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PREDICTING MOLAR COMPOSITION OF BIOGAS BY REACTION KINETICS AND TEMPERATURE DEPENDENCE ON ANAEROBIC DIGESTION

A.L. Fagbemi, D.G.F. Adamon and S. Bouraima
University of Abomey-Calavi-Polytechnic School of Abomey,
Calavi Laboratory of Applied Energetics and Mechanics (LEMA),
01 BP. 2009, Cotonou, Bénin

ABSTRACT

Mathematical model was developed and simulated to predict the molar composition of biogas produced by anaerobic digestion. Several models have been developed for anaerobic processes with reduced number of parameters, but requiring data resolution, thus posing problem of data precision. The prediction model was based on reaction kinetics of anaerobic digestion, while Ratkowsky's formulation was used to examine the dependence of temperature on methanogenic process. The reaction kinetics model was simulated using SciLab coding of fourth order Runge Kutta numerical algorithm. Comparison of numerical experimentation results with published experimental data gave satisfactory agreement. The cumulative volume of methane was predicted in the temperature range of 20 - 40 °C, and the maximum volume of methane generated was 26.39 L at 35 °C for mesophilic bacteria.

Keywords: Anaerobic Digestion, Hydrolysis, Acidogenesis, Acetogenesis, Methanogenesis, Mesophilic Bacteria

1. INTRODUCTION

Anaerobic digestion is a natural process of decomposing organic matter by bacteria in environment that lacks free oxygen, leading to generation of biogas rich in methane (CH_4), a source of renewable energy. Anaerobic digestion is a multistep process involving hydrolysis, acidogenesis, acetogenesis and methanogenesis; whereby each product synthesized at one step becomes substrate for the microorganisms of the next step; and is therefore of stepwise rate limiting.

The composition of biogas was predicted to evaluate the quality and quantity of gas production, and modeling and simulation of biogas reactor were adopted as flexible and cost saving methods of investigation. The first mathematical models of anaerobic bioreactors were developed in the 1970s, and since then, many complex models, depending on the number of bio-chemical processes have been proposed.

Anaerobic Digestion Model No. 1 (AD M1) was developed by International Water Association to simulate anaerobic reactors [1]; but was very complex, requiring 19 bio-chemical processes, 3 kinetic processes of liquid/gas transfer, 7 different bacterial populations, and analysis of 80 reaction parameters. A simpler model, Anaerobic Model No. 2 (ADM 2), developed by Bernard *et. al*. [2], is commonly used to reconcile precision and complexity, because fewer reaction parameters are required. Numerous estimation of parameters of ADM2 based on different techniques have also been carried out. Given the complexity of bio-chemical processes and the specific experimental conditions of each bioreactor, parameters of different models show different dispersion values. Computer simulations and software codes have been used to model biogas reaction kinetics [3].

The research presented in this paper involved developing mathematical model for prediction of molar composition of biogas and dependence of production of the gas mixture on temperature. Anaerobic digestion is unstable process and operational design and configuration required to improve system performance could be achieved by numerical simulations to estimate process rates for stable and cost effective operations. Values of the simulation parameters for the prediction were sourced from published literature. The model validation by comparing simulation and literature data under the same biogas operating conditions was satisfactory.

2. STAGES OF ANAEROBIC DIGESTION

The stages of anaerobic degradation of organic feedstock are hydrolysis, acidogenesis, acetogenesis and methanogenesis; as shown in Fig. 1 [4]. Hydrolysis, acidogennesis and methanogenesis kinetics reactions [5, 6, 7, 8], and effects of temperature were modelled for the anaerobic digestion. Products from sequence of the three stages served as substrates.

2.1. Hydrolysis Stage

The first stage of anaerobic degradation was hydrolysis, where solid organic material S_0

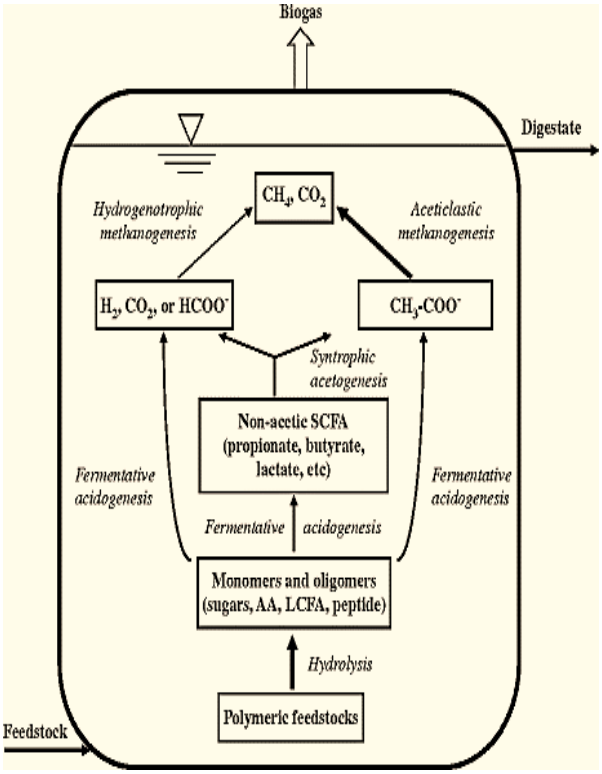

Fig. 1. Metabolic fluxes of anaerobic digestion [4].

was converted into soluble organic substrate S_1, according to the reaction [9, 10];

$$S_0 + H_2O \xrightarrow{r_0} k_h S_1 \quad (1)$$

where k_h is hydrolysis constant and r_0 is reaction rate.

