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# Comparative Analysis of Kinetic Models for Anaerobic Digestion of Abattoir Waste

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**Key words:** Kinetic model, non-linear regression, biogas production, abattoir waste, COD/VSS

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**Abstract:** Comparative analysis of the kinetic models was done by evaluation of the bio-kinetics constants of the abattoir waste based on some selected existing models; Monod, Logistics, Chen amd Hashimoto, Contois and Teissier. A 10 L locally fabricated Biodigester was used in this research with samples taken on a weekly basis over a period of 64 days and analyzed for COD, TSS, VSS, pH using standard methods (ASTM). The COD/VSS time series data was fitted into the five microbial growth kinetic models using non-linear regression analysis with MATLAB 7.9. The data fitting also led to the determination of these model's biokinetic parameters and their 95% confidence intervals. The data fitted well into all the models with corellation coefficients $R^2$>0.9 for all the models with Monod's Model having the highest $R^2$ of 0.979. The biogas produced has a high content of methane, 72.73% which is greater than the minimum (>60% mol.) quality requirement for used in internal combustion gas engines.

## INTRODUCTION

Biogas is a gas obtained by anaerobic decomposition of organic wastes such as vegetables, plants, crop residues, human and animal wastes and consists of methane as a major component with impurities such as $CO_2$, $N_2$, $H_2$ and $H_2S$. Biogas reactors 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 biochemistry and operational characteristics of biogas reactors have led to development of various types of biogas reactors, Batch, sequencing batch and continuous reactors[1, 2]. To develop a reliable design of biogas reactor 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[3, 4]. Gerber and Span[5] presented a comprehensive review on models available for biogas reactor. However, the complexity of biogas reactors (in terms of process variables), the presence of microbial-colonies, the interaction between different microbial species and the complex nature of substrates complicates such modeling. There is no single universal model to represent anaerobic digestion of substrate but each substrate has to be tested on the available models.

Anaerobic digestion models are classified into; kinetic and empirical models. This work focuses on fitting experimental data to existing kinetic models with the aim of determining the best model that will adequately describe the anaerobic digestion process. Most of the kinetic models are nonlinear and hence more difficult to correlate data than linear models in this research model parameters will be estimated using MATLAB "nlinfit" function based on an experimental data set of bacterial growth rate.

Though, there are numerous kinetic models available for describing rate of anaerobic digestion, this research will consider the models of Monod, Logistics, Chen and Hashimoto, Contois and Teissier.

**Anaerobic digestion kinetic models and models parameters evaluation:** Several kinetic models have been proposed to describe the growth of microbes during their life cycle[5]. The growth of microbial cells includes four major phases namely; lag phase, exponential phase, stationary phase and the decline phase.

Various models have been used for studying microbial growth kinetics. In all models, the focus is on the important factors that influence the growth rate of bacteria. The simplest microbial cell growth model is the Malthusian model commonly known as Malthus law or exponential law[6] mathematically expressed as:

$$\frac{dC_x}{dt} = \mu C_x \quad (1)$$

Where:
$C_x$ = Concentration of cells (microbes) (mg $L^{-1}$)
$\mu$ = Specific growth rate ($day^{-1}$)
t = Time (day)

The microbial growth rate is related to rate of substrate utilization according to the following Eq. 2:

$$\frac{dC_x}{dt} = Y\frac{dC_s}{dt} \Rightarrow -\frac{dC_s}{dt} = \frac{1}{Y}\frac{dC_X}{dt} = \frac{\mu C_X}{Y} \quad (2)$$

Where
$C_X$ = Concentration of microbes (mg $L^{-1}$)
Y = Microbial growth yield defined as

$$Y = \frac{\text{Mass of biomass (cells) produced}}{\text{Mass of substrate used}} \quad (3)$$

The specific growth rate $\mu$ is not a constant but depends on many factors which include; Concentration of substrate, concentration of microbes, time, pH, presence of inhibitory substances, temperature etc. This led to the development of many model equations for $\mu$ such as Monod's, Logistics', Contois etc.

**Monod's Model:** This model[7] is considered as one of the unstructured models which depend on the concentration of substrate and showed a hyperbolic relationship between the exponential microbial growth rate and substrate concentration. Monod's Model is presented as follows:

$$\mu = \frac{\mu_m C_s}{K_s + C_s} \quad (4)$$

Where:
$\mu$ = Specific microbial growth rate ($d^{-1}$)
$\mu_m$ = Maximum specific microbial growth rate ($d^{-1}$)
$K_S$ = Half-saturation constant (Monod's constant) (mg $L^{-1}$)
$C_s$ = Substrate concentration (mg $L^{-1}$)

In this model, the raw kinetic parameters, namely, microorganism's growth rate and half velocity constant are deterministic in nature and these predict the conditions of timing of maximum biological activity and its cessation. This model coupled with Malthus law can be used to determine the rate of substrate utilization ($r_s$).

