

Estimation of Biogas Potential of Liquid Manure from Kinetic Models at Different Temperature

Abdulhalim Musa Abubakar^{1*}, Luqman Buba Umdagas², Abubakar Yusuf Waziri³, Ehime Irene Itamah⁴

^{1,3}Department of Chemical Engineering, Faculty of Engineering, Modibbo Adama University (MAU), P.M.B 2076, Yola, Adamawa State, Nigeria

²Department of Chemical Engineering, Faculty of Engineering, University of Maiduguri (UNIMAID), P.M.B 1069, Maiduguri, Borno State, Nigeria

⁴Faculty of Engineering, Department of Electrical and Electronics Engineering, Federal Polytechnic Daura, P.M.B 1049, Daura, Katsina State, Nigeria

*Corresponding Author: abdulhalim@mautech.edu.ng, Tel.: +2347050244277

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Abstract— The target when using models to analyse results of biogas yield from manure or similar substrate is mostly to determine their kinetic parameters, which help significantly in knowing the bioreactor behavior and efficiency. This work aims at utilizing experimental biogas data obtained at 25, 30, 35, 40 and 45°C to estimate these parameters, including the biogas potential of liquid manure from existing biogas models, first and second order biogas rate equations and the basic arithmetic equations using Excel Solver coupled with POLYMATH by regression. Best models are Cone, Proposed model, Transference, Logistic and Modified Gompertz as they give high coefficient of determination and fits the measured biogas yield data at 25-45°C. Estimated biogas potential from Modified Gompertz model ranges from 7143-13584 mL/gVS; Logistic, 6556-12779 mL/gVS; Cone, 7713-14403 mL/gVS and; Transference, 35639-44932 mL/gVS, over the temperature range. The biogas potential parameter is not found in the Proposed model, first and second order biogas rate equations, linear, exponential and polynomial equations but are useful in finding fitted estimates of the empirical data. Most accurate or correct model among the best models obtained here, as per future studies, can be determined using model comparison parameters such as the Bayesian Information Criterion, Akaike's Information Criterion and F-test.

Keywords – Biogas, Liquid manure, Digestion temperature, Biogas potential, Kinetic model

I. INTRODUCTION

Liquid manures are principally formulated from plants and animal remains. They are mixtures of animal waste (e.g. blood, bone, fur, rumens of slaughtered ruminants, feathers etc.), water, plants (such as leguminous plants, sea weed, spent grain, among others) and other organic matter used as agricultural fertilizer for crop production. Manures from guano, cattle, deer, turkey, pigs, rabbit, chickens, horses, and sheep are rich in microorganisms that recycle the organic matter to help provide NPK and other nutrient elements needed for plant growth. When liquid manures are applied on farms, they have the advantage of immediate percolation into the soil, resulting in faster access by the plants. Addition of insect repellent leaves such as *Azadirachta indica* while making manures is good for insect control around farmyards [1]. Livestock production and other agricultural products are increasing worldwide, leading to the accumulation of manures that constitute a waste to the surrounding environment. Without appropriate attention, they can cause serious problems such as pest, rodent and insect attraction, odour, soil pollution, disease-

causing microbes and surface and groundwater pollution [2]. Also, high concentration of liquid manure can burn plant's root system leading to its death. To stabilize liquid manures for the environment as well as crop plants, anaerobic digestion (AD) can prove very effective [3]. Because, it can help transform these manures or wastes into clean energy, reducing dependency on fossil fuels, odor and waste reduction, replenishing lost nutrients of arable farmlands through production of biofertilizers and controlling environmental pollution [2, 4, 5].

The source from which clean energy is derived from all anaerobic processes is biogas. During biogas synthesis, factors inherent to its production from liquid manures such as pretreatment method, carbon-to-nitrogen ratio, pH, chemical oxygen demand, additives, volatile fatty acid content, inoculation ratio, inhibitors, temperature, retention time, organic loading rate, pressure, substrate mixing or agitation, presence of micro/macro-nutrients, effect of co-digestion, moisture content and particle sizes of the feedstock are often considered [6, 7]. Of all these, particle sizes are not sufficiently studied, even though they had a

notable effect on the feedstock biodegradability. Fine substrate particle sizes create a huge surface area for the microbial species and subsequent rise in substrate utilization rate and product gas generation [8]. Equations mainly used for estimating and inter-relating some of these parameters of biogas production had been presented in the literature. The equations can help in estimating the biogas potential of organic waste; liquid manure inclusive. In order to analyze the cumulative biogas yield (CBY) of substrate with time obtained from experimental setup of biogas production, kinetic models had often been used. It is worthy of note that these model kinetic equations deviate in number and type of parameters for estimation of biogas potential of substrate and do not satisfactorily fit all empirical biogas data. This is the reason, in most cases for the selection of specific kinetic model for analysis of CBY of feedstock. Kinetics of biogas generation essentially targets the changes in gas production as a function of time [9]. Microorganisms are necessary to enable AD of feedstock to product as most kinetic models assumes that biogas produced are function of bacterial growth [10, 11]. AD is regarded as a dynamic process affected by different other parameters including inoculum

source, heating, mixing, addition or non-addition of nutrients, pretreatment and storage condition [12]. Thus, caution should be taken while carrying out the batch analysis test using the fermentation process, as this is key to evaluating the kinetics of biogas production [13]. Empirical observations obtained from experimental data are sources for most kinetic growth models [14]. Kinetic studies help in knowing the suitability of kinetic models to define the significance of relationship present among variables to direct the empirical design, assess the observed results, and to define the specific parameters of the system performance [15]. With real kinetic parameters, performing diverse simulations to explore the effect of varying experimental circumstances is conceivable [16]. In addition, these parameters, which are maximum biogas production rate, biogas yield potential and duration of the lag phase of the reaction, will facilitate the design and scale-up of laboratory experiment into industrial size application, after obtaining them by fitting experimental values with the models [11, 17]. It is pertinent to emphasize the significance of kinetic study of biogas production using liquid manure as feedstock as shown in Table 1.

Table 1: Merits of Biogas Kinetic Study

S/No.	Importance	Reference
1.	Regulate and maximize the flow of gas generated	[18]
2.	Plant sizing and to formulate relationship amongst dissimilar parameters upsetting the AD process	[19]
3.	Evaluate empirical results, check initial hypothesis, control and predict the process performance, aid plant design optimization	[20, 21]
4.	Scale up analysis and estimation of treatment efficiencies of full-scale bioreactors	[15]
5.	Empirical kinetic studies results can be used for simulating the digester behavior and predicting biogas production	[15]
6.	Construction/formulation of chemical and/or biochemical procedures	[16]
7.	Gain insight on features of the process for possible optimization	[16]
8.	Understanding basic mechanism of complex AD process involving different microorganisms for process design and control	[10]
9.	Evaluate the metabolic pathways and mechanisms involve throughout the AD process	[4]
10.	Predict bioreactor efficiency	[4]
11.	Appraise the hydrolytic method and compare similarity between diverse lignocellulosic species.	[22]

Table 2 presents different models listed by Abubakar (2022) on biogas kinetics together with their parameters,

Table 2: Equations of Models of Cumulative Biogas Production

No.	Models Name	Equations	Reference
1.	First-Order	Main: $CBY = BP(1 - e^{-kt})$ Linearized: $\ln CBY = \ln BP + \ln(1 - e^{-kt})$	[24–26]
2.	Modified First-Order	Main: $CBY = BP[(1 - \beta) - (1 - \beta)e^{-kt}]$ Linearized: $\ln CBY = \ln BP + \ln[(1 - \beta) - (1 - \beta)e^{-kt}]$	[27]
3.	Modified Gompertz	Main: $CBY = BP e^{-e^{\left[\frac{k_e}{BP}(LP-t)+1\right]}}$ Linearized: $\ln CBY = \ln BP - 2.718282 e^{\frac{k_e}{BP}(LP-t)}$	[28–30]
4.	Logistic	Main: $CBY = \frac{BP}{1 + e^{\left[\frac{4.k(LP-t)}{BP} + 2\right]}}$ Linearized: $\ln CBY = \ln BP - \ln \left\{ 1 + e^{\left[\frac{4.k(LP-t)}{BP} + 2\right]} \right\}$	[15, 31, 32]

