Modeling of Anaerobic Digestion of Complex Substrates

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ABSTRACT: A structured mathematical model of anaerobic conversion of complex organi-
materials in non-ideally cyclic-batch reactors for biogas production has been developed. Th-
model is based on multiple-reaction stoichiometry (enzymatic hydrolysis, acidogenesis,
acetogenesis and methanogenesis), microbial growth kinetics, conventional material balances in th-
liquid and gas phases for a cyclic-batch reactor, liquid-gas interactions, liquid-phase equilibrium
reactions and a simple mixing model which considers the reactor volume in two separate sections
the flow-through and the retention regions. The dynamic model describes the effects of reactant’
distribution resulting from the mixing conditions, time interval of feeding, hydraulic retention tim
and mixing parameters on the process performance. The model is applied in the simulation of an
anaerobic digestion of cattle manure under different operating conditions. The model is compared
with experimental data and good correlations are obtained.

KEY WORDS: Anaerobic digestion, Dynamic modeling, Two-region mixing model, Cyclic-batch
reactor, Complex substrates, Biogas

INTRODUCTION
In the past 30 years a number of different anaerobic processes have been developed. Modeling studies are
important because the experiments on the

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expensive. The development of an up-to-date model for anaerobic digestion of organic matter is accomplished with considerable difficulties, due to the numerous variables existing in the anaerobic system. Large-scale anaerobic digestion of organic wastes has received growing attention during the recent years in Iran and elsewhere as a more efficient method for utilizing organic wastes for the production of energy and fertilizer [1]. Consequently, the need for accurate modeling of the anaerobic degradation of complex wastes has increased in recent years. The simplified models such as those by Andrews [2] and Buhr [3] have only considered the acetate degradation rate. Hill and Barth [4] included the hydrolysis and the acidogenesis steps in computing the organic overload effect in the methane production rate. Angelidaki [5] developed a structured kinetic model for ideal CSTR reactors. Today there are reports of rigorous simulators that consider the different phenomena involved, such as inhibition, ionic equilibrium, gas-liquid transfer and biofilm growth [6,7,8,9].

In general, all these models describe the ideal bioreactors but not the real systems. In real systems, the mixing device is an important component of the reactor. Good mixing promotes the effective transfer of the substrates and heat to the microorganisms, maintains uniformity in the other environmental factors and assures the effective use of the entire reactor volume by preventing stratification. Conversely, incomplete mixing jeopardizes the efficiency of the treatment process and therefore, the stability of the sludge produced. Scum formation can also be greatly reduced or even eliminated by suitable agitation. It is recognized that heterogeneities in the medium can have a profound influence, especially, on the production of the metabolites [10].

While the imperfect mixing patterns are more common than the ideal ones in a real reactor, the anaerobic digestion models often assume the complete mixing conditions. The ideal assumption of the completely mixed reactors may be valid in some cases, where due to the small scale of the experimental reactors used, perfect mixing may effectively be achieved or when the characteristic time constants for the kinetic parameters are much larger than the mixing and the mass transfer time constants. However, the difficulty in achieving complete mixing increases with the reactor size and as a result, the inevitable compromises: increasing costs and the loss of the equipment mixing in the large reactors may not be as p the small ones. The residence time distribut conducted in the full-scale primary digesters l that the actively mixed volumes can be as low the total volume [11].

Farm animals are ideal for the applicat anaerobic digestion to convert cattle manure to energy generation and fertilizer production manure is a complex substrate containing and the insoluble organic matter such as polylipids, proteins, and the volatile fatty : cyclic batch operation is one of the most c methods for the animal waste treatment. Y previous researches on the dairy wastewat have been based on this type of the anaerol [5,12,13,14].

The objective of this paper is to present model for the anaerobic digestion of complec such as cattle manure in a cyclic batch reactor following criteria:

1- Making a model capable of consider important factors involved in the anaerobic pro
2- Reducing the dimensions of the mos needed numerical calculations could be carry a personal computer.
3- Providing a rational explanation of effects between mixing parameters and digestion kinetics in non-ideal cyclic batch r

**Microbial kinetic model**

The kinetic model used in this study is: Angelidaki [16] kinetic model for the anaerob of the cattle manure. The kinetic model disting different processes: the hydrolysis of the substrate by the extracellular enzymes, the o of the soluble substrates by the acidogenic b consumption of the volatile fatty acids (VF formation of acetate by the propionate ar degrading acetogenic bacteria, and f consumption of acetate and the generation of the methanogenic bacteria. The model includ inhibition of the hydrolysis step, the acetate is the acetogenic steps, the free ammonia inhib methanogenic step and the pH inhibition