The accuracy of the Monod Model for pure cultures and simple substrates is very high[8]. The model is appropriate for homogenous cultures but not for heterogeneous cultures or complex substrates[9]. Also Pfeffer[10], concluded that the Monod kinetic model cannot be relied upon in describing the degradation of municipal wastes as a complex substrate. Furthermore, the lag phase is not included in the Monod Model. Therefore, a number of modifications have been done to improve this model.

**Contoi's model:** Contois proposed his model based on the fact that in some cases such as for certain filamentous bacteria, the bacterial growth rate is dependent on the concentration of both substrate and bacterial cells:

$$\mu = \frac{\mu_m C_s}{K_s + C_X + C_s} \quad (5)$$

The effects of inhibition and of inoculum are directly included, even though the lag phase is neglected. This model yields good results both for batch and continuous processes but its capability to model dynamic processes are strongly limited[11].

In this model, $K_C$ which is Contoi's saturation constant is proportional to microorganism concentration. According to this model, the specific growth rate decreases with substrate depletion and under extreme conditions when substrate is depleted completely the specific growth rate is inversely proportional to the cell concentration.

**Chen and Hashimoto's Model:** Chen and Hashimoto in 1978 modified Contoi's Model by including the cell concentration [12] which depends on the level of substrate degradation. This inclusion is via. the relation between substrate concentration $C_S$ and initial substrate concentration $C_{S0}$:

$$\mu = \frac{\mu_m C_s / C_{S0}}{K_s + \frac{(1-K)C_S}{C_{S0}}} \quad (6)$$

Where:
K = Kinetic constant
$C_{S0}$ = Initial substrate concentration (mg $L^{-1}$)

In this model, the integration of inhibition by substrate or products is limited [13]. As a result, no prediction of process failures due to inhibition of microorganisms is possible but process failures due to wash-out effects can be predicted[13].

**Logistic's Model:** This model incorporated inhibition term, that means the model project inhibition coefficient which is proportional to the concentration of the microbes. The specific growth rate may be inhibited by high substrate concentration. In this case, the growth kinetics of microorganism is determined more accurately using the logistics model. The specific microbial growth rate for this model is defined by the following Eq. 7:

$$\mu = \mu_m \left(1 - \frac{C_X}{C_m}\right) \quad (7)$$

where, $C_m$ = maximum cell dry weight (mg $L^{-1}$). The logistics model leads to a lag phase, exponential initial growth rate and a stationary growth concentration $C_x$ which is described in the following Eq. 8:

$$C_x = \frac{C_{xo} \exp(\mu_m t)}{\frac{C_{xo}}{C_m}(1 - \exp)(\mu_m t)} \quad (8)$$

This equation gives the concentration of microbes with respect to time.

**Teissier kinetic model:** Teissier's Model just like Monod's is another unstructured model which depends on the concentration of the substrate[14]. The model equation is given as:

$$\mu = \mu_m \left(1 - \exp\left(-C_S / K_S\right)\right) \quad (9)$$

Teissier's Model's takes into account the substrate inhibition factor, however, the model render algebraic solution of the growth equations much more difficult than the Monod Model.

There are numerous other models that described microbial growth rate[5], some of which take into cognizance the process parameters such as temperature, pH, inhibition, etc.

**Determination of models parameters:** The model equations are nonlinear and hence non-linear fit analysis of data can be used for determination of models parameters. Non-linear regression tool such as "Solver" in Microsoft Excel and "nlinfit" in MATLAB are effective for such analysis. In nonlinear regression analysis, the objective function is to minimize the sum of the squared error defined as:

$$SSE = \sum_{i=1}^{N} \left(y_{exp} - y_{pre}\right)^2 \quad (10)$$

Where:
$y_{exp}$ = Experimental value (actual value)
$y_{pre}$ = Predicted value (from model equation)
$y_{exp}$-$y_{pre}$ = Error

MATLAB uses the "nlinfit" function to carry out nonlinear regression analysis which is based on minimizing sum of squares of errors. The nlinfit function takes the following syntax[15]:

```
[beta, Resid, Jacobian, CovB, MSE] =
    nlinfi (X, Ym modelfun, beta0)
```