5.	Transfert	Main: $CBY = BP e^{-e^{[1 - \frac{k \cdot e}{BP}(LP-t)]}}$ Linearized: $\ln CMY = \ln BP - e^{[1 - \frac{k \cdot e}{BP}(LP-t)]}$	[9]
6.	Richards	Main: $CBY = BP \left\{ 1 + SF e^{(1+SF)} \cdot e^{\left[\frac{k}{BP}(1+SF) \left(1 + \frac{1}{SF} \right) (LP-t) \right]} \right\}^{1/SF}$ Linearize: $\ln CBY = \ln BP + \frac{1}{SF} \ln \left\{ 1 + SF e^{(1+SF)} \cdot e^{\left[\frac{k}{BP}(1+SF) \left(1 + \frac{1}{SF} \right) (LP-t) \right]} \right\}$	[9, 33]
7.	Cone	Main: $CBY = \frac{BP}{1+(kt)^{-SF}}$ Linearized: $\ln CBY = \ln BP - \ln[1 + (kt)^{-SF}]$	[34, 35]
8.	Transference	Main: $CBY = BP \left\{ 1 - e^{\left[-\frac{k(t-LP)}{BP} \right]} \right\}$ Linearized: $\ln CBY = \ln BP + \ln \left\{ 1 - e^{\left[-\frac{k(t-LP)}{BP} \right]} \right\}$	[31]
9.	Fitzhugh	Main: $CBY = BP \left[1 - e^{(-kt)^{SF}} \right]$ Linearized: $\ln CBY = \ln BP + \ln \left[1 - e^{(-kt)^{SF}} \right]$	[36, 37]
10.	BPK Model	Main: $CBY = BP \left\{ 1 - e^{\left[(m-1) \left(\frac{t}{t_0} \right)^{\frac{1}{m}} \right]} \right\}$ Linearized: $\log \left(\ln \frac{BP}{BP - CBY} \right) = \left[\log(1 - m) - \frac{1}{m} \log(t_0) \right] + \frac{1}{m} \log(t)$	[28]
11	Proposed Model	Main: $CBY = A + BX_1 + CX_2 + DX_1^2 + EX_2^2 + FX_1X_2 + GX_1^3 + HX_2^3 + IX_1X_2^2 + JX_1^2X_2$	[37]
12.	Chen & Hashimoto	Main: $CBY = BP \left(\frac{K_{CH}}{t \mu_{max} + K_{CH} - 1} \right)$ Linearized: $\ln CBY = \ln BP + \ln \left(\frac{K_{CH}}{t \mu_{max} + K_{CH} - 1} \right)$	[25]

where, CBY = cumulative biogas yield at digestion time t days (mL/g VS); BP = maximum biogas potential of the substrate (mL/g VS); β = non-degradable fraction of the substrate; k = specific (maximum) biogas production rate (day^{-1}); LP = lag phase (day); e = logarithmic constant (= 2.718282); t = incubation or retention time (day); SF = shape factor or shape coefficient of the curve; X_1 represents the hydraulic retention time in days; X_2 stands for the ratio of the reactor ranges from 1 to 5 (i.e. for reactor 1, $X_2 = 1$, for reactor 2, $X_2 = 2$, for reactor 3, $X_2 = 3$, for reactor 4, $X_2 = 4$ and for reactor 5, $X_2 = 5$); A to J are constant values; K_{CH} is Chen and Hashimoto kinetic dimensionless constant; m = specific constants for the kinetic process; t_0 = constant parameter and; μ_{max} = maximum specific growth rate of microorganisms (day^{-1}). Apart from CBY and t , all other parameters are referred to as kinetic parameters. Kinetic parameters are essential for biodigester design and optimal operation of large-scale anaerobic plants – because they can be used to survey the effect of the substrate ratios on biogas production to see whether values of kinetic constants is hinged on feedstock and degree of fragmentation [3, 38, 39].

Modified Gompertz model stands among the best, popular, most adequate and comprehensive biogas kinetic models for simulating batch organic waste anaerobic decomposition [13, 40, 41]. The semi-empirical model, is a modified form of the Gompertz equation that assumes cumulative biogas

production is a function of hydraulic retention time [28, 40, 42–45]. It is important in analyzing product formation rate or cell growth rate because it provides a direct relationship between microbes and biogas yield [41, 46]. For this reason, the modified Gompertz model is the most reliable model for defining bacterial growth [11]. The model can describe cell density with respect to the lag phase duration and exponential growth rates during bacterial growth in AD processes [31, 44, 47]. However, it fails to explain the start of the process, and no-sense of LP constant has been considered [28]. It is common to estimate kinetic constants from the modified Gompertz models data gotten from experimental study and checked for fitness of the model [9, 31, 48]. The growth rate of the modified Gompertz equation curve is greater than zero (positive), and its curved shape is directly linked to the equation parameters, assuming growth is inhibited by substrate level logarithmically [28, 49]. Cone model is less popular in the literature in terms of its application to simulate biogas formation [41]. It is one of the models that points to digestion efficiency and substrate biodegradability [35].

The logistic kinetic model is used to describe a time-dependent process in which at the initial stage, the growth is exponential and upon saturation, the growth will slow down and achieve plateau at the end [15]. Logistic kinetic model is among the complex models specifically developed to study the LP [32]. It is a sigmoid curve used to explain a time-dependent procedure in which at the starting stage, the

exponential growth is witnessed and upon saturation, the growth slows down and achieve plateau at the end [15]. Logistic function model finds application in biomethane potential tests and solid waste methanation/fermentation in landfills, taking into account that the rate of biogas production is directly proportional to k , BP and the amount of gas already generated [31]. The model describes CBY from batch digesters, assuming that the gas generation is a function of microbial growth [50]. An extension of the Logistic model is the Bi-logistic model [4]. It tried to include the diauxic growth effect in biogas production [51]. First order kinetic model is practical in finding the rate and extent of bio-decomposition by assuming the substrate hydrolysis stage of the AD as the rate-limiting step [20]. It is hard to accurately simulate the degradation of lignocellulosic material using the first order model owing to the fluctuation or instability of the non-degradable fraction. To solve the problem with degradability of complex substrate, a modified first order kinetic model can be used to improve the precision of the simulation [27].

Just like the Fitzhugh and Richards' models, they are the only model that incorporates the shape factor (SF), a parameter that signals the presence or absence of LP [20, 21]. Essentially, it allows the determination of k and the behavior of biogas production which is based on 'SF'. Also, the Fitzhugh model try to explore the hydrolytic and methanogenic performances of different digesters [22]. The transference function is applied traditionally to measure the efficacy of conventional pretreatments, always there to fit inputs and outputs mathematically in reaction black box or

curve-type model [27]. The model predicts maximum biogas production uniquely based on methane production using a sigmoid curve following the principle that a process could be analyzed as a system getting inputs and generating output – what is called control [31]. Venkateshkumar et al. (2020) proposed a new model they called the 'Proposed model' that relates CBY which depends on input parameters like specific substrates and its blends and inoculation time. The Chen and Hashimoto model has been applied successfully for both batch and continuous AD processes for the evaluation of anaerobic fermentation reactions [25, 52]. Lots of other models developed are not common in field applications.

Regression analysis is the most widely applied statistical technique which has to do with identifying, evaluating and analyzing the relationship between dependent and independent variable [53]. Independent variables are also referred to as explanatory or predictor variables. The dependent variable is a single variable that is predicted with the help of one or multiple independent variables [54]. Questions answered by regression analysis are: (i) how does changes in one or more of the explanatory variable(s) affects the dependent variable? (ii) which variable matters most? and most importantly, (iii) how certain are we about these variables [53, 55]. The statistical analysis techniques is applied in physical, social and behavioral sciences as well as finance to predict GDP growth and product sales [54, 56]. Three types of regression analysis can be distinguished, as depicted in Table 3.

Table 3: Types of Regression Analysis

Regression Type	Equation
Linear	$y = a_0 + a_1x_1 + \varepsilon$
Multiple Linear	$y = a_0 + a_1x_1 + a_2x_2 + \dots + \varepsilon$
Nonlinear	polynomial; exponential equations

where, y = dependent variable; x = predictor variable; a = constants; and ε = error or residuals
 "Subscript" is used to differentiate multiple number of variables and constants

Linear regression corresponds with the equation of a straight line having a single independent variable (x_1), slope (a_1) and an intercept (a_0). Multiple linear regression consists of multiple independent variables (x_1, x_2, \dots) with their respective coefficients (a_1, b_2, \dots) and a constant (a_0). Nonlinear regression results in a curved plot as seen in Figure 1. The coefficient of determination (R^2) and the adjusted R^2 are mostly used wisely to explain outcome of regression fitting of observed data. R^2 ranges from 0-1 and is a measure of the proportion of variance of a predicted outcome as well as how well a regression model fits the data. A value of 1 means every point on the regression line fits the data. Also, R^2 is commonly used to show how accurately a regression model can predict future outcomes.