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In the model the primary substrates in the manure are represented as the soluble (s) and the insoluble (is) carbohydrate units, with the basic formula (C\(_6\)H\(_{10}\)O\(_5\)nNH\(_3\))\(_s\) and (C\(_6\)H\(_{10}\)O\(_5\)nNH\(_3\))\(_{is}\) respectively. The cell mass is represented by the empirical formula C\(_{73}\)H\(_{108}\)O\(_{60}\)N. Also it is assumed that the volatile fatty acids contain only the acetic, the propionic and the butyric acids. The model expressions are as follow:

\[ (C_6H_{10}O_5nNH_3)_s \rightarrow Y_e(C_6H_{10}O_5)_s + (1-Y_e)(C_6H_{10}O_5.mNH_3)_s + (a-(1-Y_e)m)NH_3 \]

\[ (C_6H_{10}O_5)_s + 0.1115 \text{NH}_3 \rightarrow 0.1115 \text{C}_4\text{H}_7\text{NO}_2 + \text{0.744 CH}_3\text{COOH} + 0.5 \text{CH}_3\text{CH}_2\text{COOH} + 0.4409 \text{CH}_3(\text{CH}_2)_2\text{COOH} + 0.6909 \text{CO}_2 + 0.0254\text{H}_2\text{O} \]

\[ \text{CH}_3\text{CH}_2\text{COOH} + 0.06198 \text{NH}_3 + 0.314 \text{H}_2\text{O} \rightarrow 0.06198 \text{C}_4\text{H}_7\text{NO}_2 + 0.9345 \text{CH}_3\text{COOH} + 0.6604 \text{CH}_4 + 0.1607\text{CO}_2 \]

\[ \text{CH}_3(\text{CH}_2)_2\text{COOH} + 0.0653\text{NH}_3 + 0.5543\text{CO}_2 + 0.5543\text{H}_2\text{O} \rightarrow 0.0653\text{C}_4\text{H}_7\text{NO}_2 + 1.8909\text{CH}_3\text{COOH} + 0.4452\text{CH}_4 \]

In Reaction 1, \( Y_e \) is the enzymatic efficiency or yield factor and the subscripts in represents the undegradable inert organic material. The coefficients \( Y_e \), \( n \), and \( m \), together with the ratio of the soluble to the insoluble substrate depend on the type of the manure. In the model, the hydrolytic step and the biomass decay are described by the first order kinetics, while the consumption of the soluble substrates and the volatile acids as well as the growth of the anaerobic microorganisms are assumed to obey the Monod-type kinetics with the noncompetitive inhibition function of the intermediate substrates and the pH inhibition on the microbial growth rates, according to the expressions presented in the following:

The hydrolysis rate:

\[ r_h = k \ C_is \]

\[ k = k_0 \sum VFA + k_{i,VFA} \]

\[ \sum VFA = C_{ac} + C_{pr}C_{pr} + C_{but}C_{but} \]

The biomass decay rate, the substrate cons generation rate and the biomass growth rate respectively as follow:

\[ r_d = k_d X \]

\[ r_s = Y_{e,x} \mu X \]

\[ r_x = \mu X \]

The specific growth rates are as follow:

\[ \mu_A = \mu_{maxA} \frac{C_i}{K_{ac} + C_i} \]

\[ F_{AP} = \mu_{maxAP} \frac{C_{pr}}{K_{spr} + C_{pr}} \times \frac{K_{i,pr}}{K_{i,pr} + C_{ac}} \]

\[ F_{AB} = \mu_{maxAB} \frac{C_{but}}{K_{sb,ut} + C_{but}} \times \frac{K_{i,ut}}{K_{i,ut} + C_{ac}} \]

\[ F_{M} = \mu_{maxM} \frac{C_{ac}}{K_{ac} + C_{ac}} \times \frac{K_{i,am}}{K_{i,am} + C_{am}} \]

**Liquid mixing model**

A simple mixing model referred to as the model was used in combination with the kinetic conceptual representation of the two-regi model is illustrated in Figure 1. The model assumes that the reactor volume is split into \( t \) the flow-through (\( \alpha \)) region and the retention. Both regions are assumed to be perfectly mixed: the materials between the zones is 1 retention region has the features of the behavio
a stagnant zone. The different levels of mixing are accomplished by adjusting the relative volume of the flow-through region (a) and the ratio of the exchange flow rate between regions to the feed flow rate (b).

Despite its simplicity, this classical model is used in chemical engineering for the description of the retention time distribution in the real reactors [15] and has proved to be a useful tool for the theoretical study of the effects of heterogeneity in the chemical and biological systems. By definition, for a relative volume in the flow-through region (a) close to unity and, for any value of ‘a’, with an interchange rate of the material between regions to the feed flow rate ratio (b) approaching infinity, the dynamic model produces results closely approaching those of a completely mixed reactor. Otherwise, for any ‘a’ with ‘b’ close to zero (i.e. no interchange of material between regions) the system consists of a reactor with a completely dead zone of volume (1-a)Vf. For values of the mixing parameters other than those mentioned above, the mathematical model simulates the performance of an imperfectly mixed digester.

**Cyclic batch reactor**

In an ideal cyclic batch reactor, a volume of the manure is rapidly introduced into the reactor. The mixture is stirred and the reaction takes place for a specified period of time. Afterwards, a volume of the reactor contents, equal to that introduced, is discharged from the reactor. The reactant medium is mixed with a new addition of feed in the following cycle with the same reaction time as in the previous one. After several cycles, and when the reactant concentrations are the same for all the input volumes fed, and the operating conditions are kept constant, the concentration of the products in the discharged volume can reach constant values. Under these conditions, the system is at quasi-steady state.

The descriptions that follow represent the cycle of the batch operation, in four steps. In the first step, the reactor is operated batch-wise for a time known initial conditions. In this step the mass equations in the liquid phases of α and β for volume cyclic batch reactor have been described next section. In the second step, after a reaction volume Vf of the reaction mixture is drained out of the reactor. In the third step the reactor is filled with the original volume with the feed. Finally, the mixture is mixed in the last step and the initial conditions for the new cycle are obtained.