2.2. Acidogenesis Stage

The second stage of decomposition was acidogenesis, where population of acidogenic bacteria X_1 broke down the organic substrate S_1 into volatile fatty acids (VFAs) S_2 and carbon dioxide (CO_2) by the kinetic reaction [9, 10];

$$K_1 S_1 \xrightarrow{r_1} X_1 + K_2 S_2 + K_4 CO_2 \quad (2)$$

where K_1, K_2, K_4 represent stoichiometric coefficients, respectively associated with the consumption of the organic substrate (S_1), production of VFA (S_2) and CO_2, during acidogenesis. The reaction rate r_1 was given as

$$r_1 = \mu_1 X_1 \quad (3)$$

and μ_1 is acidogenic bacteria growth rate.

The specific growth rate of acidogenic bacteria was given by Monod formula [11];

$$\mu_1 = \mu_{1max} \frac{S_1}{S_1 + K_{S1}} \quad (4)$$

where μ_{1max} is maximum rate of bacteria growth, and K_{S1} is half saturation rate associated with S_1.

2.3. Methanogenesis Stage

For the third stage of kinetic reaction, X_2 methanogenic bacteria grew at specific rate by consuming the substrate S_2 at a rate proportional to the bacteria growth rate and producing methane (CH_4) and carbon dioxide (CO_2), by the reaction [9, 10];

$$K_3 S_2 \xrightarrow{r_2} X_2 + K_5 CO_2 + K_6 CH_4 \quad (5)$$

where K_3, K_5, K_6 represent stoichiometric coefficients, respectively associated with the consumption of VFAs, production of CO_2 and CH_4 during methonogenesis. The reaction rate r_2 was given as,

$$r_2 = \mu_2 X_2 \quad (6)$$

and μ_2 is methanogenic bacteria growth rate.

The specific growth rate of the bacteria was given by Haldane formula [12],

$$\mu_2 = \mu_{2max} \frac{S_2}{S_2 + K_{S_2} + \frac{S_2^2}{K_{12}}} \quad (7)$$

where μ_{2max} is maximum growth rate of bacteria, K_{S2} is half-saturation rate associated with S_2, and K_{12} is inhibition constant associated with the substrate S_2.

3. MATHEMATICAL FORMULATION

3.1. Model Assumptions

The mathematical description of dynamics of the processes relating to production of biogas was based on assumptions which defined the framework of the model and simplified the reaction equations by considering only the predominant phenomena. A batch type digester was used for the physical design and operation. The gas produced was composed of mainly CH_4 and CO_2. The production and consumption of hydrogen was neglected during the digestion process, and gas/liquid phase exchanges were not considered.

3.2. Mass Balance Equations

Denoting X_1 (g/L) as concentration of acidogenic bacteria, X_2 (g/L) as concentration of methanogenic bacteria, S_0 (g/L) as concentration of input solid organic matter, S_1 (g/L) as concentration of soluble substrate and S_2 (g/L) as concentration of volatile fatty acids (VFAs), the mass balance equations for anaerobic digestion are listed in eqn. (8) [9, 10], where D is dilution rate, S_{0e} is input concentration of organic matter, S_{1e} is input concentration of acidogenesis phase of the soluble substrate and S_{2e} is input concentration of the methanogenesis phase

$$(S_1):\begin{cases}\frac{dS_0}{dt} = D(S_{0e} - S_0) - K_h S_0 \ (input\ balance)\\ \frac{dX_1}{dt} = -DX_1 + \mu_1 X_1 \ (acidogenesis)\\ \frac{dS_1}{dt} = D(S_{1e} - S_1) + K_h S_0 - K_1\mu_1 X_1 (substrate\ balance)\\ \frac{dX_2}{dt} = -DX_2 + \mu_2 X_2 \ (methanogenesis)\\ \frac{dS_2}{dt} = D(S_{2e} - S_2) + K_2\mu_1 X_1 - K_3\mu_2 X_2 \ (substrate\ balance)\end{cases} \quad (8)$$

of VFA. The kinetics for variation of production of CO_2 and CH_4 as function of time were,

$$\frac{dCO_2}{dt} = K_4\mu_1 X_1 + K_5\mu_2 X_2 \quad (9)$$

$$\frac{dCH_4}{dt} = K_6\mu_2 X_2 \quad (10)$$

3.3. Effect of Temperature on Digestion Kinetics

Operating temperature range was critical for functioning of the biogas generator. Very high temperatures caused death of microorganisms required for biogas production, whereas very low temperatures slowed down the process of anaerobic digestion. The temperature range for optimal biogas production was determined from Ratkowsky formula [13] for maximum bacterial growth rate as a function of temperature.