Where:
beta = Vector of fit coefficients
Resid = Vector of residuals
Jacobian = Jacobian matrix
CovB = Variance-covariance matrix for coefficients
MSE = Mean squared error (estimate of variance of the error)
nlinfit = MATLAB function name for nonlinear fit analysis
X = Independent variable
Y = Dependent variable
modelfun = Function to fit
beta0 = Vector of initial guesses for fit coefficients

The outputs can be used to calculate descriptive statistics about the fit most notably 95% confidence intervals for the calculated coefficients and the $R^2$ value. The syntax for the 95% confidence intervals is as follows: betaci = nlparci (beta, Resid, Jacobian). This will return a vector of two columns and n rows where n is the total number of estimated coefficients. To calculate the correlation coefficient $R^2$ value, the following formula can be used:

$$R^2 = 1 - \left(\frac{SS_{residuals}}{SS_{Total}}\right) \times SS_{residuals} \quad (11)$$

Where:
$SS_{Total}$ = Sum of squares between the data points and their mean
$SS_{residuals}$ = Sum of squares of the residuals
$SS_{residuals}$ = Sum (Resid.$^2$)
$SS_{Total}$ = Sum ((y-mean (y)$^2$)

Table 1: Nutrients content of the substrate and digestate

| | Composition wt.% | | |
|---|---|---|---|
| Components | Substrate | Digestate | Increase (%) |
| Total nitrogen | 0.350 | 0.385 | 10.00 |
| Phosphorus | 0.148 | 0.135 | -8.78 |
| Carbon | 0.433 | 0.361 | -16.63 |
| Potassium | 0.085 | 0.067 | -21.18 |
| Sodium | 0.120 | 0.175 | 45.83 |

Table 2: Composition of the biogas produced

| Component | Mole (%) |
|---|---|
| CO | 0.000 |
| $CO_2$ | 27.27 |
| $CH_4$ | 72.73 |
| $H_2$ | 0.000 |

Table 3: Substrate/Microbial concentrations time data for the biodigester

| Time (d) | COD = $C_S$ (mg $L^{-1}$) | VSS = $C_x$ (mg $L^{-1}$) | TSS (g $L^{-1}$) | pH | Temperature (°C) |
|---|---|---|---|---|---|
| 0 | 20800 | 625 | 3.200 | 6.5 | 25.0 |
| 8 | 18622 | 658 | 3.100 | 6.3 | 28.5 |
| 15 | 16616 | 731 | 3.200 | 6.4 | 27.0 |
| 22 | 14534 | 786 | 3.201 | 6.3 | 30.0 |
| 29 | 12399 | 840 | 3.202 | 6.4 | 26.0 |
| 36 | 10252 | 897 | 3.204 | 6.2 | 27.5 |
| 43 | 8146 | 962 | 3.205 | 6.5 | 27.0 |
| 50 | 6160 | 1003 | 3.206 | 6.4 | 25.0 |
| 57 | 4380 | 1050 | 3.207 | 6.3 | 26.0 |
| 64 | 2900 | 1088 | 3.209 | 6.4 | 30.0 |

## MATERIALS AND METHODS

**Characterization of the substrate and digestate:** Sample of the abattoir waste (paunch and intestinal content) was collected and analyzed for the following parameters; COD, TSS, VSS, pH as shown in Table 1-3. The substrate and the digestate were also analyzed for nutrients (K, Na, P, C and total nitrogen). All the analytical determinations were performed according to the standard methods[16].

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

**Substrate preparation and digestion:** The abattoir waste was collected from Zango-Zaria, mixed with water in the ratio[17] 1:1, to form slurry which was then inoculated with the inoculums at 100 ml $L^{-1}$. The 2.5 kg of the waste was used to form 5.7 L of slurry which was loaded into a 10 L locally fabricated Biodigester shown in Fig. 1. Samples were taken on a weekly basis over a period of 64 days and analyzed for COD, TSS, VSS using standard methods[16]. The pH was measured using pH meter (Meacon, MIK-PH-100). The temperature of the digester was monitored throughout the experiment. The COD/VSS time series data was fitted into five microbial growth kinetic models using non-linear regression analysis with MATLAB 7.9.