The characteristic parameters of the cyclic reactor are the interval of feeding time (tR) and the remaining volume in the reactor to t discharged from the reactor (R):

\[ t_R = \frac{V_i}{Q_f} \]

\[ R = \frac{a V_i}{V_f} \]

Therefore, the initial conditions for any n cycle described by the relation:

\[ C_i = \frac{C_f + R C_f}{R + 1} \]

Also the relation between the interval of feeding time (HRT) is as follow

\[ HRT = \frac{V_i}{Q_f} - \frac{t_R (R + 1)}{a} \]

The value of tR can thus be chosen from [1/HRT, 0] hence R ∈ (0,∞) respectively. The R = ∞ corresponds to the continuous flow operation. R=0 denotes repeated the batch-wise operation.

**Mathematical model**

The mass balances on the α and β liquid gas phase of the cyclic batch reactor under conditions for different components in the reactor led to a set of ordinary differential equations which must be simultaneously solved by known conditions. These components include the substrate, the soluble substrate, acetate, butyrate, ammonia, carbon dioxide, me acidogenic bacteria, the propionate degrading
bacteria, the butyrate degrading acetogenic bacteria, and the methanogenic bacteria. The component material balances in different phases led to 25 ordinary first order differential equations and three algebraic equations as described in the following (Equations 21-38 and 41-43).

**Liquid phase**

Biomass balance for different groups of bacteria (Xi, i=A, AP, AB, M)

\[
\frac{dX_i^a}{dt} = \frac{X_i^0 - X_i^a}{a \theta / b} + \left[ \mu_i^a - (1-a) \theta \right] X_i^a
\]

(21)

\[
\frac{dX_i^b}{dt} = \frac{X_i^0 - X_i^b}{(1-a) \theta / b} + \left[ \mu_i^b - (1-a) \theta \right] X_i^b
\]

(22)

**Insoluble substrate material balance**

\[
\frac{dC_i^n}{dt} = \frac{C_i^n - C_{is}^n}{a \theta / b} - k^a C_i^n
\]

(23)

\[
\frac{dC_i^b}{dt} = \frac{C_i^b - C_{is}^b}{(1-a) \theta / b} - k^b C_i^b
\]

(24)

**Soluble substrate material balance**

\[
\frac{dC_i^n}{dt} = \frac{C_i^n - C_{is}^n}{a \theta / b} + \frac{162 y_n}{12.858 \mu_A^a X_A^a} - 162 + \frac{17n}{162} + \frac{12.858 \mu_A^a X_A^a}{X_A^a}
\]

(25)

\[
\frac{dC_i^b}{dt} = \frac{C_i^b - C_{is}^b}{(1-a) \theta / b} - \frac{162 y_n}{12.858 \mu_A^b X_A^b} + 162 + \frac{17n}{162} + \frac{12.858 \mu_A^b X_A^b}{X_A^b}
\]

(26)

**Acetic acid material balance**

\[
\frac{dC_{ac}^a}{dt} = \frac{C_{ac}^a - C_{ac}^a}{a \theta / b} + \frac{3.54 \mu_A^a X_A^a + 8.006 \mu_{AP}^a X_{AP}^a}{15.366 \mu_{AB}^a X_{AB}^a - 24.135 \mu_M X_M}
\]

(27)

\[
\frac{dC_{ac}^b}{dt} = \frac{C_{ac}^b - C_{ac}^b}{(1-a) \theta / b} + \frac{3.54 \mu_A^b X_A^b + 8.006 \mu_{AP}^b X_{AP}^b}{15.366 \mu_{AB}^b X_{AB}^b - 24.135 \mu_M X_M}
\]

(28)

**Propionic acid material balance**

\[
\frac{dC_{pc}^a}{dt} = \frac{C_{pc}^a - C_{pc}^a}{a \theta / b} + \frac{9.233 \mu_A^a X_A^a - 10.566 \mu_{AP}^a}{15.366 \mu_{AB}^a X_{AB}^a - 24.135 \mu_M X_M}
\]

(29)

\[
\frac{dC_{pc}^b}{dt} = \frac{C_{pc}^b - C_{pc}^b}{(1-a) \theta / b} + \frac{9.233 \mu_A^b X_A^b - 10.566 \mu_{AP}^b}{15.366 \mu_{AB}^b X_{AB}^b - 24.135 \mu_M X_M}
\]

(30)

**Butyric acid material balance**

\[
\frac{dC_{ba}^a}{dt} = \frac{C_{ba}^a - C_{ba}^a}{a \theta / b} + \frac{3.079 \mu_A^a X_A^a - 11.919 \mu_{AP}^a}{15.366 \mu_{AB}^a X_{AB}^a - 24.135 \mu_M X_M}
\]

(31)

\[
\frac{dC_{ba}^b}{dt} = \frac{C_{ba}^b - C_{ba}^b}{(1-a) \theta / b} + \frac{3.079 \mu_A^b X_A^b - 11.919 \mu_{AP}^b}{15.366 \mu_{AB}^b X_{AB}^b - 24.135 \mu_M X_M}
\]

(32)

