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Modelling the Kinetics of Biogas Production Potential of a Closed System Digester: The Effect of Algae on Production Yield

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ABSTRACT: The quest for better techniques of harnessing biomasses and increasing the biogas production yield as a renewable energy source which is not only readily available but also cheap has been on the increase since its discovery. This research employed the mass balance equation in developing mathematical models for computing biogas production yield, biodegradability constant (K) and the biogas production flow rate with respect to time for a bioreactor (with consideration to the material advection from the control volume after biogas production commencement). The biogas substrates used in the experiment for validating the model are cow dung and algae in varying cow dung-algae proportions of 1:0, 1:1, 2:1 and 3:1 respectively. The experimental result showed that, algae in co-digestion with cow dung is feasible at a blend ratio not exceeding average value because as the proportion of algae in the sample increases the carbon to nitrogen (C: N) ratio drifts away from optimum performance value. The goodness of fit (R^2) gotten from the non-linear plot of the MS-Excel was above 0.9 for all the samples for production yield and biodegradability constant which indicates that the model is more appropriate than the exponential rise and linear model for yield computation. Furthermore, the developed models can be used to generate charts that can be read to estimate the yield and K-value for related substrates

I. INTRODUCTION

The recent focus on renewable energy as an alternative energy source to fossil fuel for both domestic and industrial energy generation has led to increased research on better ways of harnessing these renewable energy sources. Anaerobic digestion (AD) of biomass which is one of such renewable energy sources has gained popularity and interest in the last decades not only because it is a useful energy source but also because it supports improved waste management practices resulting in better water quality protection and aesthetic beauty [5]. The gaseous products of AD commonly known as biogas comprises basically methane (60-70%) and carbon dioxide (30-40%) with hydrogen sulfide and other gases like nitrogen, oxygen and ammonia in minute quantity [1]. The biogas production yield from different biomasses varies because of the difference in biochemical composition of the substrate resulting from variation in biodegradability rate and fraction of readily degradable substrate during the production life time examination. In the light of this, it is imperative to develop mathematical models for estimating these parameters influencing production yield to enhance biomass selection for biogas production especially under limited experimental study time. This research employed the mass balance equation for developing mathematical models to validate the experimental biogas production parameters from co-digestion of cow dung and algae in varying proportions. From previous studies, algae when used independently as biomass for biogas production results in low production yield because of the carbon to nitrogen ratio (C: N) value which ranges between 8-9 (below optimum value of about 20-30) [6], nevertheless, production yield could be enhanced when it is used as co-digestate [8]. In the work of K. Gaurav et al, co- digestion of algae with cow dung increased biogas production yield by about 20%, similar result was also obtained by K. Sanjeev et al, in their study but the effect of increased algae quantity ratio above average value was not mentioned. Several authors have also simulated biogas production yield using different models including linear and exponential model and the kinetic model developed from

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the mass balance equation. Mashert, p. et al, compared the R^2 plot result of employing both linear and exponential model for biogas production yield and arrived at a better result for the exponential plot. Gaurav, K. et al, modelled co-digestion of cow dung production yield using exponential growth model and obtained an increased yield by about 18% and R^2 value of 0.85. O. L Momoh et al, developed a model for evaluating production yield (because of the limitation of the linear and exponential model) from mass balance equation and obtained a R^2 value of about 0.88. In their study, the effect of biogas advection from the bioreactor was considered negligible, but in this research, the material advection from the bioreactor after bio-degradation was accounted for in the mass balance equation used in developing the model for production yield computation. A mathematical model was also developed from the differential of the polynomial plot for estimating the flow rate from the bio-reactor.

II. MATERIALS AND METHODS

A SUBSTRATE COLLECTION AND PREPARATION: THE SUBSTRATES USED IN THIS WORK ARE COW DUNG AND ALGAE

(a) The cow dung was collected from the farm of the Faculty of Agricultural science located in University park of the University of Port Harcourt. The cow dung was matched into fine particles after which the physiochemical analysis (that is the fraction of volatile solid in each substrate and the moisture content of each substrate) were determined using moisture analysis method. The pH of each slurry was also determine using Orion-620 PH meter while the daily biogas production was measured by first determining the empty volume of the tube and subtracting each incremental value from it.