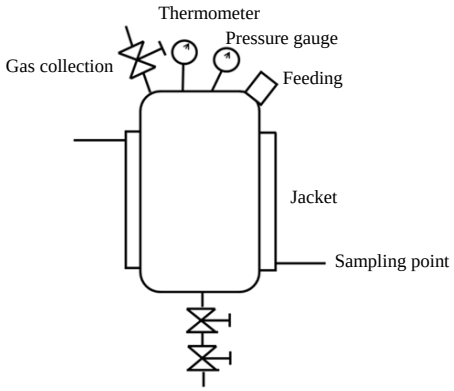


Fig. 1: Schematic diagram of the fabricated 10 L laboratory bioreactor

The biogas produced was analyzed at National Research Institute for Chemical Technology NARICT using NDIR Gas Analyzer, GASBOARD-3100P.

## RESULTS AND DISCUSSION

The results of analysis of the substrate/digestate and the biogas produced are presented in Table 1 and 2, respectively. Concentrations time data results for the bioreactor were tabulated in Table 3 and fitted into five kinetic models; Monod, Contois, Logistics, Chen and Hashimoto and Teissier and presented graphically in Fig. 2 through Fig. 2-6. The models parameters/confidence intervals were tabulated in Table 3-5.

**COD/VSS time series data:** The substrate concentration measured in terms of COD decreases with time and eventually remains constant after 64 days while the concentration of the microbes measured in terms of VSS increases with time as shown in Fig. 1. This behaviour is expected based on the fact that the microbes consumes the substrate and multiply rapidly under favourable conditions.

**Fitting the COD/VSS time series data:** The data was fitted to five models; Monod, Teissier, Logistics, Chen and Hashimoto and Contois. The data fitted well into all the models as shown in Fig. 2 through Fig. 6 with corellation coefficients $R^2$>0.9 for all the models. Monod's Model has the highest $R^2$ of 0.979. Table 1 shows the $R^2$ (goodness of fit) for the four models tested. Monod's Model havinng the highest $R^2$ indicates that the substrate is not a complex one and that inhibition is minimal.

**Analysis of substrate and digestate:** The analysis of the digestate shows an increase in the total nitrogen and sodium while phosphorus, poatassium and carbon

Table 4: Model's kinetic coefficients determined using nonlinear regression method

| Model | $\mu_{max}$ ($d^{-1}$) | $K_S$ (mg $L^{-1}$) | $K_K$ | $C_m$ (mg $L^{-1}$) | K | Coefficient of determination, $R^2$ | MSE |
|---|---|---|---|---|---|---|---|
| Monod | 0.0138 | 4279.2 | | | | 0.979 | 9.8E-8 |
| Contois | 0.0126 | | 3.343 | | | 0.959 | 9.6E-8 |
| Logistics | 0.0194 | | | 1677.9 | | 0.949 | 2.2E-7 |
| Teissier | 0.0113 | 4760.0 | | | | 0.946 | 2.9E-7 |
| Chen and Hashimoto | 0.0115 | | | | 0.1706 | 0.921 | 9.8E-8 |

Table 5: The 95% confidence intervals for the models' parameters

| Model/Parameters | Monod | Contois | Logistic | Teissier | Chen and Hashimoto |
|---|---|---|---|---|---|
| **$\mu_{max}$ ($d^{-1}$)** | | | | | |
| Lower bound | 0.0129 | 0.0102 | 0.0175 | 0.0105 | 0.0110 |
| Upper bound | 0.0147 | 0.1320 | 0.0214 | 0.0121 | 0.0118 |
| **$K_S$ (mg $L^{-1}$)** | | | | | |
| Lower bound | 3324.2 | | | 3649.1 | |
| Upper bound | 5234.2 | | | 5870.8 | |
| **$K_K$** | | | | | |
| Lower bound | | 2.673 | | | |
| Upper bound | | 4.0134 | | | |
| **K** | | | | | |
| Lower bound | | | | | 0.1391 |
| Upper bound | | | | | 0.2022 |
| **$C_m$ (mg $L^{-1}$)** | | | | | |
| Lower bound | | | 1521.3 | | |
| Upper bound | | | 1834.4 | | |

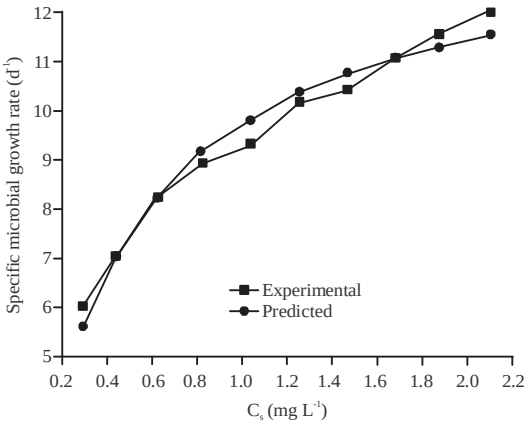


Fig. 2: Specific microbial growth rate against substrate concentration Cs for Monod's model