In anaerobic digestion, all the controlling factors influencing bacteria growth rate (μ) were assumed to be independent and operated in a multiplicative way, expressed by [14],

$$\mu = f(\text{temperature, T}) \times f(pH) \times f(other\ 1) \times \ldots \times f(other\ n) = \prod_{i=1}^{n} f_i \quad (11)$$

where f_i represented environmental factors controlling anaerobic process, such as temperature (T), pH, water content, etc. The effect of each factor, $\gamma(f_i)$, on growth rate was represented as a fraction of the maximum growth rate [14],

$$\gamma(f_i) = \frac{\mu(f_i)}{\mu_{Opt}} \quad (12)$$

where $\mu(f_i)$ is maximum factor of growth rate and μ_{Opt} is optimum growth rate.

The maximum rate of bacterial growth was defined by [14];

$$\mu_{max} = \mu_{Opt} \prod_{i=1}^{n} \gamma(f_i) \quad (13)$$

Considering only temperature effect, eqn. (11) was reduced to $\mu_{max} = \mu_{Opt}\,\gamma(T)$. From eqn. (12), $\gamma(T) = \mu(\text{T})/\mu_{Opt}$, and eqn. (13) became $\mu_{max} = \mu_{Opt}\,\mu(\text{T})/\mu_{Opt}$ or $\mu_{max} = \mu(T)$. Hence, the influence of temperature on the digestion process was expressed as,

$$\mu_{max} = \mu(T) \quad (14)$$

Ratkowsky 3 square root relationship for the maximum growth rate as a function of temperature was expressed by [13];

$$\mu_{max} = [b(T - T_{min})]^2(1 - \exp[c(T - T_{max})]) \quad (15)$$

where b and c are regression constants, T_{min} is minimum growth temperature and T_{max} is maximum growth temperature.

3.4. Differential Equations for Reaction Kinetics

The dilution rate D in eqn. (8) was assumed to be zero for batch digester, where the substrate was loaded at the start of the methanation process, such that at the end of the operation, the digester was emptied of the residue of digestion. The system excluded any form of continuous and periodic recharging of the reactor.

3.4.1. System of Ordinary Differential Equations (ODEs) for Reaction Kinetics

The system of equations for the reaction kinetics consisted of 7 coupled first order ODEs, composed of 16 parameters $b_1, b_2, c_1, c_2, T_{Sub}, T_{min}, K_h, K_1, K_2, K_3, K_4, K_5, K_6, K_{S_1}, K_{S_2}, K_{12}$, as shown in eqn. (16), in addition to the bacteria growth equations.

3.4.2. Matrix Representation of System of ODEs

The numerical algorithm for prediction was developed by reformulating the system of ODEs in matrix form to facilitate computation by Runge Kutta method, as given in eqn. (17).

A state vector Y defined for the matrix representation of the system of equations (16) and (17), was expressed by eqn. (25).

4. RUNGE KUTTA NUMERICAL SOLUTION

The 4th order Runge Kutta method is explicit and efficient method for solving problems of ODEs with initial values and guaranteed stable calculation time, was adopted for numer-

$$(S_2):\begin{cases} \frac{dS_0}{dt} = -K_h S_0 \\ \frac{dX_1}{dt} = \mu_{1max}\frac{S_1}{S_1+K_{S_1}}X_1 \\ \frac{dS_1}{dt} = K_h S_0 - K_1\mu_{1max}\frac{S_1}{S_1+K_{S_1}}X_1 \\ \frac{dX_2}{dt} = \mu_{2max}\frac{S_2}{S_2+K_{S_2}+\frac{S_2^2}{K_{12}}}X_2 \\ \frac{dS_2}{dt} = K_2\mu_{1max}\frac{S_1}{S_1+K_{S_1}}X_1 - K_3\mu_{2max}\frac{S_2}{S_2+K_{S_2}+\frac{S_2^2}{K_{12}}}X_2 \\ \frac{dCO_2}{dt} = K_4\mu_{1max}\frac{S_1}{S_1+K_{S_1}}X_1 + K_5\mu_{2max}\frac{S_2}{S_2+K_{S_2}+\frac{S_2^2}{K_{12}}}X_2 \\ \frac{dCH_4}{dt} = K_6\mu_{2max}\frac{S_2}{S_2+K_{S_2}+\frac{S_2^2}{K_{12}}}X_2 \\ \mu_{1max} = [b_1(T_{Sub}-T_{min})]^2(1-\exp[c_1(T_{Sub}-T_{max})]) \\ \mu_{2max} = [b_2(T_{Sub}-T_{min})]^2(1-\exp[c_2(T_{Sub}-T_{max})]) \end{cases} \quad 16$$