(b) The algae (*chroccoccus specie*) were obtained from an abandoned residential site in Obio-Akpor Local Government Area of Rivers state Nigeria. The algae were pre-treated by soaking them in hot water of about 100°C for 20min as recommended by K., Sanjeev to break down the ligno-cellular cell wall that is recalcitrant to biodegradation. The attached soil particles were removed by decantation and filtration before grinding with a manual grinder into fine particles to increase the surface area available for biodegradation and also prevent digester clogging during feeding and discharge. Similar method for determining the physiochemical properties, PH and biogas production measurement are employed as in (a).

B EXPERIMENTAL DESIGN AND SETUP

The reactor used in this research are two biogas digesters of the same dimensions designed as a closed system with the substrates fed into them in batches. The gas collection point is positioned at the top just above the storage space designed for gas at the upper section of the digester.

Digester A: Comprised 100% cow dung in 16l of water (that is, 8kg of cow dung in 16l, a cow dung -algae ratio of 1:0)

Digester B: Comprised 50% cow dung and 50% algae in 16l of water (that is, 4kg of cow dung and 4kg of algae in 16l, a cow dung -algae ratio of 1:1).

Digester C: Comprised 66.3% cow dung and 33.6% algae in 16l of water (that is, 5.32kg of cow dung and 2.68kg of algae in 16l, a cow dung -algae ratio of 2:1).

Digester D: Comprised 75% cow dung and 25% algae in 16l of water (that is, 6kg of cow dung and 2kg of Algae in 16l, a cow dung -algae ratio of 3:1).

III. RESULTS AND DISCUSSION

A MODEL DEVELOPMENT

The evaluation of the biogas production yield at any given time(t) was assessed by developing a kinetic model using the mass balance equation. In the model development, the biogas digester was considered as a control volume since it is not an inverted system as shown in the experimental setup in Figure 1. Therefore, the mass balance equation which is given by Eq (1) and mathematical expression depicted in Eq (2) was used to model the relationship between the biodegradability of the substrate and the biogas production yield at any given time(t).

$$\begin{bmatrix} \text{The rate of} \\ \text{increase in storage of } i \text{ in the cv} \end{bmatrix} = \begin{bmatrix} \text{Net rate of advection} \\ \text{of } i \text{ into the CV} \end{bmatrix} + \begin{bmatrix} \text{Net rate of ormation} \\ \text{of } i \text{ by reaction inside the CV} \end{bmatrix} \quad (1)$$

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$$\frac{dVC}{dt} = \sum Q_i C_{i_{inflow}} - \sum Q_i C_{i_{outflow}} + rv \qquad (2)$$

The net rate of advection of materials into the controlled volume is not neglected since there is outflow of materials from the controlled volume after biodegradation into the storage tube although, material inflow is absent. Therefore, Eq (2) is reduced to Eq (3) given below.

$$\frac{VdC}{dt} = -QC + rV \qquad (3)$$

Where, Q is the volume flow rate of materials, C is the concentration of the substrate, r is the rate of reaction within the control volume and V is the material volume. Dividing Eq (3) through with V and replacing r with $-KC$ gives:

$$\frac{dC}{dt} = -\left(\frac{Q}{V} + K\right)C \qquad (4)$$

Taking the integral from the time production begins to any time (t), we have:

$$\ln\frac{C_t}{C_0} = -\left(\frac{Q}{V} + K\right)(t - t_0) \qquad (5)$$

The above equation gives a relationship between the substrate degradation in terms of initial concentration of the volatile solid and the volatile solid concentration at any given time without any information of the biogas production. A transformation of the biodegradable solids into biogas can described by Figure 1. [1].