**Ammonia material balance**

\[
\frac{dC_{am}}{dt} = \frac{C_{am}^a - C_{am}^a}{a \theta / b} + \frac{17 \mu_A^a X_A^a + \mu_{AP}^a X_{AP}^a + \mu_{AB}^a X_{AB}^a + \mu_M X_M}{15.366 \mu_{AB}^a X_{AB}^a - 24.135 \mu_M X_M} - \frac{0.15 \mu_A^a X_A^a + \mu_{AP}^a X_{AP}^a + \mu_{AB}^a X_{AB}^a + \mu_M X_M}{15.366 \mu_{AB}^a X_{AB}^a - 24.135 \mu_M X_M}
\]

(33)

**Carbon dioxide material balance**

\[
\frac{dC_{co}^a}{dt} = \frac{C_{co}^a - C_{co}^a}{a \theta / b} + \frac{2.413 \mu_A^a X_A^a + 1.01 \mu_{AP}^a X_{AP}^a}{15.366 \mu_{AB}^a X_{AB}^a - 24.135 \mu_M X_M} - \frac{3.030 \mu_{AB}^a X_{AB}^a + 16.726 \mu_M X_M - \frac{N_A^n}{a V_t}}{15.366 \mu_{AB}^a X_{AB}^a - 24.135 \mu_M X_M}
\]

(34)

\[
\frac{dC_{co}^b}{dt} = \frac{C_{co}^b - C_{co}^b}{(1-a) \theta / b} + \frac{2.413 \mu_A^b X_A^b + 1.01 \mu_{AP}^b X_{AP}^b}{15.366 \mu_{AB}^b X_{AB}^b - 24.135 \mu_M X_M} - \frac{3.030 \mu_{AB}^b X_{AB}^b + 16.726 \mu_M X_M}{15.366 \mu_{AB}^b X_{AB}^b - 24.135 \mu_M X_M}
\]

(35)

**Methane material balance**

\[
\frac{dC_{m}^a}{dt} = \frac{C_{m}^a - C_{m}^a}{a \theta / b} + \frac{1.509 \mu_{AP}^a X_{AP}^a + 0.956 \mu_{AB}^a X_{AB}^a}{15.366 \mu_{AB}^a X_{AB}^a - 24.135 \mu_M X_M} - \frac{6.082 \mu_M X_M - \frac{N_A^n}{a V_t}}{15.366 \mu_{AB}^a X_{AB}^a - 24.135 \mu_M X_M}
\]

(36)

\[
\frac{dC_{m}^b}{dt} = \frac{C_{m}^b - C_{m}^b}{(1-a) \theta / b} + \frac{1.509 \mu_{AP}^b X_{AP}^b + 0.956 \mu_{AB}^b X_{AB}^b}{15.366 \mu_{AB}^b X_{AB}^b - 24.135 \mu_M X_M} - \frac{6.082 \mu_M X_M - \frac{N_A^n}{a V_t}}{15.366 \mu_{AB}^b X_{AB}^b - 24.135 \mu_M X_M}
\]

(37)
Where

\[ \theta = \frac{V_1}{Q_t} \quad \text{(39)} \]

\[ b = \frac{Q_1}{Q_t} \quad \text{(40)} \]

**Gas phase**

Carbon dioxide material balance

\[ \frac{dP}{dt} = \frac{RT}{V_g} \left( \frac{N_{A}^2}{44} - \frac{P}{P} \right) F_i \quad \text{(41)} \]

Methane material balance

\[ \frac{dP_m}{dt} = \frac{RT}{V_g} \left( \frac{N_{A}^2}{16} - \frac{P_m}{P} \right) F_i \quad \text{(42)} \]

Total material balance

\[ F_i = \frac{P}{P - P_w} \left( \frac{N_{A}^2}{16} + \frac{N_{A}^2}{44} \right) \quad \text{(43)} \]

In addition, to apply the pH inhibition effects to the kinetic rate expressions and calculation of the free ammonia and carbon dioxide in the liquid phases, the pH variations with time should be simulated. For this purpose the ionic charge balance equations for the two liquid phases, the dissociation rate equations and the expressions of the total concentration of the ionic components in the liquid phases are developed as a function of the pH. In general, the model is based on the following assumptions and considerations:

1- The uniformity assumptions were considered in the gas phase and the two liquid phases of \( \alpha \) and \( \beta \).
2- The Monod-type kinetics was applied for the microbial steps (acidogens, acetogens, and methanogens).
3- The non-competitive type inhibition model was considered in all the microbial steps as described in the previous sections.
4- The first order rate was applied to the bacterial decay reaction and the enzymatic hydrolytic steps.
5- The decay rate constants of the different bacterial groups were assumed to be 5% of their maximum growth rate.
6- The mass transfer to the gas phase was only done by the liquid phase of \( \alpha \).
7- Only the flow-through region was fed with the influent and the effluent streams.
8- The \( \beta \) liquid phase would exchange materials only with the \( \alpha \) liquid phase.