$$(S_3):\begin{cases} \frac{dS_0}{dt} = f_1(t,S_0,X_1,S_1,X_2,S_2,CO_2,CH_4) \\ \frac{dX_1}{dt} = f_2(t,S_0,X_1,S_1,X_2,S_2,CO_2,CH_4) \\ \frac{dS_1}{dt} = f_3(t,S_0,X_1,S_1,X_2,S_2,CO_2,CH_4) \\ \frac{dX_2}{dt} = f_4(t,S_0,X_1,S_1,X_2,S_2,CO_2,CH_4) \\ \frac{dS_2}{dt} = f_5(t,S_0,X_1,S_1,X_2,S_2,CO_2,CH_4) \\ \frac{dCO_2}{dt} = f_6(t,S_0,X_1,S_1,X_2,S_2,CO_2,CH_4) \\ \frac{dCH_4}{dt} = f_7(t,S_0,X_1,S_1,X_2,S_2,CO_2,CH_4) \end{cases} \quad (17)$$

where

$$f_1(t,S_0,X_1,S_1,X_2,S_2,CO_2,CH_4) = -K_h S_0 \quad (18)$$

$$f_2(t,S_0,X_1,S_1,X_2,S_2,CO_2,CH_4) = \mu_{1max}\frac{S_1}{S_1+K_{S_1}}X_1 \quad (19)$$

$$f_3(t,S_0,X_1,S_1,X_2,S_2,CO_2,CH_4) = K_h S_0 - K_1\mu_{1max}\frac{S_1}{S_1+K_{S_1}}X_1 \quad (20)$$

$$f_4(t,S_0,X_1,S_1,X_2,S_2,CO_2,CH_4) = \mu_{2max}\frac{S_2}{S_2+K_{S_2}+\frac{S_2^2}{K_{12}}}X_2 \quad (21)$$

$$f_5(t,S_0,X_1,S_1,X_2,S_2,CO_2,CH_4) = K_2\mu_{1max}\frac{S_1}{S_1+K_{S_1}}X_1 - K_3\mu_{2max}\frac{S_2}{S_2+K_{S_2}+\frac{S_2^2}{K_{12}}}X_2 \quad (22)$$

$$f_6(t,S_0,X_1,S_1,X_2,S_2,CO_2,CH_4) = K_4\mu_{1max}\frac{S_1}{S_1+K_{S_1}}X_1 + K_5\mu_{2max}\frac{S_2}{S_2+K_{S_2}+\frac{S_2^2}{K_{12}}}X_2 \quad (23)$$

$$f_7(t,S_0,X_1,S_1,X_2,S_2,CO_2,CH_4) = K_6\mu_{2max}\frac{S_2}{S_2+K_{S_2}+\frac{S_2^2}{K_{12}}}X_2 \quad (24)$$

$$Y = [S_0 \;\; X_1 \;\; S_1 \;\; X_2 \;\; S_2 \;\; CO_2 \;\; CH_4 \;]^T \quad (25)$$

$$Y' = F(Y,t) \quad (26)$$

where $F = [f_1 \;\; f_2 \;\; f_3 \;\; f_4 \;\; f_5 \;\; f_6 \;\; f_7 \;]^T$ was solved.

ical solution of the ODEs, because of the inherent precision. The 4th order Runge Kutta method is an improvement of Euler method, and induces a total error in $O(h^4)$ [15], where h is discretization of the time interval.

4.1. Runge-Kutta Solution

The numerical solution scheme of the system of ODEs represented by eqn. (26), $Y' = F(Y,t)$, and $y(t_0) = y_0$ was solved for discrete times $t_0 < t_1 \ldots < t_n$ by Runge Kutta method, at intermediate points $\{(t_{n,i}, y_{n,i})\}_{1\le i\le q}$ to recursively calculate values (t_n, y_n), where $t_{n,i} = t_n + c_i h_n$, h_n was time step and c_i was in interval [0, 1]. For each intermediate point, the corresponding slope was $p_{n,i} = F(t_{n,i}, y_{n,i})$, and for each time step h, the calculations followed the representations given by the set of eqns. (27).

$$(S_4):\begin{cases} Y(t+h) = Y(t) + \frac{1}{6}(k_1 + 2k_2 + 2k_3 + k_4) \\ k_1 = hF(t,Y(t)) \\ k_2 = hF\left(t+\frac{1}{2}h, Y(t)+\frac{1}{2}k_1\right) \\ k_3 = hF\left(t+\frac{1}{2}h, Y(t)+\frac{1}{2}k_2\right) \\ k_4 = hF(t+h, Y(t)+k_3) \end{cases} \quad (27$$

The next value (y_{n+1}) was approximated by the sum of the current value (y_n) and product of interval size (h) by the estimated slope. The slope was obtained by weighted average of the slopes, where k_1 was the slope at beginning of the interval; k_2 was slope in middle of the interval (using slope k_1 to calculate value of y at the point $t_n + h/2$); k_3 was slope in middle of the interval (obtained using slope k_2 to compute

y); and k_4 was the slope at end of the interval, (with the value of y calculated using k_3).

4.2. Initial Conditions & Model Parameters

The initial conditions served as input data, and were taken from published experimental data [14, 16, 17]. To validate the accuracy of the model, the simulated data were compared with literature data, for biogas operating under identical conditions in order to evaluate the residual errors.