II. RELATED WORK

Ciborowski (2001) assessed the utilization of livestock manure to solve pollution problem and energy generation in

consonance with Liebetrau et al. (2021) who collectively assessed the potential of the substrate for biogas production in 7 countries where they found that Norway has 26000 animal farms, Ireland had approximately 33 million livestock in 2018 while in Germany, 2/3 of manure generated is not used for biogas generation. Mohammed et al. (2020)'s record indicate that Nigeria has more than 14.73 million cattle capable of generating large volumes of biogas. Based on search regarding the exploration of liquid manure for kinetic study of biogas generation done in this work, the use of majority of the kinetic models presented in Table 2 is scanty for most feedstock, including manure. The following research had been carried out: Abdulsalam and Umar (2015) studied kinetics of biogas production by co-digesting elephant and cow dung; microbial kinetic study of biogas generation from chicken manure by Ulukardeşler and Atalay (2018), where Contois with decay rate model was reported as the best; animal manure and organic waste kinetic study in Arifan et al. (2021a) & Arifan et al. (2021b) where Modified Gompertz model with $BP = 3273.20$

mL/gTS and higher R^2 compared to First-Order model (BP = 3517.95 mL/gTS) is considered the best, because the later deviates between measured and correlated data; and in Zhang et al. (2022) where Modified Gompertz model fits more efficiently than the First-Order kinetic model by sorghum-vinegar residue enhancement of biogas production using livestock manure. Since most researchers dwell on co-digestion of manure with other substrate, Tufaner and Avsar (2016) collectively review the effect on biogas generation, without the kinetic aspect. So, the difference between literature work and this one, are in areas of codigestion and the type of kinetic model utilized.

For instance, Shitophyta et al. (2021) compared the linear, exponential and the Gaussian model used to estimate the constants 'x' (mL/gVS/day) & 'y' (day) and t_m – time when the peak biogas production rate ensued as given in Equation (1)

$$BY = x e^{\left[-0.5\left(\frac{t-t_m}{y}\right)^2\right]} \quad (1)$$

Fakkaew & Polprasert (2021) also presented the Arrhenius equation (or Equation 2), frequently applied to determine the energy parameters of some models,

$$k = A e^{-\frac{E}{RT}} \quad (2)$$

where, T represents the absolute temperature (K); A represents the pre-exponential factor; E represents the reaction activation energy (J/mol) and; R represents the ideal gas constant (8.314 J/mol.K). Eronmosele et al. (2020) in their work, measured the temperature of the digesting multiple substrate over the retention period but did not use equation 2 to determine E and A, as they require running the system at constant temperature to obtain 'k'; and repeating the step at another constant temperature with a different reactor. Examples of nonlinear regression tools used by authors in bioprocess analysis so far to estimate these constants includes Microsoft Excel program [22, 68–71], POLYMATH educational version [11, 41], nonlinear curve fitting toolbox of MATLAB [19, 24, 72], Sigma Plot [4], SPSS software [8], OriginPro [15, 22, 25, 73], Statistica [74, 75], Datafit [37], 1stOpt 15 Pro (7D-Soft High Technology Inc. China) [63] and PAST [76] among other regression tools mentioned by Abubakar et al. (2022).

III. METHODOLOGY

Biogas Yield (BY) Data: Laboratory experiment carried out by Fhooe2021 resulting in the formulation of an Excel calculator was used to access the BY of liquid manure with retention time for different temperature.

The temperature range taken by Fhooe was 10-45°C for retention time ranging from 25-150 days, where at constant retention time (RT), the Excel calculator recorded an increase in BY with increasing digestion temperature. BY (L/kgVS or mL/gVS); where VS stands for volatile solid at varying interval of the RT from 26-150 days at temperatures

of 25, 30, 35, 40 and 45°C as presented in Table 4 was used to determine the CBY.

Cumulative Biogas Yield (CBY): Since in all the model equations shown in Table 2, CBY is the dependent variable; hence, it was determined by successive addition of the previous and next BY in the column for each temperature. The kinetic models were linearized where necessary for better parameter estimation.

Regression with Excel Solver: The Excel Solver add-in program found under the Data menu in Microsoft Excel was used to estimate the unknown kinetic parameters. The Solver was used to estimate the R^2 in regression analysis, determine maximum and minimum values of the objective functions in linear programming and finding roots of nonlinear equations. For nonlinear equations involving exponential functions as in kinetic models of Table 2, they were linearized by taking common or natural logarithm of the equations. The linearized form of the model equations was then used instead of the main or original formula for regression purpose. Where linearization will not fit any regression model type, POLYMATH was explored for the similar reason. R^2 was determined for the respective models following the listed steps.

Step 1: The average value of the natural log of the experimental data, $(\ln CBY_{Expt. avg})$ which is equal to, $\left(\frac{\ln CBY_{Expt.}}{N}\right)$, where N represents the number of data points, was computed.

Step 2: Total sum of squares (TSS) as, $\sum(\ln CBY_{Expt.} - \ln CBY_{Expt. avg})^2$, was calculated.

Step 3: Appropriately, the values of the unknown constant parameters of the equations, which can then be used to compute the correlated or fitted values of CBY, $(\ln CBY_{Corr.})$, were guessed.

Step 4: The error or the difference between the experimental and fitted/predicted values of their respective logarithms, as in $(\ln CBY_{Expt.} - \ln CBY_{Corr.})$, was computed.

Step 5: Sum of squared error (SSE), $\sum(\ln CBY_{Expt.} - \ln CBY_{Corr.})^2$, was calculated.

Step 6: Model/predicted values of CBY ($CBY_{Corr.}$), by taking the antilog of $(\ln CBY_{Corr.})$ in (iii) above, was found.

Step 7: Equation 3 was used to set the value of R^2 .

$$R^2 = 1 - \frac{SSE}{TSS} = 1 - \frac{\sum(\ln CBY_{Expt.} - \ln CBY_{Corr.})^2}{\sum(\ln CBY_{Expt.} - \ln CBY_{Expt. avg})^2} \quad (3)$$

Step 8: The calculated value of R^2 after following the seven computation steps above was maximized using Excel Solver by changing the respective values of the guessed parameters

in (ii) above. If the new $CBY_{Corr.}$ values deviates too much from the empirical values ($CBY_{Expt.}$) or the estimated unknown parameters falls out of range of their typical values, new guesses were made and then Excel Solver is invoke to compute R^2 again. When exhaustive guesses fails to give the desired unknown estimates, it was concluded that the experimental data doesn't fit the proposed model equation.

Adjusted R^2 was determined based on Equation (4), where, n represents the number of points in the data set, while q represents the number of independent variables from the model, excluding the constant.

$$\text{Adj. } R^2 = 1 - \frac{(1-R^2)(n-1)}{(n-q-1)} \quad (4)$$

Biogas rate constant: The first and second order biogas rate constant, k (in mL/gVS/day) were determined using Equations (5) and (6) respectively, given by Shitophyta and Maryudi (2018) and Nwosu-obieogu et al. (2020) at 5 different temperature values.

$$\text{First Order: } \ln\left(\frac{BY_m}{BY_m - BY_t}\right) = kt \quad (5)$$

$$\text{Second Order: } \left(\frac{BY_m}{BY_m - BY_t}\right)^{-1} = kt \quad (6)$$

Where, BY_m = biogas yield generated in 150 days or the final BY value (mL/gVS), BY_t = biogas yield generated at time, t (mL/gVS) and t = biogas production time or RT (day).

Constants from Basic Mathematical Functions: The constants a , b , c , d , and e (mL/gVS/day) in the linear, exponential and polynomial equations relating BY and t were estimated by regression using equations presented by Ghatak and Mahanta (2014), Nwosu-obieogu et al. (2020) and Shitophyta and Maryudi (2018). Respectively, the linear, exponential and polynomial equations are as shown in Equations (7), (8) and (9).

$$BY = a + bt \quad (7)$$

$$BY = a + bte^{ct} \quad (8)$$

$$BY = a + bt + ct^2 + dt^3 + et^4 \quad (9)$$

On the ascending graph of biogas production, the constant 'c' in the exponential function is often predicted to approach a positive value, as stated by Ghatak and Mahanta (2014).

IV. RESULTS AND DISCUSSION

Over a 150 days retention period, biogas yield from anaerobic digestion of liquid manure, at five different temperatures were recorded from the simulated Excel Biogas Calculator as shown in Table 4.

Table 4. Biogas Yield at Different Temperature

Run	Retention Time (day)	Biogas Yield (mL/gVS)				
		25°C	30°C	35°C	40°C	45°C
1.	26	177.56	250.71	323.86	397.01	470.16
2.	27	179.86	252.83	325.79	398.75	471.71
3.	30	186.79	259.18	331.58	403.97	476.36
4.	32	191.41	263.42	335.44	407.45	479.46
5.	35	198.34	269.78	341.22	412.67	484.11
6.	36	200.64	271.9	343.15	414.41	485.66
7.	40	209.88	280.38	350.87	421.37	491.87
8.	42	214.50	284.62	354.73	424.85	494.97
9.	45	221.42	290.97	360.52	430.07	499.62
10.	50	232.97	301.57	370.17	438.77	507.37
11.	53	239.90	307.93	375.96	443.99	512.02
12.	57	249.13	316.41	383.68	450.95	518.23
13.	59	253.75	320.64	387.54	454.43	521.33
14.	61	258.37	324.88	391.40	457.91	524.43
15.	64	265.29	331.24	397.19	463.13	529.08
16.	68	274.53	339.72	404.91	470.10	535.28
17.	69	276.84	341.84	406.84	471.84	536.84
18.	75	290.69	354.55	418.42	482.28	546.14
19.	77	295.31	358.79	422.27	485.76	549.24
20.	82	306.85	369.39	431.92	494.46	556.99
21.	96	339.18	399.06	458.94	518.82	578.70
22.	100	348.41	407.54	466.66	525.78	584.91
23.	110	371.50	428.73	485.96	543.18	600.41
24.	127	410.75	464.76	518.76	572.77	626.77
25.	128	413.06	466.88	520.69	574.51	628.32
26.	131	419.99	473.24	526.48	579.73	632.98
27.	135	429.22	481.71	534.20	586.69	639.18
28.	143	447.70	498.67	549.64	600.61	651.58
29.	144	450.00	500.79	551.57	602.35	653.13
30.	150	463.86	513.50	563.15	612.79	662.44

Twelve models shown in Table 2 were regressed as shown in Figure 1, 3, 4 and 5. Richards and Chen & Hashimoto lines of CBY against time, forms a concave-like shape that

curves upward, regardless of temperature set chosen as shown in Figure 1.

