND**	**0.00**
Test Method	**ASTM D1688-12**	**ASTM D1687-92**	**ASTM D1886-14**

ND = Not detectable.

Table 4: Analysis of the biogas produced (Using NDIR Gas Analyzer, GASBOARD - 3100P)

S/N	Component	% mole
1	CO	0.00

ISSN 2229-5518

2	CO_2	31.13
3	CH_4	67.76
4	H_2	0.00
5	Others	1.11

Figure 2 shows the variation of cummulative volume of biogas per gram of substrate with time and Figures 3 & 4 show the graphical representation of the data-fitting with Gompertz and modified logistic models respectively.

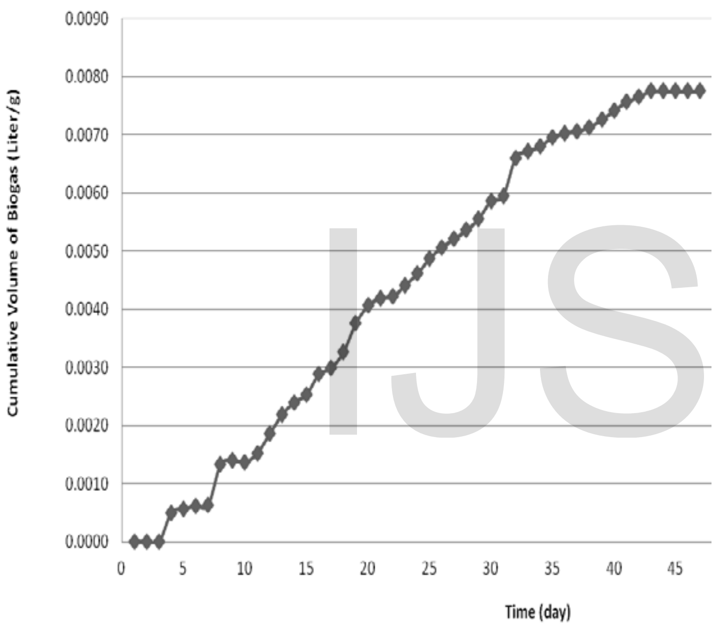

Fig. 2 Plot of cummulative volume of biogas (L/g of Substrate) against time

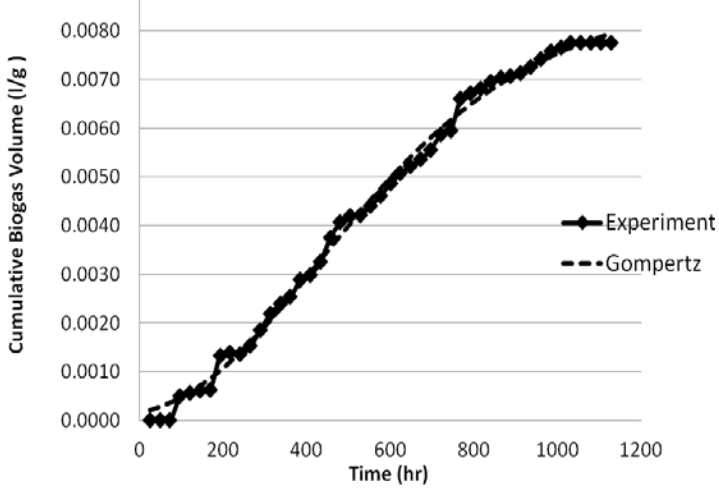

Fig. 3 Experimental data fitting with Gompertz Model

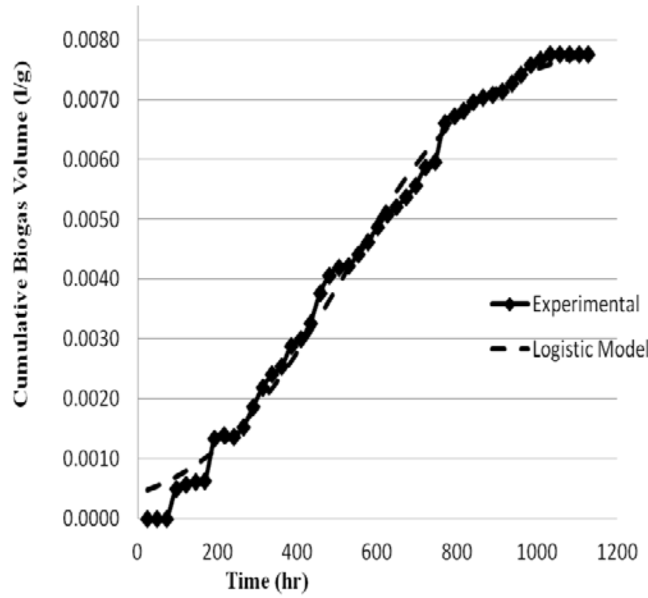

Fig. 4 Experimental data fitting with Modified Logistic Model

Using non-linear regression method with Microsoft Excel, the results for parameters and the goodness of fit for the Gompertz and Modified Logistic models are shown in Table 4.

Table 4: Goodness of fit for the Gompertz and Modified Logistic Models

Model	Model Parameters			Correlation Coefficient
Gompertz	A (L/g)	R_{max} (L/g.hr)	λ (hr)	0.998
	0.0087	0.000011	120.7	
Modified Logistics	a	b	C	0.996
	0.0079	17.7755	0.006	

5. DISCUSSIONS

Zango-Zaria abattoir solid waste was characterized for its suitability as substrate for biogas production based on the major characteristics of substrate that affect biogas production such as organic content, carbon to nitrogen ratio, and presence of inhibitory substances. The results indicate high content of organic matter (COD = 19350 mg/L) and low concentrations (below the inhibitory limit) of toxic substances that will hinder biogas production. The carbon to nitrogen ratio

(C: N = 14.97), though less than the optimum for anaerobic digestion (optimum C:N ratio = 30-20), but is within the range for cow slurry which is 10-20. Cumulative volume of 19.3929 liters of gas at 15.5 ^{o}C, 1 atm was produced in 43 days after which the digester was observed for further four days but no gas was produced. The biogas produced from the waste has a relatively high content of methane (67.76 % mol).

Plot of cumulative volume against time showed a steady increase in the volumetric rate of biogas produced until the 30th day when the rate started declining and finally remains constant (gas production stop). Digester failure was not observed; this may be attributed to the low concentration/absence of toxic substances.

The cumulative volume-time data obtained from the digester was fitted to two empirical models; the Gompertz and Modified Logistic models with the aim of determining the empirical model to be used in predicting the rate of the biogas production. Correlation coefficients of 0.998 and 0.996 for Gompertz and Modified Logistics models respectively indicate that both the two models can adequately be used for predicting the rate of biogas production with Gompertz model slightly giving a better prediction.

The two models' parameters were determined using non-linear regression tool "Solver" in Microsoft Excel. The lag time λ = 120. 72 h determined by the non-linear regression data fitting method is higher than the actual value of 3 days (72 h)

6. Conclusion

Based on the results obtained, the substrate has high content of organic matter (COD = 19350 mg/L) and low concentrations (below the inhibitory limit) of toxic substances. Furthermore, the relatively high content of methane in the biogas produced makes the substrate suitable for biogas production.

The rate of biogas production using Zango-Zaria abattoir solid waste can be predicted using Gompertz and the Modified Logistics models with Gompertz model slightly giving a better prediction.

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