The first-order differential equations in matrix form were solved numerically by using initial values of the substrate and bacteria concentrations at start of bioreactor operations [16]; $S_0(0) = 10\ g/\text{L}, S_1(0) = 10\ g/\text{L},\ X_1(0) = 0.4\ g/\text{L};\ S_2(0) = 0\ g/\text{L},\ X_2(0) = 0.01g/\text{L},\ CO_2(0) = 0\ g/\text{L}, CH_4(0) = 0\ g/\text{L}$.

The growth parameters were [16]; KS_1 = 35 mg/L, KS_2 = 4 mg /L, K_{12} = 170 mg /L, μ_{1max}= 0.4 J^{-1}, μ_{2max}= 0.4 J^{-1}; while the kinetic parameters were: K_h = 0; K_1 = 50; K_2 = 50; K_3 = 15; K_4 = 15; K_5 = 75.

For methane production, the value of parameter K_6 was 75 L^2/mg [17]. The regression parameters were $b_1 = 0.041$, $b_2 = 0.04$, $c_1 = 0.161$, $c_2 = 0.161$; while the temperatures were T_{min}= 2 °C and T_{max}=43.7 °C [14].

5. NUMERICAL SIMULATION

The non-linear ODEs (eqn. 16) were solved using 4th order Runge Kutta numerical algorithm, while the function pdex4 in Scilab software for initial value problems was used for the computations.

5.1. Numerical Algorithm

The Steps for Runge Kutta function 4 algorithm for resolution of Y'= F(Y, t), with parameters y_0 for initial condition, n for number of discretization points, and h as discretization of time interval were:

(i). Initialization:

Initialization of the step h; and initial conditions: t = 0 and Y = Y (0)

ii). For Loop or While Loop:

Calculation of $k_1 = hF\big(t, Y(t)\big)$; $k_2 = hF(t + + \frac{1}{2}h, Y(t) + \frac{1}{2}k_1)$; $k_3 = hF\left(t + \frac{1}{2}h, Y(t) + \frac{1}{2}k_2\right)$; $k_4 = hF(t + h, Y(t) + k_3)$; and $Y(t) = Y(t) + \frac{1}{6}(k_1 + 2k_2 + 2k_3 + k_4)$; t = t + h;

End Function

(iii). Construction of Prediction Function:

Input Initial conditions and values of model parameters; Call to Function Runge Kutta 4

(iv). Outputs from Model:

Graphs of production of CH_4 and CO_2; Proportions of CH_4 and CO_2 gases

5.2. SciLab Code

SciLab programs were developed and implemented for simulation of bio-reactor operations, and for validating the numerical data. The results representing numerical solution of the system ODEs were plotted using graphical interface in SciLab.

Comparative analysis between the numerical data and published experimental data on batch type digester served to validate the model performance. Listings of the SciLab code are shown in Appendices 1 and 2.

6. SIMULATION RESULTS

On implementing the SciLab codes, the volume of methane gas produced, molar composition of the biogas, and influence of operating temperature on bioreactor performance were examined.

6.1. Volume of Gas Produced

The cumulative volume of biogas generated served as important parameter for the control and monitoring of the anaerobic digestion; as significant production of biogas was reflection on both the stability and functioning of the digester.

The temporal evolution of cumulative volume of biogas is presented in Fig. 2 for substrate temperature at 30 °C, indicating the volume of biogas generated was 26 L. The trendline equation and the regression coefficient are also shown on the plot for volume (V)-time(t) relationship. Figure 2 indicates that the kinetics of biogas production occurred in three main phases of latency, exponential and stabilization.

The latency phase corresponded to adaptation of microorganisms to the input culture medium, and had very short period or duration. During the exponential growth phase, the multiplication of microorganisms led to significant production of biogas. The stabilization phase corresponded to the terminal stage, characterized by absence of substrate in the medium, resulting in built up of accumulated biogas.

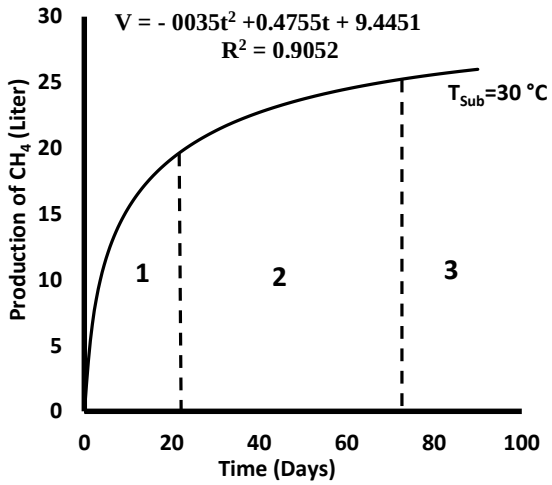

Fig. 2. Cumulative production of CH_4 as a function of time at operating temperature of 30 ° C; indicating (1) latency, (2) exponential, and (3) stabilization phases of kinetics of biogas production

6.2. Molar Composition of Biogas

The molar composition of biogas output by SciLab simulation of anaerobic digester at 30 °C was methane at 66.16 % and carbon dioxide at 33.84 % of total volume produced. There was predominance of methane in the gas mixture, indicating that the biogas exhibited fuel characteristics of the same composition similar to published data for experimental produced biogas.