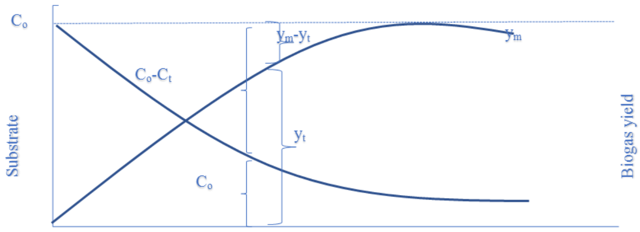

Figure 1. *Pattern of transformation of volatile solid into biogas.*

$$\frac{C_t}{C_0} = \frac{y_m - y_t}{y_m} \qquad (6)$$

C_t and $C_0$are the volatile solid concentration at any time(t) and the initial concentration of volatile solid respectively. Substituting Eq (6) into Eq (5) and taking the natural logarithm of both sides gives;

$$y_t = y_m\left[1 - e^{-\left(\frac{Q}{V}+K\right)(t-t_0)}\right] \qquad (7)$$

But, $Q = \frac{V}{t_0}$, replacing the expression for Q in eq (9) gives;

$$y_t = y_m\left[1 - e^{-\left(\frac{1}{t_0}+K\right)(t-t_0)}\right] \qquad (8)$$

But, $K = \frac{1}{t_0}$, replacing the expression for K in Eq (8) gives;

$$y_t = y_m\left[1 - e^{-(2K)(t-t_0)}\right] \qquad (9)$$

Where; y_t is biogas production yield at any given time, y_m is maximum biogas production yield, K is degradability rate and t_0 is initial production time

The above equation can be used to compute the biogas production yield at any given time prior to maximum production (if information about the maximum production yield, the rate constant associated with the degradation and the observed initial production time is known) in a reactor that is assumed not to be in steady state during biodegradation but accounts for the outflow of biogas from the system.

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In order to determine the rate of biodegradability(k) the derivative of Eq (9) with respect to time was computed.

$$\frac{dy_t}{dt} = y_m\left(\frac{1}{t_0} + K\right)\left[e^{-\left(\frac{1}{t_0}+K\right)(t-t_0)}\right] \qquad (10)$$

Taking the natural logarithm of Eq (10) one obtains:

$$ln\frac{dy_t}{dt} = lny_m + ln\left(\frac{1}{t_0} + K\right) - \left(\frac{1}{t_0} + K\right)(t - t_0) \qquad (11)$$

Rearranging Eq (11) it becomes:

$$ln\frac{dy_t}{dt} = \left[lny_m + ln\left(\frac{1}{t_0} + K\right) + 1 + kt_0\right] - \left(\frac{1}{t_0} + K\right)t \; (12)$$

A plot of $ln\frac{dy_t}{dt}$ against t gives a straight-line equation with slope $-\left(\frac{1}{t_0} + K\right)$ Hence, the value of k can be calculated from Eq (12) if the slope is denoted by M.

$$K = -\left(\frac{1}{t_0} + M\right) \qquad (13)$$

$$M = -(2K) \qquad (14)$$

$$K = -\left(\frac{1}{M}\right) \qquad (15)$$

A comparison of the experimental and model biogas production yield at any given time (t) before maximum production is obtained and computed using MS non- linear regression model is shown in Figure 4-7 for the four samples with their respective goodness of fit.

B. EXPERIMENTAL RESULT AND DISCUSSION

The daily biogas production yield plot for a 40-day period at ambient temperature range of 27ºC-32ºC for the four samples are shown in Figure 2. The observed curve is typical of a production profile curve which comprises production build up, apex and decline phases. There was an observed time lag in biogas production for all the four samples due to the difference in biochemical composition of the substrate (i.e., the bacteria activities during the hydrolysis, acidogenesis and methanogenesis stage). The production start-up time was observed to be 11 days, 12 days, 13 days and 9 days for samples A, B, C and D respectively with corresponding volume yield of 3.52L, 2.64L, 5.9L, and 5.89L. This delay can be attributed to the susceptibility of cow dung to biodegradation as a result of its cellulose content. A lower production start-up time was observed for sample A, which comprises 100% cow dung followed by D, B and C with algae percentage of 25, 33.3 and 50 which can be attributed to the complex ligno-cellular cell wall of algae which makes it recalcitrant to biodegradation, however, the thermal pre-treatment used in this experiment has reduced the effect [7]. From the production profile curve shown in Figure 2, a steady production rate was observed for sample A which gradually got to the peak yield value before production finally stopped but for the blend samples B, C, and D, production was slow at the initial phase and suddenly increased linearly until it gradually reduced before it stopped. The sudden increased yield of the blend samples can be attributed to the increase in the normal low carbon to nitrogen ratio (C:N) value of algae by the cow dung in the blend mixture thereby increasing the production yield.