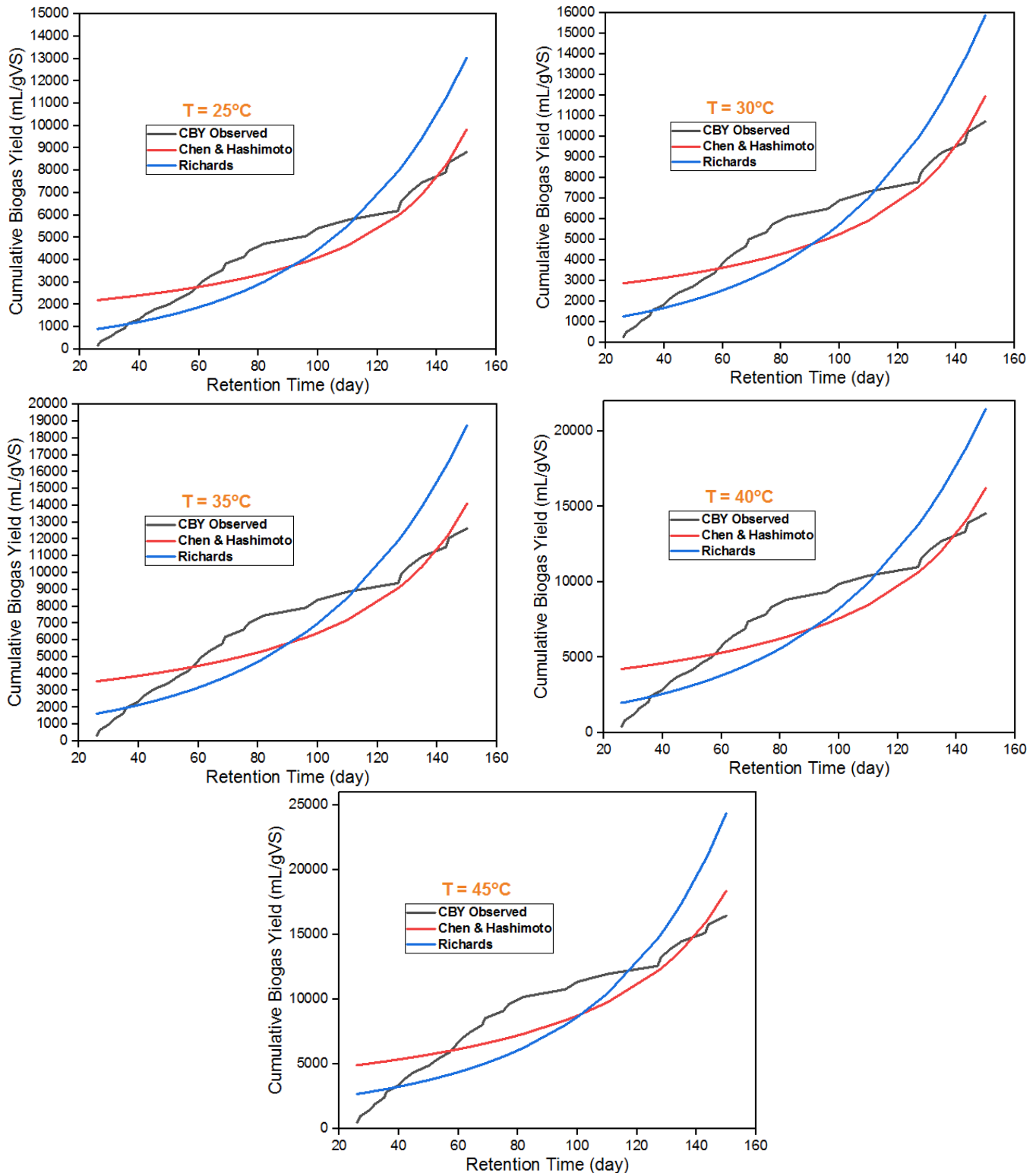


Figure 1: Chen & Hashimoto and Richards Models Fitted to CBY Observed at Selected Temperatures

The models did not fit the observed CBY data as well as each other; only intersecting at approximately 90 days RT at $T = 25\text{--}40^\circ\text{C}$ and 100 days when $T = 45^\circ\text{C}$. The mid-way intersection feature exhibited by Chen & Hashimoto and

Richards models when plotted together has no significant implication but perchance shows that number of fitted data point is unity. The two biogas kinetic models are the only models with this feature, where BP is the only unique

parameter estimated from them. It ranges from 98.39-222.54 mL/gVS in Richards model, increasing with increase in temperature from 25-40°C and 275.61-2365.09 mL/gVS in Chen & Hashimoto models. Estimated μ_{max} at all temperatures in Chen & Hashimoto model is negative, implying a negative growth and might explains the reason why the line is curved inward, unlike Monod, Contois, Moser and other growth models that have the same parameter, but curves outwards. Since μ_{max} is negative, the higher the μ_{max} , the lower should be the BP values estimated from Chen & Hashimoto model. In this work, a high $\mu_{max} = -0.0009189 \text{ day}^{-1}$ at $T = 25^\circ\text{C}$ gives BP = 275.6131 mL/gVS, of which a decrease to $-0.0019753 \text{ day}^{-1}$ at $T = 45^\circ\text{C}$ increases BP to 1184.239 mL/gVS. However, this assertion is not valid at random temperatures, but is presumed correct only at specific temperatures. At $T = 30^\circ\text{C}$ where μ_{max} is very small, its BP value of 1633.205 mL/gVS can be considered the most valid prediction, since it is illogical to have a system generating high amount of biogas when the growth rate is low (or the case where microorganisms are dying). At 40°C , Richards model (a member of the twin-shape models) gives the maximum BP which is 2365.09 mL/gVS and according to Ali et al. (2018) is the best model for biogas plant sizing.

When BP is known, the main Chen & Hashimoto model in Table 2 can be re-written in form of an equation of a straight line as shown in Equation (10),

$$t = \frac{1}{\mu_{max}} + \frac{K_{CH}}{\mu_{max}} \frac{CBY}{BP - CBY} \quad (10)$$

with slope = $\frac{K_{CH}}{\mu_{max}}$ and intercept = $\frac{1}{\mu_{max}}$. The plot of retention time, t , against $\frac{CBY}{BP - CBY}$ is linear, where $\frac{K_{CH}}{\mu_{max}} = 1080.6$ days and $\frac{1}{\mu_{max}} = 1359.7$ days using predicted CBY at $T = 25^\circ\text{C}$ as shown in Figure 2.