6.3. Dependence on Operating Temperature

Figure 3 shows cumulative volume of methane produced in the temperature range of 20 - 40 °C, and reaching peak value of 26.39L at 35 ° C, after 90 hours of operation. The cumulative volume decreased when the temperature exceeded the optimum value of 35 °C. The variation of cumulative volume of biogas produced with temperature was consistent with published data [18, 19, 20].

The dependence of molar composition of biogas on temperature was examined by varying the temperature for different proportions of CH_4 and CO_2 in the gas mixture as shown in Table 1, which agreed with published experimental data. The proportions of CH_4 in Table 1 were higher than published data, because of approximations made in the kinetics of biological reactions, by not taking gas/liquid phase exchanges into account in the model formulation.

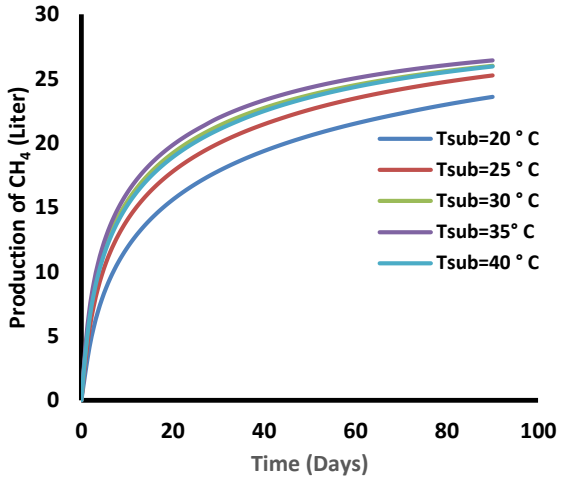

Fig. 3. Cumulative production profile of methane at different temperatures

Table 1. Composition of the gas mixture for simulated batch digester

Gas %	Temperature (°C)					
	20	24	28	32	36	40
CH_4	85.48	69.39	71.19	62.86	59.10	69.24
CO_2	14.52	30.61	28.81	37.14	40.90	30.76

6.4. Model Validation

The numerical results were compared with experimental data of Rakotoniaina [21] on batch digester. Figure 4 illustrates the model prediction of evolution of cumulative volume of methane as a function of time (excluding gas/liquid phase exchanges); whereas Fig. 5 shows evolution of cumulated production of methane using a mixture of cow manure. The simulated model and Rakotoniaina data [21] are shown in Table 2, with the residual errors.

Table 2. Comparison of Numerical and Experimental data

Data Source	Cumulated Volume of Methane (L)	Absolute Error (L)	Residual Error (%)
Model Numerical Data	402.71	**4.71**	**1.2**
Experimental Data [21]	398.00		

The comparison shows good agreement, with residual error of ~ 1.2 %. The difference is justified because the gas/liquid phase exchange phenomena were not considered in formulating the model. Hence, the model equations developed, solved by Runge Kutta method, and simulated by SciLab code, were appropriate for setting up operating parameters and conditions for generating biogas for batch digester.

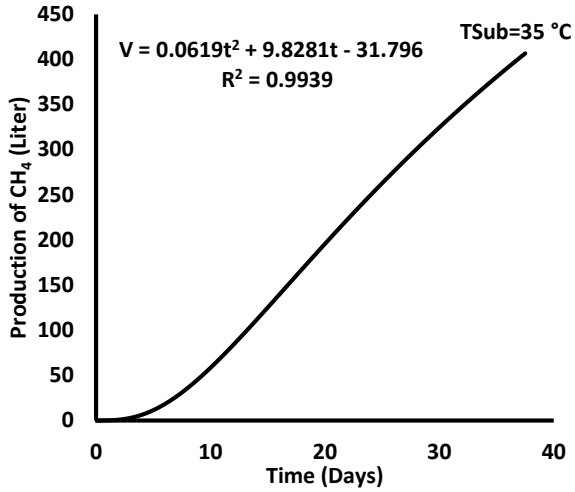

Fig. 4. Cumulative CH_4 production (model) at 35 °C

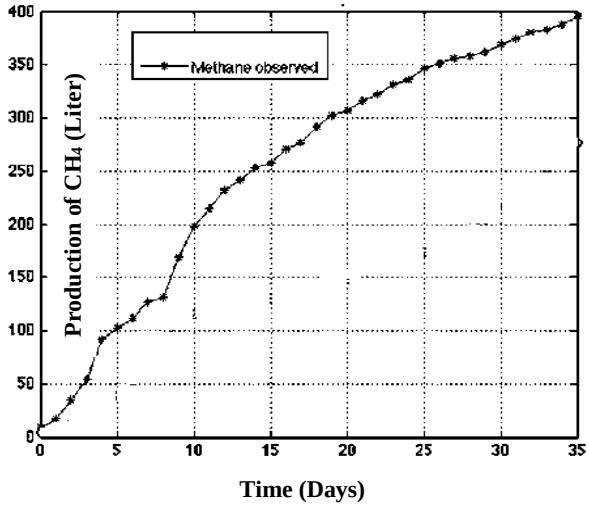

Fig. 5. Cumulative production of CH_4 [16]

7. LIMITATIONS OF THE STUDY

In anaerobic digestion, the compounds are first formed in the liquid phase before being converted into the gas phase. The conversion process is a limiting phenomenon influencing the overall performance of the bio-reactors, because the conversion influences the mixing of the liquid phase and the gaseous fraction in the digestion media. Compounds such as methane or hydrogen which are relatively sparingly soluble, can then be supersaturated.