Maximum production volume was observed for sample A, B, C and D on day 19, 19, 21 and 19 with a corresponding value of 16.89L, 17.67L, 23.6L and 17.67Lwhile production was observed to end on day 32, 35, 36 and 34 with a corresponding yield of 0.29L, 0.12L, 0.296L and 0.296L respectively.

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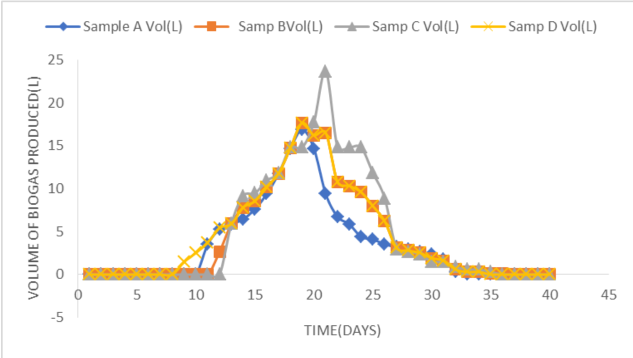

Figure 2. Daily biogas production in volume.

Digester C recorded the highest biogas production of 196.84L as shown in Figure 3 followed by digester D, B and A with values 180.50L, 170.2L and 143.36L respectively. The result indicates that, as the proportion of algae in the blend increases the production potential also increases but further increase in algae proportion above the average value reduces the production yield which is in line with the findings of of K. Gaurav et al and K. Sanjeev et al. This can be attributed to the large quantity of algae present in the blend producing almost the same effect as when algae are used alone as a substrate.

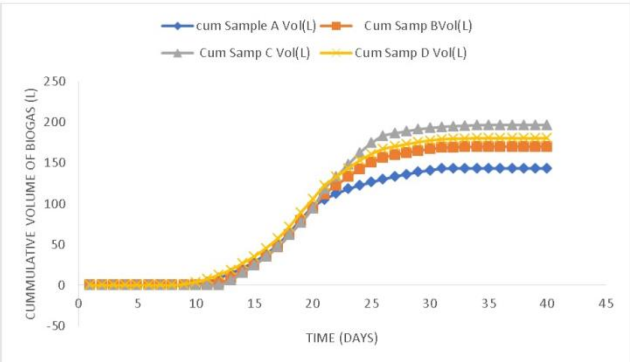

Figure 3. Cumulative biogas production in volume.

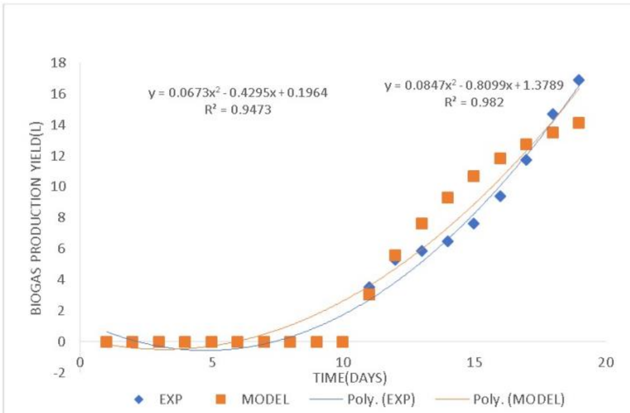

Figure 4. Comparison of biogas production yield for modelled and experimental result for Sample A.