9- The system pressure and reaction \( \chi \) considered constant.
10- The energetic effects were not consi temperature was perfectly controlled.
11- At the operational temperature and \( \rho \) biogas was considered to be an ideal gas.
12- The biogas consisted of methane, \( \text{CO}_2 \) a.
13- The water vapor in the biogas stream saturation state.
14- The \( \text{CO}_2 \) present in the \( \alpha \) liquid phase thermodynamic equilibrium with the \( \text{CO}_2 \) phase and it obeyed Henry’s law as follows:

\[ \left[ \text{CO}_2 \right]_p = \frac{C_{\text{CO}_2}^p / 44}{1 + k_{a1} / \left[ \text{H}^+ \right] + k_{a1} k_{a2} / \left[ \text{H}^+ \right]^2} = \frac{I}{H} \]

15- The concentration of methane in the \( \beta \) phase was assumed to be negligible, i.e. immediately transferred to the gas phase due to solubility.
16- In the ionic charge balance (Equation algebraic sum of the concentrations of the compounds in the process, \( [\text{AC}^-] \), was ass constant during the anaerobic digestion process calculated from the initial pH of the system to and \( \beta \) liquid phases.

\[ \begin{align*}
[\text{H}^+] &+ [\text{OH}^-] &+ [\text{HCO}_3^-] &+ 2 [\text{CO}_3^{2-}] &+ [\text{Ac}^-] &+ [\text{Pr}^-] &+ [\text{Bar}^-] &+ [\text{A}^-] &+ [\text{C}^+] \\
17- The times for feeding, draining and mixing were assumed negligible compared to the le batch operation.

The assumptions made in developing the mostly based on our previous work [16] and the to the two-region mixing model was the Levenspiel [15].

**Computer simulations**

The computer simulations were conducted evaluate the effect of the incomplete mixing anaerobic digestion performance of the cat through the changes on the characteristics parameters \( a \) and \( b \) and also on the operating of the cyclic batch reactor. These simula performed by the numeric first order integrrelevant equations with a fixed time step by
program based on the Euler’s method. The program was written in a generalized form in Fortran, where a variable number of steps, feed composition, initial conditions and the operating conditions as well as the kinetic and the mixing parameters of the model could be specified through an input file.

The values of the applied mixing parameters were selected on the basis of the information found in the literature. The tracer studies conducted in the full-scale anaerobic digesters have revealed the well-mixed portions of the digester volumes ranging widely from 23% to 88% [11]. There is less evidence regarding the average interchange rates of the contents in the anaerobic digesters. The kinetic model parameters were taken directly from the literature and are given in Table 1. Also the physio-chemical model parameters at 35 °C are given in Table 2. The manure composition used in the model simulations is given in Table 3 and it was based on the cattle manure used in the experiments of Angelidaki [5].

The ionic charge balance equations should be iteratively solved for the pH calculation since the concentrations of the ionic compounds, in turn, are functions of the pH according to Equations 46 to 52 presented in the following:

\[ \text{NH}_4^+ = \frac{C_{am}/17}{1 + k_{a6}/[H^+]} \]

\[ \text{OH}^- = k_w/[H^+] \]

\[ \text{HCO}_3^- = \frac{C_e/44}{1+[H^+] / (k_{a1} + k_{a2} / [H^+]^2)} \]

\[ \text{CO}_3^{2-} = \frac{C_e/44}{1+[H^+] / (k_{a2} + [H^+]^2 / k_{a1} k_{a2})} \]

\[ \text{Ac}^- = \frac{C_{ac}/60}{1+[H^+] / k_{a3}} \]

\[ \text{Pr}^- = \frac{C_{pr}/74}{1+[H^+] / k_{a4}} \]

\[ \text{But}^- = \frac{C_{but}/88}{1+[H^+] / k_{a5}} \]

### Table 1: Kinetic parameters used in the model [6]

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<tr>
<th>Parameter</th>
<th>( K_w )</th>
<th>( K_{spr} )</th>
<th>( K_{byst} )</th>
<th>( K_{am} )</th>
<th>( K_{VFA} )</th>
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<th>( \mu_{maxAP} )</th>
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<th>( \mu_{maxM} )</th>
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<th>( m )</th>
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### Table 2: Physio-chemical parameters at 35 °C [17]

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<th>Parameter</th>
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<th>( K_{a1} )</th>
<th>( K_{a2} )</th>
<th>( K_{a3} )</th>
<th>( K_{a4} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit</td>
<td>molar</td>
<td>molar</td>
<td>molar</td>
<td>molar</td>
<td>molar</td>
</tr>
<tr>
<td>Value</td>
<td>2.065×10^{-4}</td>
<td>4.909×10^{-7}</td>
<td>5.623×10^{-11}</td>
<td>1.73×10^{-3}</td>
<td>1.445×10^{-1}</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( K_{w} )</th>
<th>( K_{a6} )</th>
<th>( H_\infty )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit</td>
<td>molar</td>
<td>molar</td>
<td>atm.l/mol</td>
</tr>
<tr>
<td>Value</td>
<td>1.445×10^{-5}</td>
<td>1.567×10^{-9}</td>
<td>37.67</td>
</tr>
</tbody>
</table>

[11]...

[5]...