Based on the assumptions, the model presented did not include transfer kinetics of gaseous compounds from the liquid phase. Therefore, the model is applicable for conditions where the liquid/gas phase transfer phenomena are neglected.

8. DISCUSSION

The research presented was aimed at developing a mathematical model for predicting the molar composition of biogas from kinetics reaction schemes, and dependence on temperature of production of biogas.

The methodologies adopted were modeling kinetics of biogas production from biochemical reactions based on hydrolysis, acidogenesis and methanogenesis of anaerobic digestion; and modifying Ratkowsky's formula to examine the influence of temperature on molar fractions of the gas mixture produced. Comparative analysis was made between the simulated model data and experimental data.

The model predicted molar composition of 66.16 % methane and 33.84 % carbon dioxide produced at 30 °C; which were in agreement with published data. The maximum value of cumulative volume of methane produced was 26.39 L at optimal temperature of 35 °C in the mesophilic regime. From analysis of results of the simulations, the choice of appropriate temperature range was critical for biogas production, as either very high temperatures or very low temperatures limited the gas production. Therefore, outside the critical operating temperature range, temperature had negative effect on efficient anaerobic digestion process, as well as the quality and quantity of the gas produced.

9. CONCLUSIONS

Considering that experimentation for examining anaerobic digestion process is expensive and time consuming, mathematical model was developed for the physico-chemical and biological processes involved, and simulated using SciLab Code to predict the molar mass composition and temperature dependence on biogas production.

The numerical model predicted accurately the influence of temperature on efficient operations of batch type digester. The simulation data agreed with published experimental results. The cumulative volume of methane was simulated in temperature range of 20 - 35 °C and attained peak value of 26.39 L at 35 °C. The omission of the gas/liquid phase exchange in the model formulation did not significantly affect the total volume of methane gas produced and the molar composition of the gas mixture.

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APPENDIX I: Model Simulation Script

```
clear
//////////////////////*********SIMULATION
////////////////////// Runge function kutta4 for the resolution of  Y '= F (t, Y)
//////////////////////  function parameters:
////////////////////// y0:  initial condition
//////////////////////  N: number of discretization points
////////////////////// /h:  discretization of the time interval
function [Y, Z]=RK4(F, y0, N)
y=y0;
Y=[y0];
 t=0;
 Z=[t];
 h=T/N;
 for i=1:N
 k1=h*F(t,y);
 k2=h*F(t+(h/2),y+(k1/2));
 k3=h*F(t+(h/2),y+(k2/2));
 k4=h*F(t+h,y+k3);
 y=y+((k1+2*k2+2*k3+k4)/6);
 t=t+h;
 tr=90*t
 Y=[Y,y];
 Z=[Z,tr];
  end
  endfunction
//////////////////////  Construction of the prediction function [f1; f2; ...;f9]
function yp=prevision(t, y)
 yp=[-Kh*y(1);  ((b1*(TSub-Tmin))^2)*(1-exp(c1*(TSub-Tmax)))*(1/(y(3)+KS1))*(y(3))*y(2) ;
  Kh*y(1)-K1*((b1*(TSub-Tmin))^2)*(1-exp(c1*(TSub-Tmax)))*(1/(y(3)+KS1))*(y(3))*y(2);
  ((b2*(TSub-Tmin))^2)*(1-exp(c1*(TSub-Tmax)))*(1/(y(5)+KS2+((y(5))^2)/K12))*(y(5))*y(4);
  K2*((b1*(TSub-Tmin))^2)*(1-exp(c1*(TSub-Tmax)))*(1/(y(3)+KS1))*(y(3))*y(2)-K3*((b2*(TSub-
Tmin))^2)*(1-exp(c1*(TSub-Tmax)))*(1/(y(5)+KS2+((y(5))^2)/K12))*(y(5))*y(4);
  K4*((b1*(TSub-Tmin))^2)*(1-exp(c1*(TSub-Tmax)))*(1/(y(3)+KS1))*(y(3))*y(2)+K5*((b2*(TSub-
Tmin))^2)*(1-exp(c1*(TSub-Tmax)))*(1/(y(5)+KS2+((y(5))^2)/K12))*(y(5))*y(4);
  K6*((b2*(TSub-Tmin))^2)*(1-exp(c1*(TSub-Tmax)))*(1/(y(5)+KS2+((y(5))^2)/K12))*(y(5))*y(4)];
Endfunction
////////////////////// Initial conditions and values of the model parameters
T=1; N=100 ;
y0=[10;0.4;10;0.01;0;0;0];// initial conditions S0(0)=10g/L ; S1=0 g/L ;  S2(0) = 0g/L ; X1(0) = 0,4 g/L  et X2=
0.01 g/L.
Kh=0;KS1=35*0.001;KS2=4*0.001;K12=170*0.001  ;K1=50;  K2=50;K3=15;  K4=15;  K5=75;  K6=75*1000;
b1=0.0410; b2=0.040 ;/// KS1 = 35 mg/ L ; KS3 = 4 mg/L ; K23 = 170 mg/L.
TSub=30 ; Tmin=2 ;Tmax=43.7; c1=0.161
////////////////////// Calculations
[solution,temps]=RK4(prevision,y0,N);
////////////////////// calculation of the gas proportions of CH4 and CO2
PCH4=100*(solution(7,N))/( (solution(6,N))+(solution(7,N)));
PCO2=100-PCH4;
disp(PCH4)
disp(PCO2)
////////////////////// Graph giving CH4 production as a function of time
figure(1)
xlabel(' temps[jour] ');ylabel('production  du CH4 [litre]');
plot2d(temps,solution(7,:),style=[color("blue")]);
hl=legend(['T=20°C'],['T=25°C'],['T=30°C'],['T=35°C'],['T=40°C']);
```

