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Modeling of Anaerobic Digestion of Complex Substrat

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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 equilibriu 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 o anaerobic digestion of cattle manure under different operating conditions. The model is compare with experimental data and good correlations are obtained.*

KEY WORDS: *Anaerobic digestion, Dynamic modeling, Two-region mixing model, Cyclic-batc 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 process are very time-consuming, labor int

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1021-9986/03/2/61 12/$/3.20

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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 acetic 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 lov the total volume [11].

Farm animals are ideal for the applica anaerobic digestion to convert cattle manure t energy generation and fertilizer producti manure is a complex substrate containing and the insoluble organic matter such as poly lipids, proteins, and the volatile fatty cyclic batch operation is one of the most c methods for the animal waste treatment. M previous researches on the dairy wastewate 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 comple such as cattle manure in a cyclic batch reacto the following criteria:

1- Making a model capable of consider important factors involved in the anaerobic pro

2- Reducing the dimensions of the mo needed numerical calculations could be carrie 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 i Angelidaki [16] kinetic model for the anaerob of the cattle manure. The kinetic model distin different processes: the hydrolysis of the substrate by the extracellular enzymes, the c of the soluble substrates by the acidogenic b consumption of the volatile fatty acids (VF formation of acetate by the propionate a 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 i the acetogenic steps, the free ammonia inhib methanogenic step and the pH inhibition

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biological steps. 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 $(C_6H_{10}O_5)_s$ and $(C_6H_{10}O_5.nNH_3)_{is}$ respectively. The cell mass is represented by the empirical formula $C_5H_7O_2N$. 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:

(1)

$$(C_6H_{10}O_5.nNH_3)_{is} \rightarrow y_e(C_6H_{10}O_5)_s + (1-y_e)(C_6H_{10}O_5.mNH_3)_{in} + (n-(1-y_e)m)NH_3$$

(2)

$$(C_6H_{10}O_5)_s + 0.1115\ NH_3 \rightarrow 0.1115\ C_5H_7NO_2 + 0.744\ CH_3COOH + 0.5\ CH_3CH_2COOH + 0.4409\ CH_3(CH_2)_2COOH + 0.6909\ CO_2 + 0.0254H_2O$$

(3)

$$CH_3CH_2COOH + 0.06198\ NH_3 + 0.314\ H_2O \rightarrow 0.06198C_5H_7NO_2 + 0.9345CH_3COOH + 0.6604CH_4 + 0.1607CO_2$$

(4)

$$CH_3(CH_2)_2COOH + 0.0653NH_3 + 0.5543CO_2 + 0.5543H_2O \rightarrow 0.0653C_5H_7NO_2 + 1.8909CH_3COOH + 0.4452CH_4$$

(5)

$$CH_3COOH + 0.022NH_3 \rightarrow 0.022C_5H_7NO_2 + 0.945CH_4 + 0.945CO_2 + 0.066H_2O$$

In Reaction 1, y_e is the enzymatic efficiency or yield factor and the subscript *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:

$$r_h = k\ C_{is}$$

$$k = k_0 \frac{k_{i,VFA}}{\sum VFA + k_{i,VFA}}$$

$$\sum VFA = C_{ac} + f_{pr}\ C_{pr} + f_{but}\ C_{but}$$

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

$$r_d = k_d\ X$$

$$r_s = Y_{s/x}\ \mu\ X$$

$$r_x = \mu\ X$$

The specific growth rates are as follow:

$$\mu_A = \mu_{maxA} \frac{C_s}{K_{ss} + C_s}$$

$$\mu_{AP} = \mu_{maxAP} \frac{C_{pr}}{K_{spr} + C_{pr}} \times \frac{K_{ipr}}{K_{ipr} + C_{ac}} \times F_{AP}(pH)$$

$$\mu_{AB} = \mu_{maxAB} \frac{C_{but}}{K_{sbut} + C_{but}} \times \frac{K_{ibut}}{K_{ibut} + C_{ac}} F_{AB}(pH)$$

$$\mu_M = \mu_{maxM} \frac{C_{ac}}{K_{sac} + C_{ac}} \times \frac{K_{iam}}{K_{iam} + C_{am}} \times F_M(pH)$$

$$F(pH) = \frac{1 + 2 \times 10^{0.5(pK_l - pK_h)}}{1 + 10^{(pH - pK_h)} + 10^{(pK_l - pH)}}$$

Liquid mixing model

A simple mixing model referred to as the model was used in combination with the kinet conceptual representation of the two-regi model is illustrated in Figure 1. The mi assumes that the reactor volume is split into t the flow-through (α) region and the retention Both regions are assumed to be perfectly mi transfer of the materials between the zones is l retention region has the features of the behavic