The production yield result for each sample was used to validate the developed model using MS excel non-linear regression plot. The polynomial trendline was used since the observed curve was neither linear nor exponential but polynomial in nature. The coefficient of determination (R^2) for both the experimental and model were computed and the values for sample A, B, C and D were approximately 0.95 and 0.98; 0.96 and 0.98; 0.95 and 0.96 and 0.93 and 0.99 respectively. The R^2 -value of the model result which approaches unity (that is, approximately 1) is an indication that the model is close to experimental result and is more appropriate for computing production yield when compared with the linear, exponential growth model applied by Gaurav, K., and the developed model of O. L Momoh et al that neglected the effect of biogas outflow after biodegradation. A comparison of the experimental and model R^2- value for each of the samples showed that sample C had less variation followed by sample B, A and D. This is an indication that the model is most suitable when applied to sample C which comprises a blend of 2:1 of cow dung and algae proportion.

Another relevant model for estimating the flow rate of biogas from the bioreactor was arrived at by taking the derivative of the slope from each of the non-linear regression plot which is presented in Eq 11-13 with goodness of fit 0.95, 0.96, 0.95 and 0.93 respectively. Where; y is the biogas production yield (in volume) at any given time(t) and x is the examination time (t).

$$y = 0.0673t^2 - 0.4295t + 0.196 \qquad (16)$$

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$$y = 0.0804t^2 - 0.7661t + 1.1949 \quad (17)$$

$$y = 0.0847t^2 - 0.8175t + 1.2021 \quad (18)$$

$$y = 0.0477t^2 + 0.0557t - 1.1578 \quad (19)$$

The first order derivative of Eq 11-13 can be used to estimate the volume flow rate of biogas from the bioreactor which is expressed in Eq 15-18.

$$\frac{dy_t}{dt} = 0.1346t - 0.4295 \quad (20)$$

$$\frac{dy_t}{dt} = 0.1608t - 0.7661 \quad (21)$$

$$\frac{dy_t}{dt} = 0.1694t - 0.8175 \quad (22)$$

$$\frac{dy_t}{dt} = 0.0954t - 0.0557 \quad (23)$$

These equations can be applied by researchers in evaluating biogas production yield of an algae co-digestion blend with cow dung with time progression without necessarily carrying out the experimental study.

A comparison of the volume flow rate for each of the four samples A, B, C and D for a 20-day period showed that, the biogas flow commenced in Digester D with a flow rate of 0.44l/day with increasing value as more substrate conversion occurred. The initial flow rate for Digester B was observed to be 0.12l/day while that of digester C and D were 0.15l/day and 0.04l/day respectively. At the end of 20-day period, maximum flow rate was observed for Sample C followed by B, A and D these results corresponded to the actual observed experimental results.

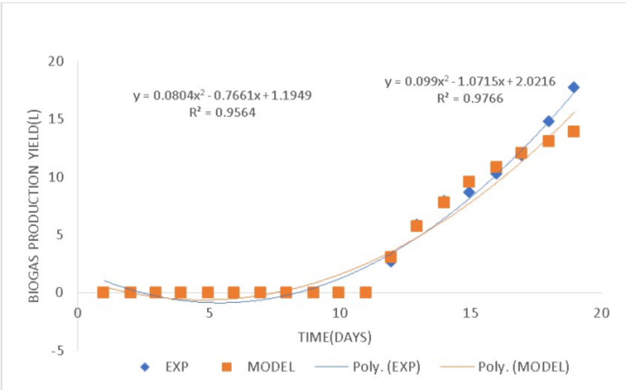

Figure 5. Comparison of biogas production yield for modelled and experimental result for Sample B.

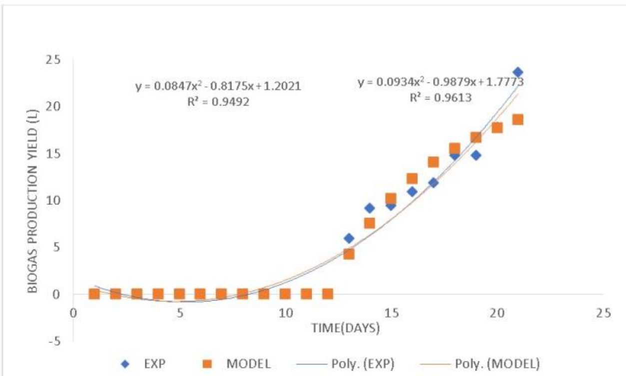

Figure 6. Comparison of biogas production yield for modelled and experimental result for Sample C.