[17]...
Table 3: Characteristics of the feed

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Insoluble substrate</td>
<td>30.4 (g/l)</td>
</tr>
<tr>
<td>Soluble substrate</td>
<td>5.4 (g/l)</td>
</tr>
<tr>
<td>Total acetate</td>
<td>4.5 (g/l)</td>
</tr>
<tr>
<td>Total propionate</td>
<td>2.3 (g/l)</td>
</tr>
<tr>
<td>Total butyrate</td>
<td>0.2 (g/l)</td>
</tr>
<tr>
<td>Total ammonia</td>
<td>3.0357 (gN\textsubscript{2}H\textsubscript{4}l)</td>
</tr>
<tr>
<td>Total carbon dioxide</td>
<td>0.0 (g/l)</td>
</tr>
<tr>
<td>Total microbial biomass</td>
<td>0.2 (g/l)</td>
</tr>
<tr>
<td>Fraction of acidogens</td>
<td>0.65</td>
</tr>
<tr>
<td>Fraction of propionate acetogens</td>
<td>0.025</td>
</tr>
<tr>
<td>Fraction of butyrate acetogens</td>
<td>0.025</td>
</tr>
<tr>
<td>Fraction of methanogens</td>
<td>0.30</td>
</tr>
<tr>
<td>pH</td>
<td>7.0</td>
</tr>
</tbody>
</table>

Of course we need to use an additional iterative procedure for the calculation of the pH of the α liquid phase, since according to Equation 44, the total concentration of the CO\textsubscript{2} in the α liquid phase is a function of the pH of this phase and the partial pressure of this gas in the gas phase. A trial-and-error procedure was used to calculate the pH and the different component concentrations of the α liquid phase.

RESULTS AND DISCUSSION

The effect of the mixing parameters a and b on the distribution of the component concentrations in a cyclic batch reactor with τ\textsubscript{c} = 1 day and HRT = 12 days are shown in Figures 2 and 3 for the insoluble substrate and propionate, respectively. In these figures the simulations results are compared for the two different sets of the mixing parameters a and b, of (0.3,0.5), and (0.3,5.0). As can be seen from Figure 2 for large values of the mixing parameter b, the value of the insoluble substrate concentration rapidly increases in the retention region and then shows the same pattern of insoluble substrate concentration change in the flow-through region. As the mixing parameter b is decreased at a constant value of the parameter a, the pattern of insoluble substrate change in both regions is similar but varies in quantity. In Figure 3, the same variations can be observed for the propionate concentration. As can be seen, the mixing parameter b has a significant effect on the distribution of components in the reactor so that with increasing this mixing parameter, the different component concentrations of the α and β liquid phases become entirely similar. The resulting homogeneous and non-uniform medium concentrations throughout the total reactor due to the high and low interchanging in tested ranges, shows that the two-region model is used to simulate anaerobic reactors with the non-ideal mixing conditions.

The effects of the mixing parameters a and b on the methane yield and the CO\textsubscript{2} composition in the α liquid phase are shown in Figures 4 and 5. As can be seen, the yield shows high fluctuations as function of the mixing parameters a and b equal to 0.3 and 0.3, respectively. However, these variations are less frequent for the other mixing group consi.

observation could be accounted for the concentration profile of the different components in the α methane yield was increased with increasing mixing parameter b from 0.5 to 5.0 so that the methane production for (a = 0.3 and b = 0.3) were equal to 165, and 5.1 respectively. Also the methane production was less frequent for the latter mixing parameters group with b of mixing in the case of the former parameters group. On the other hand, at the steady-state conditions, concentration in biogas increases with the mixing. Therefore, it is necessary to apply a mixing condition in the reactor that leads to a lower CO\textsubscript{2} percent with having lower biogas refinement cost.

The steady-state methane yield as a function of τ\textsubscript{c} (in days) is shown in Figure 6 for the batch reactors with HRTs of 12, 18, 24, and 24 days, respectively. The mixing parameters a and simulations were chosen 0.3 and 0.5, respectively. As can be seen, there is an optimum τ\textsubscript{c} corresponding to maximum methane yield for all three cases. The value increases with the increase in HRT of 12, 18, and 24 days, respectively. This means that for systems a ratio 3/12, 4/18, and 5/24 of reactor replaced with entering new raw materials the reactors. Also, the ratio of τ\textsubscript{c}/(a,HRT), the flow-through region volume that is replaced for these three cases is equal to 0.83, 0.7,
Figure 2. Dynamic simulation of the anaerobic digestion of the cattle manure in a daily cyclic batch reactor with HRT=12 days and the different degrees of mixing for the prediction of the methane yield.

Figure 3. Dynamic simulation of the anaerobic digestion of the cattle manure in a daily cyclic batch reactor with HRT=12 days and the different degrees of mixing for the prediction of the propionate concentration.

Figure 4. Dynamic simulation of the anaerobic digestion of the cattle manure in a daily cyclic batch reactor with HRT=12 days and the different degrees of mixing for the prediction of the methane yield.

Figure 5. Dynamic simulation of the anaerobic digestion of the cattle manure in a daily cyclic batch reactor with HRT=12 days and the different degrees of mixing for the prediction of the CO$_2$ mole percent in biogas.
respectively. It is seen that the methane yield at the optimum conditions for the system with the ratio of $\tau/\text{(a.HRT)}$ equal to 0.69 is higher than two other systems. Therefore, it can be concluded that there is an optimum ratio of $\tau/\text{(a.HRT)}$ for cyclic-batch reactors in the range of 0.6-0.8 that gives the maximum methane yield.