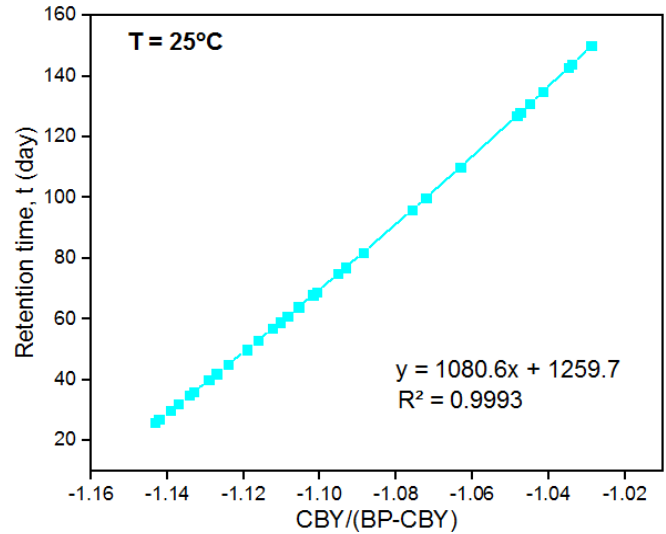
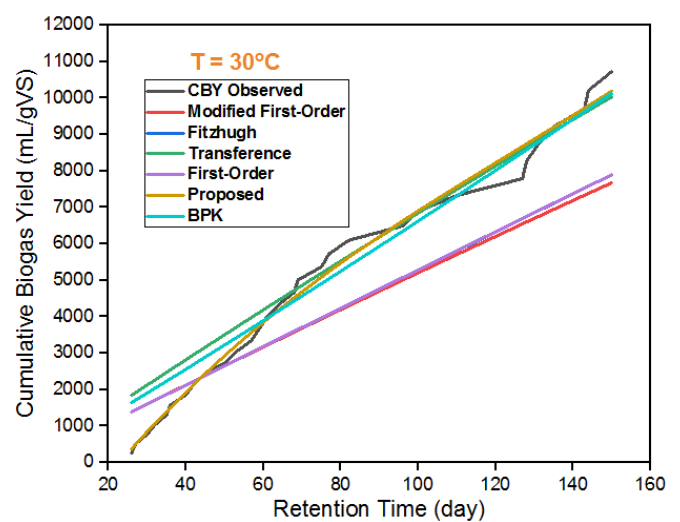
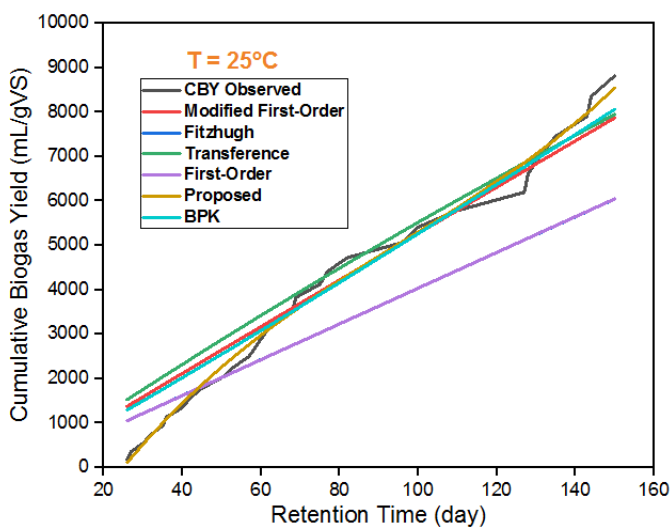


Figure 2: Determination of K_{CH} and μ_{max} in Chen & Hashimoto Model at Temperature of 25°C

The peak specific growth rate, μ_{max} , that was estimated from Figure 2 is not negative and hence negative values obtained through regression. It is logical in this case, to perform regression to determine BP, and then use this value to determine the other two kinetic parameters of the Chen & Hashimoto model graphically so as to adjust the values of K_{CH} and μ_{max} . However, not all data will give a linear plot, which makes the task of finding the slope and intercept tedious (as in plot at 30°C). In the literature, Richards and Chen & Hashimoto models had not been used specifically to analyse biogas output and determine BP of liquid manure. At all the temperatures BY of liquid manure was obtained, six biogas kinetic models are linear after parameter estimation by regression with Excel Solver as shown in Figure 3.



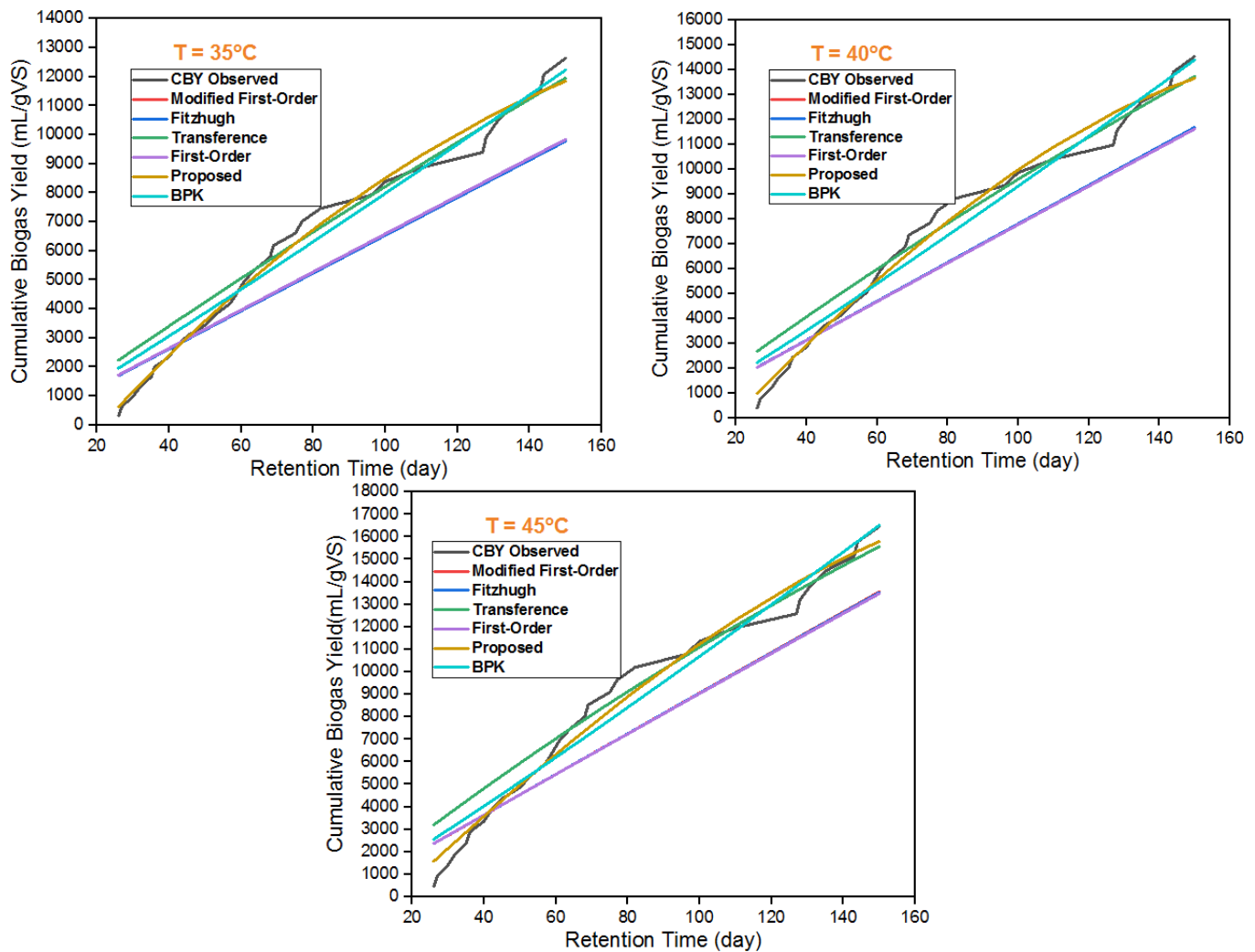


Figure 3: Fitting Six Biogas Kinetic Models to Observed CBY for Temperatures 25°C, 30°C, 35°C, 40°C and 45°C.

None of the six kinetic models in Figure 3, namely, Modified First-Order, Fitzhugh, Transference, First-Order, Proposed and the Biogas Production Kinetic (BPK) models fit the experimental results (perfectly). Clearly, at 25°C, BPK, Fitzhugh and Modified First-Order models fit each other, while at the remaining temperatures, First-Order, Modified First-Order and Fitzhugh models fit each other. Starting from the parameter, k , Proposed and BPK models has nothing to do with this constant and is incapable of explaining the maximum gas production rate. The maximum biogas production rate, k is a temperature-dependent parameter expressed in form of an Arrhenius equation that explains the trends of the biogas generation. That is, lesser volume of anaerobic digester, shorter retention time and faster degradation as highlighted by Silva et al. (2021). Transference function model gives the highest figures of ' k ' from 59.946-127.411 day⁻¹ compared to First-Order, Fitzhugh and Modified First-Order whose values are between 10⁻³-10⁻⁵ day⁻¹ given that it doesn't fit any of the other five models plotted in Figure 3. Either high or low, it is impossible to generalize the influence of ' k ', either between models or across different temperature it is estimated for a particular model. For instance, ' k ' goes up and down from 25-45°C in Fitzhugh model and the other