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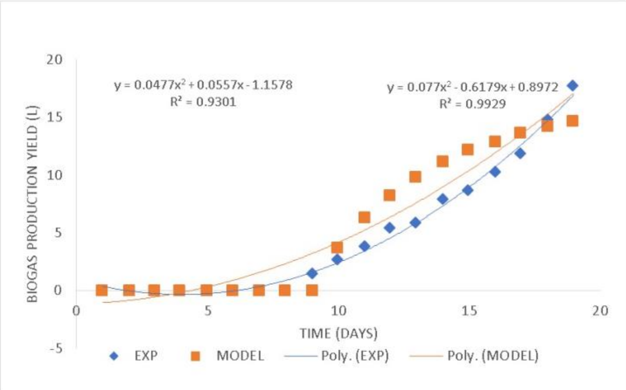

Figure 7. Comparison of biogas production yield for modelled and experimental result for Sample D.

The slope of the linear plot for samples A, B, C and D are 0.0736, 0.0848, 0.0866 and 0.0566 respectively which when computed into Eq (22) would yield the k values for each sample.

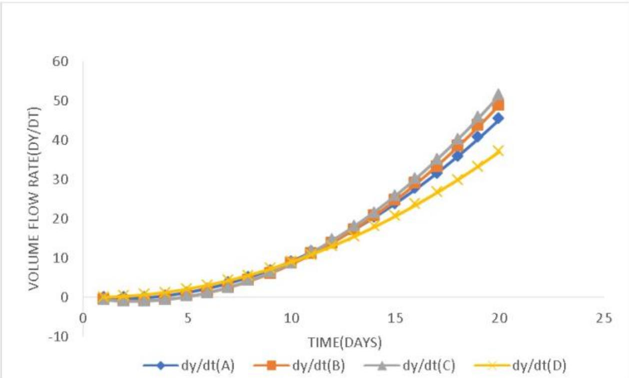

Figure 8. Comparison of the volume flow rate for the four samples.

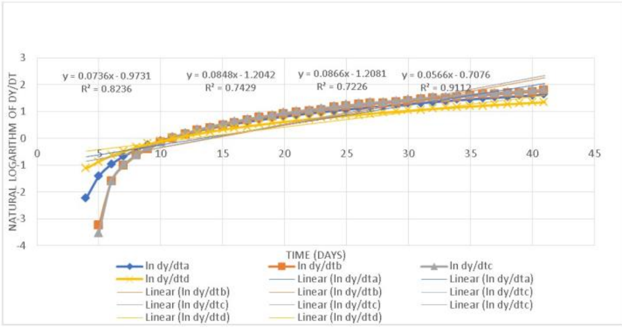

Figure 9. *Comparison of the volume flow rate for the four samples.*

Table 1. Digester sample Properties.

Digester	Weight of Cow dung (Kg)	Weight of Algae (Kg)	C:N	K(day^{-1})	y_m(l)	Methane Composition (% Vol)	R^2
A	8	0	36.7:1	0.10	16.89	49.08	0.982
B	4	4	16.5:1	0.090	18.01	54.03	0.9766
C	5.32	2.68	25.3:1	0.083	23.68	57.01	0.9613
D	6	2	31:1	0.125	17.67	49.96	0.9929

IV. CONCLUSION

The kinetic model developed from the mass balance equation for estimating the biogas production yield resulted in a R^2 value above 0.9 for all four samples which indicates that the model is a better alternative to the linear and exponential model for estimating production yield. Furthermore, the experimental result shows that, application of algae as co-digestate with cow dung is a feasible anaerobic digestion process at a blend ratio not exceeding average value because as the proportion of algae in the sample increases the C:N ratio drift away from optimum performance value. A blend ratio of 2:1 which corresponds to 5.32kg of cow dung and 2.68kg of algae in 16L of water yielded optimal performance in this

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study. The biodegradability rate of any biomass can be estimated from the developed model by plotting the yield curve and dividing the obtained slope by two. The model can be applied in generating charts for various co-digestion processes for monitoring the biodegradation of such substrates applications, AMF herein makes a trade off of those between the time of response and the cost of communication.

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