The effect of the hydraulic retention time on the methane yield was evaluated for two different reactors including a daily fed non-ideally mixed cyclic batch reactor ($a=0.3$ and $b=0.5 t=1\text{ day}$) and an approximately non-ideally mixed continuous flow reactor ($a=0.3$ and $b=0.5 t=0.1\text{ day}$). The steady-state results are shown in Figure 7. As is seen, there is an HRT critical range for both reactors. For an HRT smaller than this critical range due to the cell wash-out, the accumulation of the VFAs and a sharp decline in the pH, the anaerobic digestion process becomes unstable and a sour reactor is created. This results in a sharp decrease in the methane production. In contrast, for the HRT values greater than the critical range, the change in methane yield vs HRT depends on the type of feeding which may increase or decrease with a slow slope. The unexpected decrease of the methane yield with increase in HRT in the case of cyclic-batch regime can be explained by the change in the ratio $\tau/\text{(a.HRT)}$. This value decreases from 0.22 to 0.06 by increasing HRT from 15 to 50 days. Therefore, the methane yield decreases as the value of $\tau/\text{(a.HRT)}$ goes beyond its optimum range. As can be seen from Figure 7, the performance of the continuous flow reactor in terms of methane production is better than the cyclic batch reactor.

The effect of mixing parameter $a$, on the steady-state methane yield at conditions that the mixing parameter $b$ is equal to 0.5 is illustrated in Figure 8 for the three different systems. In the first system, a cyclic-batch reactor with a $t_i$ of 2 days and an HRT of 24 days, and in the second and third systems, an approximately continuous flow reactor ($t_i=0.1$) with an HRT of 24 and 12 days, have been simulated. As expected theoretically, in the continuous flow regime, the methane yield increases with the increase in the mixing parameter $a$ (corresponding to a decreased dead zone volume in the reactor). Also, it is seen that the effect of mixing parameter $a$ on the degree of variations of the methane yield in continuous flow reactors decreases with the increase in HRT from 12 to 24 days because the organic materials find further time for mixing and dis the reactor. Therefore, the effect of the degree on the methane yield becomes less imp. unexpected decrease in the methane yield increase in the mixing parameter $a$ for reactors can be explained, as mentioned ear change in the value of $\tau/\text{(a.HRT)}$. When parameter $a$ increases from 0.3 to 0.6, the $\tau/\text{(a.HRT)}$ decreases from 0.28 to 0.14 being optimum value of 0.69.

The effect of mixing parameter $b$ on the methane yield at conditions that the mixing parameter $a$ equal to 0.3 is illustrated in Figure 9 for different systems. In the first system, a reactor with a $t_i$ of 2 days and an HRT of 1 ratio of $\tau/\text{(a.HRT)}$ being equal to 0.55 and in and third systems, an approximately contin. reactor ($t_i=0.1$) with an HRT of 12 and 24 been simulated. As is seen, the methane yield with the increase in the mixing parameter $b$ cases. In continuous flow reactor, it is observe the effect of mixing parameter $b$ on the : increase in the methane yield reduces with an the HRT from 12 to 24 days. In other words, the degree of mixing becomes less imp. increased retention time of the materials in the.

To evaluate the applicability of the preliminary simulations were compared to experimental runs [19] measuring methan various organic loading rate for an HRT of determine the most appropriate set of mio parameters. The operating conditions of their are given in Table 4. In Figure 10, the best f the experimental data is shown. The estim HRT/b mixing parameters of the reactor are 4.0, respectively. Steady-state methane y HRT of 6 days were then predicted for differ loading rates using the mixing parameters Predicted values are compared with experime Figure 11. As can be seen, a good agreement between the predicted values and the experime

**CONCLUSIONS**

The performance of anaerobic digest is dependent on the degree of mixing achieve reactors. However, it is difficult and expensive
Fig. 6: Effect of the time period of feeding on steady-state methane yield at different HRTs.

Fig. 7: Effect of the hydraulic retention time on the steady-state methane yield.

Fig. 8: Effect of the relative volume region (a) on the steady-state methane yield at different HRTs.

Fig. 9: Effect of the internal exchange flow rate to the feed flow rate ratio (b) on the steady-state methane yield at different HRTs.
Table 4: Operating parameters of the reactor

<table>
<thead>
<tr>
<th>Operational parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total volume</td>
<td>15 liters</td>
</tr>
<tr>
<td>Temperature</td>
<td>35 °C</td>
</tr>
<tr>
<td>pH</td>
<td>Controlled at 6.7-7.3</td>
</tr>
<tr>
<td>Mixing of reactor</td>
<td>1 minute every hour</td>
</tr>
<tr>
<td>VS loading rate for HRT=3 days</td>
<td>2.3, 4.68 gVS/l/day</td>
</tr>
<tr>
<td>VS loading rate for HRT=6 days</td>
<td>2.3, 4 gVS/l/day</td>
</tr>
</tbody>
</table>

A complete mixing in full scale reactors. Therefore, the real reactors are often operated under non-ideal mixing conditions. The performance of the anaerobic digestion processes can be predicted by an appropriate mathematical model. Unfortunately, in most available models, the simplified assumptions of the complete mixing conditions are used, and consequently their applicability appears to be limited. The simulation results showed that the two-region mixing model, despite its simplicity, can be used for modeling of the non-ideally mixed reactors with different degrees of mixing. Analysis of the impact of the characteristic mixing parameters on the anaerobic digestion of the cattle manure showed that the reactor performance is a complex function of both mixing parameters. With \( m_r \) as depicted by the two-region model, the degradation of the estimated parameters, the residence time distribution of components in the reactor, cost and kinetic rates of the anaerobic digestion are influenced. Also, it is observed that for feeding as well as the mixing parameters, the distribution of components in the reactor, cost and kinetic rates of the anaerobic digestion are influenced. The obtained results show that the reactor improved when the period of feeding app.