APPENDIX II: Script for model validation

```
clear
//////////////////////Validation
////////////////////// Runge function kutta4 for the resolution of  Y '= F (t, Y)
//////////////////////  function parameters:
////////////// //////////y0:  initial condition
////////////////////// N: number of discretization points
////////////////////// h:  discretization of the time interval
function [Y, Z]=RK4(F, y0, N)
y=y0;
Y=[y0];
 t=0;
 Z=[t];
 h=1/(2*24);
 for i=1:N
  k1=h*F(t,y);
  k2=h*F(t+(h/2),y+(k1/2));
  k3=h*F(t+(h/2),y+(k2/2));
  k4=h*F(t+h,y+k3);
  y=y+((k1+2*k2+2*k3+k4)/6);
  t=t+h;
  Y=[Y,y];
  Z=[Z,18*t];
  end
endfunction
//////////////////////  Construction of the prediction function [f1; f2; ...;f9]
function yp=prevision(t, y)
yp=[-Kh*y(1);((b1*(TSub-Tmin))^2)*(1-exp(c1*(TSub-Tmax)))*(1/(y(3)+KS1))*(y(3))*y(2); Kh*y(1)-
K1*((b1*(TSub-Tmin))^2)*(1-exp(c1*(TSub-Tmax)))*(1/(y(3)+KS1))*(y(3))*y(2);((b2*(TSub-Tmin))^2)*(1-
exp(c1*(TSub-Tmax)))*(1/(y(5)+KS2+((y(5))^2)/K12))*(y(5))*y(4);K2*((b1*(TSub-Tmin))^2)*(1-
exp(c1*(TSub-Tmax)))*(1/(y(3)+KS1))*(y(3))*y(2)-K3*((b2*(TSub-Tmin))^2)*(1-exp(c1*(TSub-
Tmax)))*(1/(y(5)+KS2+((y(5))^2)/K12))*(y(5))*y(4);K4*((b1*(TSub-Tmin))^2)*(1-exp(c1*(TSub-
Tmax)))*(1/(y(3)+KS1))*(y(3))*y(2)+K5*((b2*(TSub-Tmin))^2)*(1-exp(c1*(TSub-
Tmax)))*(1/(y(5)+KS2+((y(5))^2)/K12))*(y(5))*y(4);K6*((b2*(TSub-Tmin))^2)*(1-exp(c1*(TSub-
Tmax)))*(1/(y(5)+KS2+((y(5))^2)/K12))*(y(5))*y(4)];
endfunction
//////////////////////Initial conditions and values of the model parameters
T=1; N=100 ;
y0=[39;13;0;10;0;0;0];
Kh=0.5;KS1=160;KS2=0.82;K12=5 ;K1=2.5; K2=4;K3=2.6*0.01; K4=2.6*0.01;K5=45.51;K6=74.54
;b1=0.0410;b2=0.0254 ;
////////////////////// Temperature
TSub=35 ; Tmin=2 ;Tmax=43.7; c1=0.161
////////////////////// calcul
[solution,temps]=RK4(prevision,y0,N);
disp(solution(7,N));
//////////////////////  calculation of the gas proportions of CH4 and CO2
PCH4=100*(solution(7,N))/( (solution(6,N))+(solution(7,N)));
PCO2=100-PCH4;
disp(PCH4)
disp(PCO2)
//////////////////////  Graph giving CH4 production as a function of time
figure(1)
xlabel(' temps[jour] ');ylabel('production  du CH4 [litre]');
plot2d(temps,solution(7,:),style=[color("blue")]);
hl=legend(['T=20°C'],['T=25°C'],['T=30°C'],['T=35°C'],['T=40°C'])
```