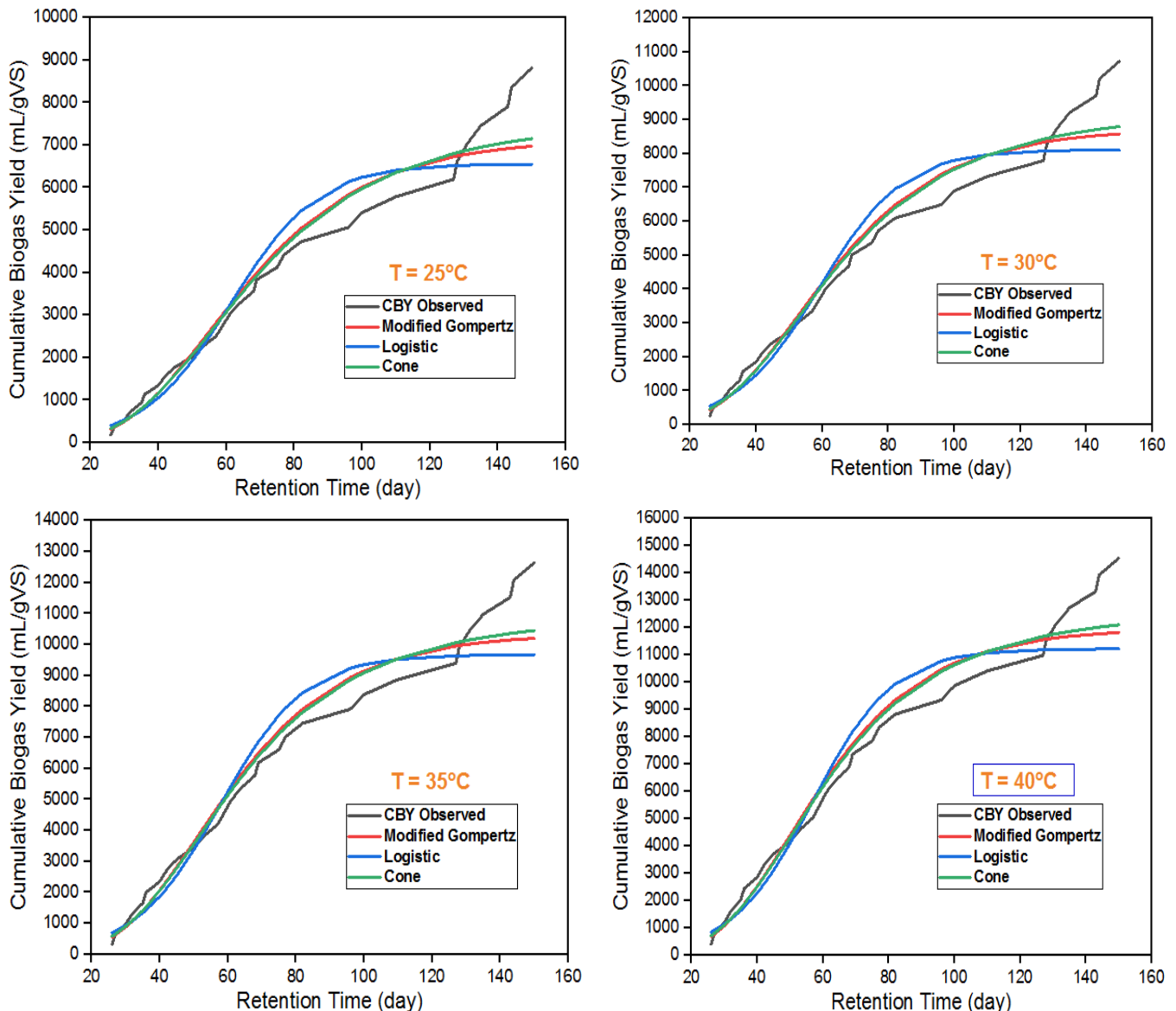
linear lines. Commonly, the higher the ' k ' value, the higher will be the value of the BP of the feedstock. Except at 30°C, BP estimated using the corrected First-Order (Modified First-Order) model is higher than its value in First-Order parameter estimate, which shows that the lower the non-biodegradable fraction the lower the feedstock potential for biogas. But in ideal situation, the lower the non-biodegradable fraction, the higher the liquid manure biogas potential. Deviation might be related to the conditions of the reactor given inaccurate empirical BY data, some of which are pH fluctuations, inhibitors and low nutrient levels.

Values of BP in BPK model is negative and it is only when BP is known that the linearized equation of BPK in Table 2 can be used to determine ' m ' and ' t_0 ' (both constant) – which is not feasible giving the kind of BP obtained in this work. The BPK is a new model which is begging for attention of researchers to use so as to compare and contrast with other models and variety of feedstock for biogas generation. BPK model, perhaps, performs poorly in giving right estimates of BP, even though it fits other model in this category. In this experiment, one biodigester is used, and hence $X_2 = 1$, in the Proposed model. The Proposed model have no common kinetic parameter compared to the

remaining models, but its lines are bent (almost fitting the observed data line) with R^2 values close to 1.

Sometimes, during AD, an initial delay is experienced at the beginning of the process, this delay is termed as the LP. According to Pecar & Gorsek (2020), there are three scenarios with regards to the LP; a case of no LP signifying immediate kick-start of methane production, a shorter LP and a longer LP. Shorter LP is because the microbial species got a suitable environment for their multiplication or the condition of the feedstock being easily degradable. Longer LP is caused by the existence of recalcitrant lignin structure repelling hydrolysis during the initial stage of decomposition or the period needed for microorganisms to fit into their new environment is prolonged due to nutrient

imbalance or population factor [10]. When LP is less than zero (or negative), it implies that the system needs no lag time to produce biogas and LP can be taken as 0 day [68]. Ideally, LP is often longer than 1 day [28]. Just like Modified First-Order model having β (a unique constant), Transference function model with the kinetic parameter 'LP' does not compare favourably with the other linear models in Figure 3. An LP = 0 day at $T = 35-45^\circ\text{C}$ gives high BP and implies quick onset of biogas production without any delay compared to low BP = 35638.60 mL/gVS at $T = 25^\circ\text{C}$ in the model. LP can hence be compared to those obtained in Modified Gompertz, Logistic, Transfert and Richards models shown in Figure 1, 4 and 5.



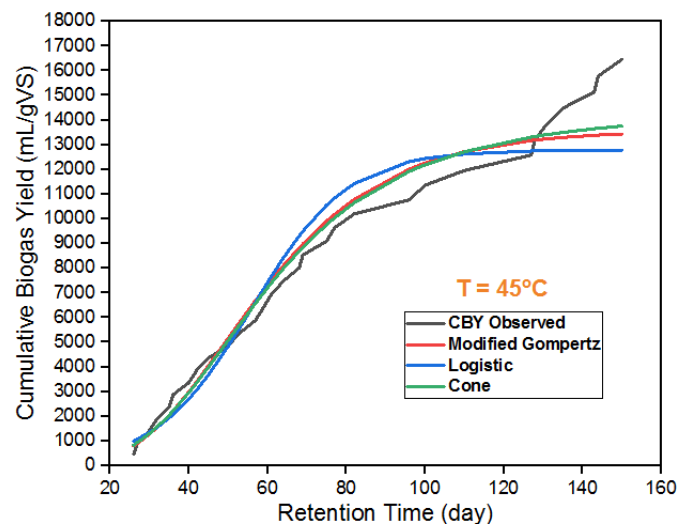


Figure 4: CBY Observed at Different Temperatures Fitted to Modified Gompertz, Cone and Logistic Function Models

Figure 4 is a curve depicting the Logistic, Cone and Modified Gompertz models at different temperatures. Estimates of BP are much closer than models in Figure 1 and 3 and shows that Cone fits the Modified Gompertz model better. The line of the observed CBY is not as smooth as the curves in Figure 4, nor is it linear as lines of Figure 1 and 3, but looks somewhat between the two depictions. In the literature, observed CBY is often presented as a curve line similar to bacterial growth curve in microbiology where the lag, exponential, stationary and death phases is observable and can be differentiated. In all three models, as the temperature increases, BP also increases and it satisfy the notion that as 'k' increases, BP increases. Also, when LP is lowest, BP is optimum for all the 3 models at $T = 45^{\circ}\text{C}$. But LP in Richards model is less than a day and gives much lower estimates of BP. However, in terms of estimates of meaningful results, Transference model can be aligned with Cone, Modified Gompertz and

Logistic models, even though its BP is much higher because LP is zero, which is reasonable. At 25°C , $\text{BP} = 7143 \text{ mL/gVS}$ in Modified Gompertz, it is 6556 mL/gVS in Logistic and 7713 mL/gVS in Cone model, showing an almost tallying range of estimates. The trend is same at other temperatures. Among the sigmoid curves of Figure 4, Cone model is one that gives the highest BP and k values across all temperature exploited. According to Parralejo et al. (2019), SF, signifies the presence or absence of the LP. It is found in Richards, Fitzhugh and Cone models. It is a dimensionless constant which is between 2.95-3.25 (& negative at $T = 45^{\circ}\text{C}$) in Richards model, between 0.058-0.107 in Fitzhugh and increasing from lowest to highest temperature (i.e. 3.236-3.336) in Cone model. The extent of fit by these models to empirical CBY is indicated in regression estimates of R^2 and adjusted R^2 displayed in Table 5.