Continuous flow regime. The obtained results show the importance of mixing consideration when simulating anaerobic digestion processes. The two-region mixing model can be used for the simulation of the anaerobic process whose mixing patterns resemble such a mixing regime. The characteristic mixing parameters of the mixing model can be calculated from the tracer-response curves and by fitting the data to the model by using the least-square method.

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Dr. M. Khalagi Asadi, the head of the center.

Nomenclature

\begin{align*}
  a & \quad \text{mixing parameter} \\
  b & \quad \text{mixing parameter} \\
  C & \quad \text{liquid concentration (g/l)} \\
  [CO_2] & \quad \text{free CO}_2\text{ in liquid concentration (mol/l)} \\
  d & \quad \text{day} \\
  f_{pr} & \quad \text{mass conversion factor of propionate to} \\
 & \quad \quad \text{acetate}=0.8108 \\
  f_{but} & \quad \text{mass conversion factor of butyrate to} \\
 & \quad \quad \text{acetate}=0.6818 \\
  F_t & \quad \text{biogas transfer rate (mol/d)} \\
  F_{pH} & \quad \text{pH function} \\
  H & \quad \text{Henry’s constant (atm.l/mol)} \\
  HRT & \quad \text{hydraulic retention time} \\
  K & \quad \text{hydrolysis rate constant (d$^{-1}$)} \\
  K_0 & \quad \text{non-inhibited hydrolysis rate constant} \\
 & \quad (d$^{-1}$) \\
  K_1 & \quad \text{first dissociation constant of carbonic} \\
 & \quad \text{acid} \\
  K_2 & \quad \text{second dissociation constant of carbonic} \\
 & \quad \text{acid} \\
  K_3 & \quad \text{dissociation constant of acetic acid} \\
  K_4 & \quad \text{dissociation constant of propionic acid} \\
  K_5 & \quad \text{dissociation constant of butyric acid} \\
  K_6 & \quad \text{dissociation constant of water} \\
  K_7 & \quad \text{bacterial decay rate constant (d$^{-1}$)} \\
  K_i & \quad \text{inhibition constant (g/l)} \\
  K_m & \quad \text{Monod saturation constant (g/l)} \\
  m & \quad \text{feed constant used in Equation 1} \\
  n & \quad \text{feed constant used in Equation 1} \\
  N & \quad \text{gas transfer rate (g/d)} \\
  [NH_3] & \quad \text{free NH}_3\text{ in liquid concentration (mol/l)} \\
  P & \quad \text{pressure (atm)} \\
  pK_a & \quad \text{constant used in Equation 16} \\
  pK_i & \quad \text{constant used in Equation 16} \\
  Q & \quad \text{volumetric flow rate (l/d)} \\
  r_d & \quad \text{bacterial decay rate (g/l.d)} \\
  r_h & \quad \text{hydrolysis reaction rate (g/l.d)} \\
  r_s & \quad \text{substrate consumption rate (g/l.d)} \\
  r_g & \quad \text{bacterial growth rate (g/l.d)} \\
  R & \quad \text{gas constant (atm.l/mol.K)} \\
  R & \quad \text{recycle flow ratio defined in Equation 18} \\
  t & \quad \text{time (d)} \\
  T & \quad \text{temperature (°C)} \\
  V_g & \quad \text{gas volume of reactor (l)} \\
  V_i & \quad \text{liquid volume of reactor (l)} \\
  VFA & \quad \text{volatile fatty acids} \\
  X & \quad \text{microorganisms concentration} \\
  Y_c & \quad \text{yield factor used in Equation 1} \\
  Y_{b,m} & \quad \text{yield factor of biomass} \\
 & \quad \text{Equation 10} \\
  A & \quad \text{flow-through region} \\
  \beta & \quad \text{retention region} \\
  \theta & \quad \text{hydraulic retention time (d)} \\
  \mu & \quad \text{specific growth rate (d$^{-1}$)} \\
  \mu_{max} & \quad \text{maximum specific growth rate} \\
\end{align*}

Subscripts

\begin{align*}
  ac & \quad \text{acetate} \\
  am & \quad \text{ammonia} \\
  A & \quad \text{cidogenic bacteria} \\
  AB & \quad \text{butyric degrading acetogenic} \\
 & \quad \text{g} \\
  AP & \quad \text{propionate degrading acetogenic} \\
 & \quad \text{g} \\
  but & \quad \text{butyrate} \\
  c & \quad \text{carbon dioxide} \\
  e & \quad \text{exchange between zones} \\
  f & \quad \text{feed} \\
  i & \quad \text{component i} \\
  i & \quad \text{initial conditions} \\
  is & \quad \text{insoluble substrate} \\
  m & \quad \text{methane} \\
  M & \quad \text{methanogenic bacteria} \\
  pr & \quad \text{propionate} \\
  r & \quad \text{effluent flow} \\
  s & \quad \text{soluble substrate} \\
  w & \quad \text{water} \\
\end{align*}

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REFERENCES