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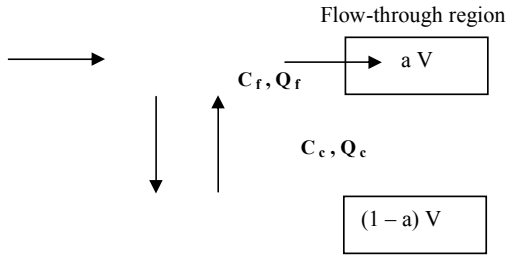

Fig. 1: Two-region mixing model

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)V_l . 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 cycle of the batch operation, in four steps. In t the reactor is operated batch-wise for a tir known initial conditions. In this step the m equations in the liquid phases of α and β for volume cyclic batch reactor have been desc next section. In the second step, after a reactio a volume V_r of the reaction mixture is drain reactor. In the third step the reactor is fille original volume with the feed. Finally tl mixture is mixed in the last step and the initia for the new cycle are obtained.

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

$$t_r = \frac{V_r}{Q_f}$$

$$R = \frac{a\,V_l - V_r}{V_r}$$

Therefore, the initial conditions for any ne described by the relation:

$$C_i = \frac{C_f + R\,C_r}{R+1}$$

Also the relation between the interval of feedi the hydraulic retention time (HRT) is as follow

$$HRT = \frac{V_l}{Q_f} = \frac{t_r\,(R+1)}{a}$$

The value of t_r can thus be chosen from (0,HRT), hence R $\in$ (0,∞) respectively. Th $R \to \infty$ corresponds to the continuous flow op R=0 denotes repeated the batch-wise operation

Mathematical model

The mass balances on the α and β liquid the gas phase of the cyclic batch reactor und conditions for different components in the me reactor led to a set of ordinary differentia which must be simultaneously solved by kr conditions. These components include th substrate, the soluble substrate, acetate, butyrate, ammonia, carbon dioxide, me acidogenic bacteria, the propionate degrading

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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)

$$\frac{dX_i^{\alpha}}{dt} = \frac{X_i^{\beta} - X_i^{\alpha}}{a\,\theta / b} + \left(\mu_i^{\alpha} - b_i\right)X_i^{\alpha} \qquad (21)$$

$$\frac{dX_i^{\beta}}{dt} = \frac{X_i^{\alpha} - X_i^{\beta}}{(1-a)\,\theta / b} + \left(\mu_i^{\beta} - b_i\right)X_i^{\beta} \qquad (22)$$

Insoluble substrate material balance

$$\frac{dC_{is}^{\alpha}}{dt} = \frac{C_{is}^{\beta} - C_{is}^{\alpha}}{a\,\theta/b} - k^{\alpha}\,C_{is}^{\alpha} \qquad (23)$$

$$\frac{dC_{is}^{\beta}}{dt} = \frac{C_{is}^{\alpha} - C_{is}^{\beta\alpha}}{(1-a)\,\theta/b} - k^{\beta}\,C_{is}^{\beta} \qquad (24)$$

Soluble substrate material balance

$$\frac{dC_s^{\alpha}}{dt} = \frac{C_s^{\beta} - C_s^{\alpha}}{a\,\theta/b} + \frac{162\,y_e}{162+17n}k^{\alpha}\,C_{is}^{\alpha} - 12.858\,\mu_A^{\alpha}\,X_A^{\alpha} \qquad (25)$$

$$\frac{dC_s^{\beta}}{dt} = \frac{C_s^{\alpha} - C_s^{\beta}}{(1-a)\,\theta/b} + \frac{162\,y_e}{162+17n}k^{\beta}\,C_{is}^{\beta} - 12.858\,\mu_A^{\beta}\,X_A^{\beta} \qquad (26)$$

Acetic acid material balance

$$\frac{dC_{ac}^{\alpha}}{dt} = \frac{C_{ac}^{\alpha} - C_{ac}^{\alpha}}{a\theta/b} + 3.54\mu_A^{\alpha}X_A^{\alpha} + 8.006\mu_{AP}^{\alpha}X_{AP}^{\alpha} + 15.366\mu_{AB}^{\alpha}X_{AB}^{\alpha} - 24.135\mu_M^{\alpha}X_M^{\alpha} \qquad (27)$$

$$\frac{dC_{ac}^{\beta}}{dt} = \frac{C_{ac}^{\alpha} - C_{ac}^{\beta}}{(1-a)\theta/b} + 3.54\mu_A^{\beta}X_A^{\beta} + 8.006\mu_{AP}^{\beta}X_{AP}^{\beta} + 15.366\mu_{AB}^{\beta}X_{AB}^{\beta} - 24.13\tilde{n}\ {}^{\beta}_{M}X_M^{\beta} \qquad (28)$$