Table 5: Kinetic Parameters Estimated from the Models at Various Temperatures

Kinetic and Regression Parameters	Temperature/Models				
	25°C	30°C	35°C	40°C	45°C
	Modified Gompertz				
BP	7143.446921	8738.820256	10347.23815	11963.22083	13583.94411
k	102.9070606	132.4317	162.5778915	193.0834214	223.8114286
LP	29.59574097	28.38909997	27.69566245	27.25107216	26.94394195
R ²	0.973467971	0.972551164	0.972131724	0.971930754	0.971835243
Adj. R ²	0.972520399	0.971570848	0.971136428	0.970928281	0.970829359
	Modified First-Order				
BP	6.04 × 10 ⁵	80119.39017	2315637.239	955426.205	1105887.731
k	0.0001456	0.000671318	2.83318 × 10 ⁻⁵	8.19456 × 10 ⁻⁵	8.22098 × 10 ⁻⁵
β	0.3964037	0	5.71904 × 10 ⁻⁵	9.9988 × 10 ⁻⁶	9.99794 × 10 ⁻⁶
R ²	0.67140365	0.753035579	0.768623974	0.772314708	0.775136352
Adj. R ²	0.659668067	0.744215421	0.760360545	0.764183091	0.767105508
	Logistic				
BP	6555.825881	8112.79793	9667.919303	11223.17414	12778.70578
k	126.9210384	159.8458665	193.6217002	227.8694536	262.4327845
LP	35.54338812	33.87650029	32.86492638	32.19090384	31.7129628

R ²	0.948637086	0.94742757	0.94683001	0.946517187	0.946349376
Adj. R ²	0.946802697	0.945549984	0.944931082	0.944607087	0.944433283
Chen & Hashimoto					
BP	275.6131	1633.205	928.8104	2365.088	1184.239
K _{CH}	1.170688	2.937349	1.434238	2.825768	1.385561
μ _{max}	-0.0009189	-0.0102411	-0.0022648	-0.0094274	-0.0019753
R ²	0.8404787	0.8272269	0.8169915	0.8089599	0.8025267
Adj. R ²	0.8286624	0.8144289	0.8034353	0.7948088	0.7878991
Richards					
BP	98.39024348	141.7002839	177.6148419	222.5392724	127.3284623
k	-1.237795043	-1.706750025	-1.953358171	-2.451225698	0.002716221
LP	0.401366638	0.320023278	0.305912329	0.387947349	0.502906926
SF	3.254296519	3.31297785	2.947841081	3.100960721	-0.004849712
R ²	0.75818568	0.743978099	0.733565574	0.725828697	0.667171253
Adj. R ²	0.749549455	0.73483446	0.724050059	0.716036865	0.655284512
Fitzhugh					
BP	611212.1474	392239.3358	579395.9104	705952.591	634192.8908
k	0.001151027	0.001646402	0.001065069	0.001054979	0.001695166
SF	0.057551315	0.082320117	0.106506913	0.105497859	0.084758185
R ²	0.747668686	0.760084539	0.767583851	0.771993338	0.774443914
Adj. R ²	0.738656854	0.75151613	0.759283274	0.763850243	0.766388339
Cone					
BP	7712.588907	9371.462283	11041.6083	12717.66541	14403.38951
k	0.014652325	0.015420558	0.015960744	0.016359478	0.01666037
SF	3.236403621	3.259472513	3.287669957	3.313975795	3.336315065
R ²	0.97395494	0.972963999	0.972449398	0.972159323	0.971985973
Adj. R ²	0.973024759	0.971998427	0.971465448	0.971165013	0.970985472
Transfert					
BP	40654.20849	53457.61924	66193.96549	78894.09123	91574.19593
k	9.99371×10^{-5}	9.99997×10^{-6}	0.000959596	9.99951×10^{-5}	9.99994×10^{-6}
LP	0.01	0.01	0.010000048	0.01	0.01
R ²	-1.28057×10^{-6}	-1.00849×10^{-7}	-7.97935×10^{-6}	-7.07302×10^{-7}	-6.1537×10^{-8}
Adj. R ²	-0.035715612	-0.03571439	-0.03572255	-0.035715018	-0.035714349
Transference					
BP	35638.60483	77149.52079	69504.4837	53044.43616	44932.10429
k	59.94627447	71.65882571	87.40749222	105.9650691	127.4106031
LP	0.001437797	0	0	2.24033×10^{-6}	0
R ²	0.996370773	0.997681601	0.99799884	0.998056701	0.998090418
Adj. R ²	0.996241158	0.997598801	0.99792737	0.997987298	0.998022218
First-Order					
BP	743417.34	416409.0572	393866.7705	533884.0698	456797.7484
k	5.44364×10^{-5}	0.000127626	0.000168595	0.000146777	0.000199662
R ²	0.747826946	0.760184733	0.766934639	0.771540768	0.773797099
Adj. R ²	0.738820765	0.751619902	0.758610876	0.763381509	0.765718424
Proposed Model					
A	-559.9421	-540.6475	-521.346	-464.6088	-333.7367
B	60.64252	60.64294	60.64311	60.64271	60.64303
C	-1170.196	-1150.902	-1131.601	-1074.864	-943.9924
D	-0.6017964	-0.442898	-0.2839993	-0.1661918	-0.1297273
E	-640.55	-621.2564	-601.9558	-545.2195	-414.3483
F	42.2444	42.24482	42.24498	42.24457	42.24489
G	0.0034667	0.0018146	0.0001626	-0.0009379	-0.0009471

H	-807.0197	-787.7255	-768.4241	-711.6871	-580.8152
I	47.12603	47.12646	47.12663	47.12623	47.12655
J	-0.3974966	-0.2385983	-0.0796996	0.0381078	0.0745723
R ²	0.9925761	0.9912222	0.989003	0.9869017	0.9826268
Adj. R ²	0.9892353	0.9872721	0.9840544	0.9810075	0.9748088
BPK					
BP	-9.94×10^{-35}	-6.19×10^{-34}	-2.16×10^{-33}	-1.88×10^{-32}	-7.54×10^{-33}
m	82.68092	81.57365	80.19316	76.81822	77.74423
t ₀	0.6191326	0.9900841	0.731614	0.2026968	0.1803201
R ²	0.95481	0.9599333	0.9615457	0.9614901	0.959278
Adj. R ²	0.9514626	0.9569654	0.9586972	0.9586375	0.9562616

In terms of best fit, the Proposed model, Cone, Modified Gompertz, Logistic and Transference models are best with R² and adj. R² values > 0.94 as shown in Table 5. Basically, R² is seen as a statistical measure of data proximity to the fitted regression line and does not show whether a regression model is enough or not – as low R² value can be obtained for a good model and high R² value can be obtained for models that does not fit the data points. Plainly, high R² values are not often good and low R² values are not often bad. For instance, under BPK model, R² estimated are

high but BP's are all negative and Transfert model where all R² are extremely low while BP estimated can be compared to the best-fit models discussed earlier. The correlated or predicted CBY in Transfert model is a constant at all temperatures, making the model the worst performing model using the experimental data. It gives meaningful predictions of BP, k and LP that can be compared with the curving-line models, but the fact that it gives a straight horizontal line as shown in Figure 5 takes it out of that category.

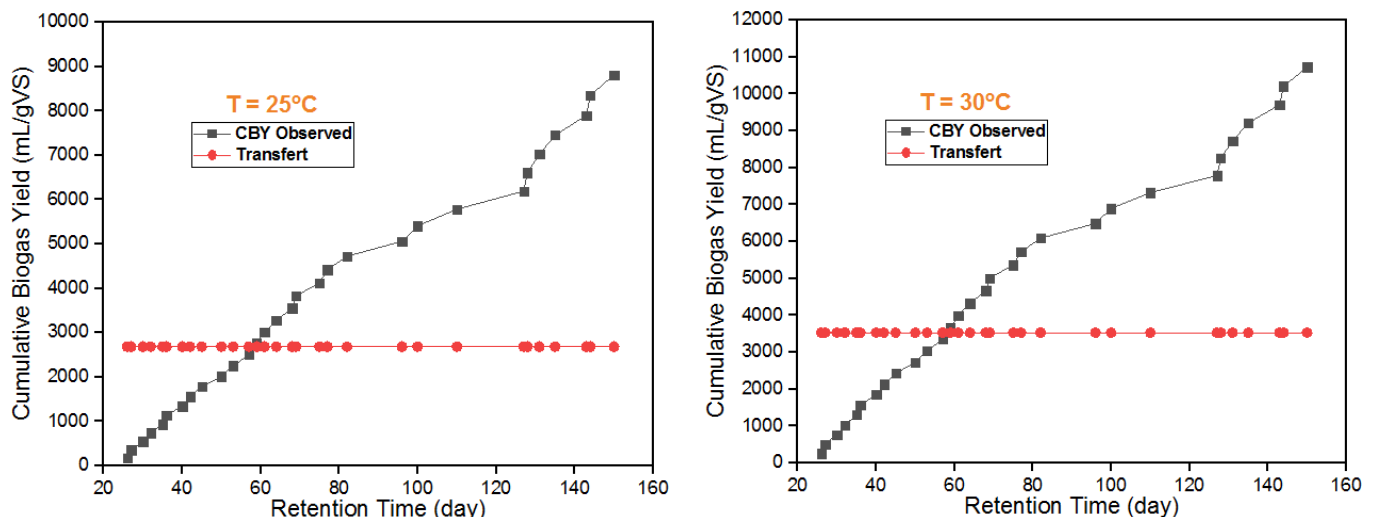


Figure 5: Transfert Model Together with CBY Observed at T = 25°C and 30°C

The nature of Figure 5 shows that the experimental data is not suitable for model fitting with Transfert model. Other researchers have presented a curve plot using predicted CBY values of Transfert model for chicken manure used as substrate. Selection of a suitable kinetic model is done to evaluate the metabolic mechanisms and pathways intricate during the AD and to predict the efficacy of certain reactors [4]. When looking at large scale AD of organic waste for biogas production, these parameters mentioned are helpful as they provide insight into the anticipated daily biogas yield from substrate(s) undergoing digestion [32].