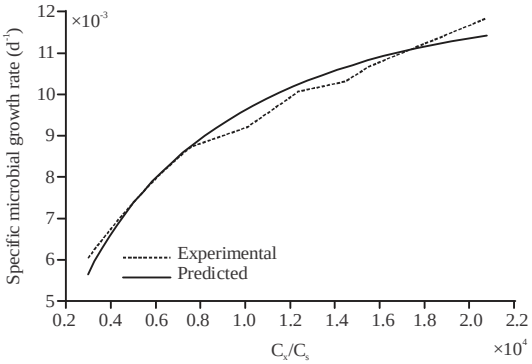


Fig. 3: Specific microbial growth rate against $C_x/C_s$ for Contoi's Model

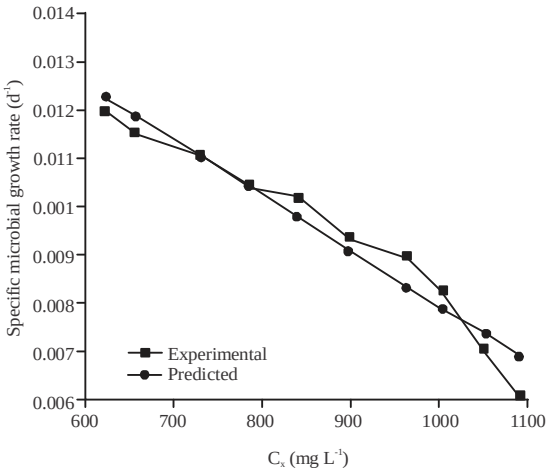


Fig. 4: Specific microbial growth rate against microbes concentration $C_x$ for Logistic's Model

decreased. A decrease in phosphorus, poatassium and carbon during anaerobic digestion was also reported by Adelekan and others[18]. Risberg [19] reported a decrease in carbon and phosphorus while total nitrogen and potassium remain unchanged. They all reported an icrease in the quality of the digested over the undigeted matter due to conversion of these plant nutrients to a mineralised form (a more useable form by plants).

**Analysis of the biogas produced:** The biogas produced has a high content of methane, 72.73% which is greater than the minimum (>60% mol.) quality requirement for used in internal combustion gas engines.

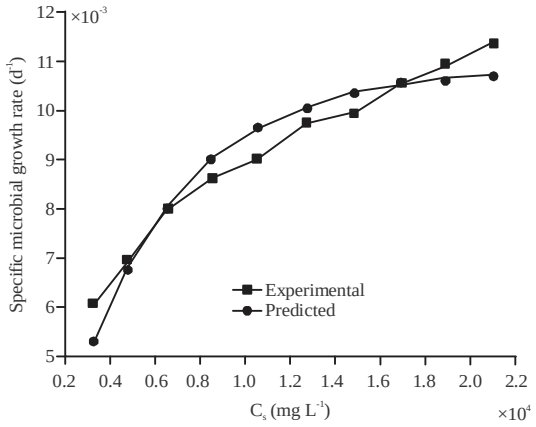


Fig. 5: Specific microbial growth rate against substrate concentration $C_s$ for Teissier's Model

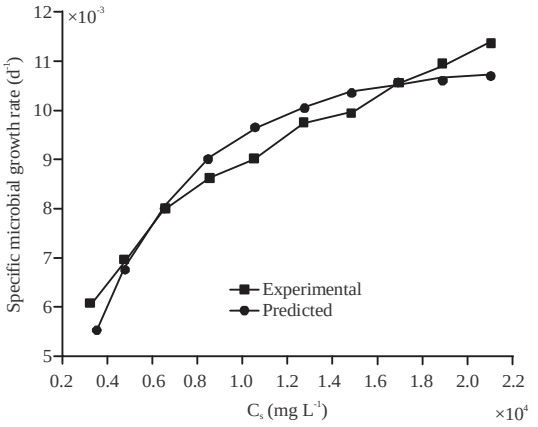


Fig. 6: Specific microbial growth rate against substrate concentration $C_s$ for Chen and Hashimoto's Model

## CONCLUSION

Based on the results obtained, Monod's kinetic model is able to describe with high accuracy the experimental results obtained for the anaerobic digestion of Zango-Zaria abattoir waste and will serve as a suitable model for describing the kinetic of Zango-Zaria abattoir waste as substrate for biogas production. This model can be used in the design of bioreactor for production of biogas from the waste. The high quality of the biogas makes it suitable for use in internal combustion gas engines without the need for purification.

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