Figure 6(a-b) is a graph showing First Order and Second Order plots obtained by writing the BY in form of a rate

equation. The first and second order equations are linear, from which k was estimated from different temperature plots. Using Excel graphing features, $k = 0.0211$ /day at T = 25-45°C by drawing a straight line over each line. This k value is hypothetical as Excel couldn't give the slope of the curve line – unmistakably even the right value of k for a first order results will approximately be the same. Second order computation of k is approximately equal at all temperatures to satisfy this assumption. Apart from this, Figure 6 also presents estimates of some constants using the three forms of basic equations, namely; linear, exponential and polynomial equations.

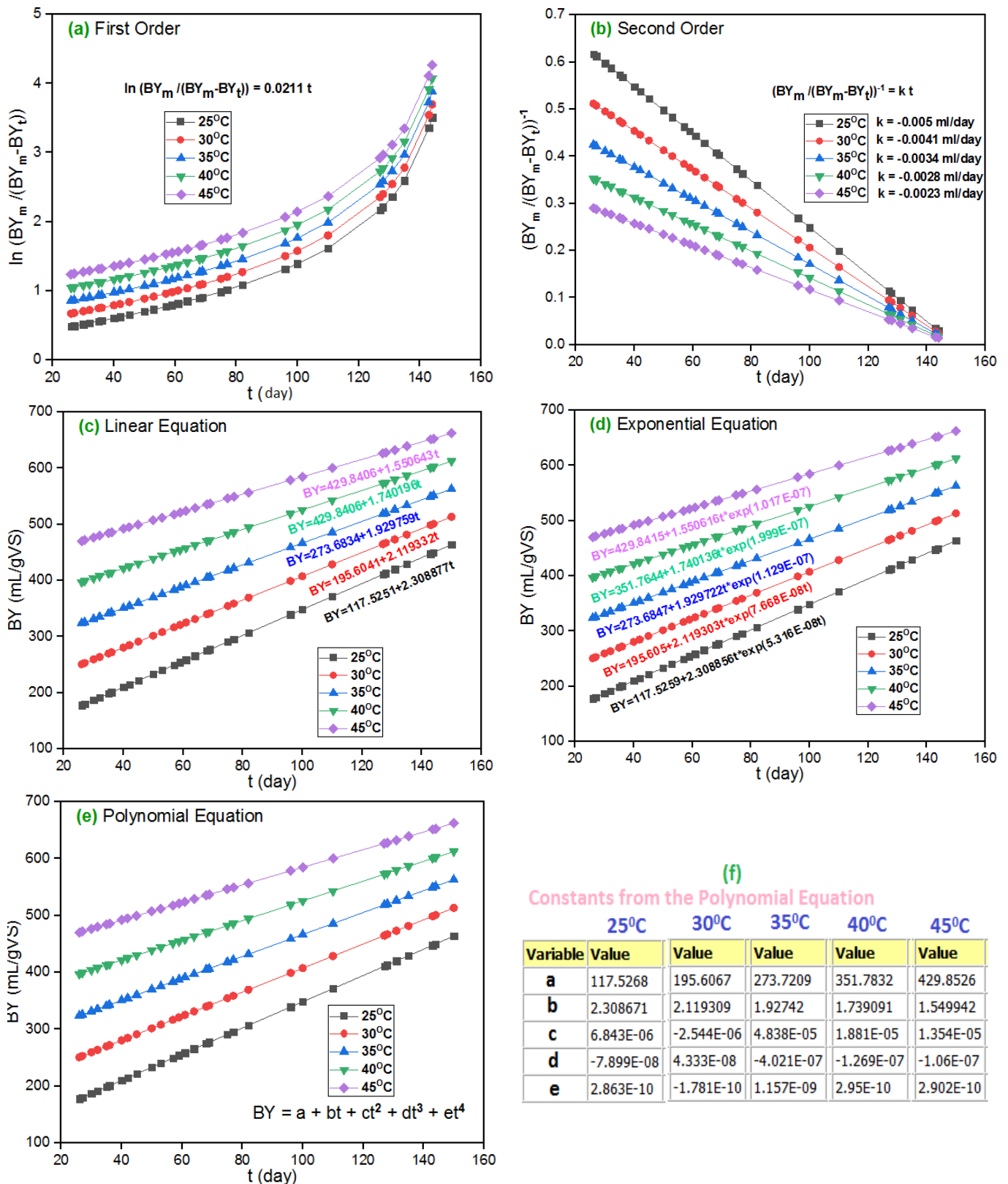


Figure 6: First and Second Order, Linear, Exponential and Polynomial Model Plots at the Experimented Temperature

The linear, exponential and polynomial lines are same, linear and gives almost identical estimates of the constants a, b, c, d, and e. Unlike the models given in Table 2, the different degree of algebraic equations in Figure 6 cannot be

used to optimize the process of producing biogas. Shitophyta et al. (2021), following the kinetic studies carried out using Tofu liquid waste, reported that exponential model correlates better than the linear equation.

The first order model can be compared almost to the Richards and Chen & Hashimoto models of Figure 1 that curves inward, though here BY is used instead of CBY and values of k is not negative as in Richards model as reported in this work.

Therefore, with known biogas potential from liquid manure, the development of biogas systems to be channeled into biogas stoves, especially in rural areas will serve as an alternative energy source apart from solar (in temperate regions) to be used for cooking and lighting [83, 84]. Since the majority of the feedstock is found in rural areas where livestock farming is prominent. In locations where animals roam for food and water, it will be impossible to develop an accurate figure of the amount of waste they generate and in turn makes biogas potential prediction difficult. Especially in Northern Nigeria where animals such as cows are moved across states in search of nutrition and water.

V. CONCLUSION AND FUTURE SCOPE

This study can be replicated in Maiduguri (in North Eastern Nigeria), which is located between latitudes $12^{\circ} 30'N$ and $14^{\circ} 30'N$ and longitudes $10^{\circ} 30'E$ and $14^{\circ} 45'E$ – an area between the Sudan Savannah and Sahel Savannah vegetation zones, with $11^{\circ}46'18'' N$ to $11^{\circ}53'21'' N$ as its latitudinal spread and $13^{\circ}03'23'' E$ to $13^{\circ}14'19'' E$ as its longitudinal extension [85–88], also known for livestock production with potential for liquid manures from animal slaughterhouses that can be channeled into biogas production. Apart from the North Eastern states of Adamawa and Borno States or the Northern part of Nigeria as a whole with huge animal population, biogas has potentials in Europe, Asia and many other African countries with high proportion of livestock waste. Results show that the temperature ranging from $25-45^{\circ}C$ is suitable for liquid manure biogas production while the kinetic models, namely, Transference, Cone, Proposed model, Logistic and Modified Gompertz are the finest models for the feedstock. Determination of energy parameters like the pre-exponential factor and activation energy using the Arrhenius equation can be further carried out at k 's obtained at different temperatures. Furthermore, the time the maximum gas production occurred can be computed using the Gaussian model reported in the literature.

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AUTHORS PROFILE

Abdulhalim Musa Abubakar holds a B. Eng. degree in Chemical Engineering from University of Maiduguri (UNIMAID)-Nigeria in 2018, also pursuing a M. Eng. Degree in the same field and institution since 2019. He works as teaching/research assistant at Modibbo Adama University (MAU) of Nigeria. His research interest revolves around water treatment, petroleum refining and petrochemicals and chemical engineering numerical analysis. He is an author of several journal articles.



Luqman Buba Umdagas is a PhD student at Abubakar Tafawa Balewa University in Nigeria. He obtained his Bachelors and Masters Degrees in Chemical Engineering from the University of Maiduguri. His research focuses on synthesis of catalysts for valorization of waste plastics into liquid fuels. His research interests are renewable and sustainable energy, process modelling and simulation and process optimization. He works as a lecturer at the Department of Chemical Engineering, University of Maiduguri.



Abubakar Yusuf Waziri was awarded B. Eng. and M.Sc. degree in Chemical Engineering from Modibbo Adama University (MAU) and Ahmadu Bello University (ABU), Zaria in Nigeria, respectively. He works as a lecturer since 2019 at MAU and is a registered member of the Council for the Regulation of Engineering in Nigeria (COREN). His research interest/area of expertise is process engineering and catalysis, where he published several journal articles and made presentation in various conferences.



Ehime Irene Itamah, holds a degree in Chemical Engineering at UNIMAID of Nigeria. He obtained a certification in solar installation from International Center for Energy, Environment and Development (ICEED). He is a Masters student of ABU, Zaria in Kaduna State of Nigeria (2021) and works as an assistant lecturer at Federal Polytechnic Daura in Katsina State since 2020.