Propionic acid material balance

$$\frac{dC_{pc}^{\alpha}}{dt} = \frac{C_{pc}^{\beta} - C_{pc}^{\alpha}}{a\theta/b} + 2.937\mu_A^{\alpha}X_A^{\alpha} - 10.566\mu_A^{\alpha}$$

$$\frac{dC_{pc}^{\beta}}{dt} = \frac{C_{pc}^{\alpha} - C_{pc}^{\beta}}{(1-a)\theta/b} + 2.937\mu_A^{\beta}X_A^{\beta} - 10.566\mu_{AP}^{\beta}$$

Butyric acid material balance

$$\frac{dC_{but}^{\alpha}}{dt} = \frac{C_{but}^{\beta} - C_{but}^{\alpha}}{a\theta/b} + 3.079\,\mu_A^{\alpha}X_A^{\alpha} - 11.919\mu_B^{\alpha}$$

$$\frac{dC_{but}^{\beta}}{dt} = \frac{C_{but}^{\alpha} - C_{but}^{\beta}}{(1-a)\theta/b} + 3.079\mu_A^{\beta}X_A^{\beta} - 11.919\mu_B^{\beta}$$

Ammonia material balance

$$\frac{dC_{am}^{\alpha}}{dt} = \frac{C_{am}^{\beta} - C_{am}^{\alpha}}{a\theta/b} + \frac{17(n - m(1-y_e))}{162+17n}k^{\alpha}\,C_{is}^{\alpha} - 0.15(\mu_A^{\alpha}X_A^{\alpha} + \mu_{AP}^{\alpha}X_{AP}^{\alpha} + \mu_{AB}^{\alpha}X_{AB}^{\alpha} + \mu_M^{\alpha}X_M^{\alpha})$$

$$\frac{dC_{am}^{\beta}}{dt} = \frac{C_{am}^{\alpha} - C_{am}^{\beta}}{(1-a)\theta/b} + \frac{17(n - m(1-y_e))}{162+17n}k^{\beta}\,C_{is}^{\beta} - 0.15(\mu_A^{\beta}X_A^{\beta} + \mu_{AP}^{\beta}X_{AP}^{\beta} + \mu_{AB}^{\beta}X_{AB}^{\beta} + \mu_M^{\beta}X_M^{\beta}$$

Carbon dioxide material balance

$$\frac{dC_c^{\alpha}}{dt} = \frac{C_c^{\beta} - C_c^{\alpha}}{a\,\theta/b} + 2.413\,\mu_A^{\alpha}\,X_A^{\alpha} + 1.01\,\mu_{AP}^{\alpha}\,X - 3.303\,\mu_{AB}^{\alpha}\,X_{AB}^{\alpha} + 16.726\,\mu_M^{\alpha}\,X_M^{\alpha} - \frac{N_c^{\alpha}}{a\,V_l}$$

$$\frac{dC_c^{\beta}}{dt} = \frac{C_c^{\alpha} - C_c^{\beta}}{(1-a)\,\theta/b} + 2.413\,\mu_A^{\beta}\,X_A^{\beta} + 1.01\,\mu_{AP}^{\beta} - 3.303\,\mu_{AB}^{\beta}\,X_{AB}^{\beta} + 16.726\,\mu_M^{\beta}\,X_M^{\beta}$$

methane material balance

$$\frac{C_m^{\beta}}{a\,\theta/b} + 1.509\,\mu_{AP}^{\alpha}\,X_{AP}^{\alpha} + 0.956\,\mu_{AB}^{\alpha}\,X_{AB}^{\alpha} + 6.082\,\mu_M^{\alpha}\,X_M^{\alpha} - \frac{N_m^{\alpha}}{a\,V_l} = 0$$

$$\frac{dC_m^{\beta}}{dt} = -\frac{C_m^{\beta}}{(1-a)\theta/b} + 1.509\mu_{AP}^{\beta}\,X_{AP}^{\beta} + 0.956\mu_{AB}^{\beta}\,X_{AB}^{\beta} + 6.082\mu_M^{\beta}\,X_M^{\beta}$$

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Where

$$\theta = \frac{V_l}{Q_f} \quad (39)$$

$$b = \frac{Q_e}{Q_f} \quad (40)$$

Gas phase

Carbon dioxide material balance

$$\frac{dP_c}{dt} = \frac{R\,T}{V_g}\left(\frac{N_c^{\alpha}}{44} - \frac{P_c}{P}F_t\right) \quad (41)$$

Methane material balance

$$\frac{dP_m}{dt} = \frac{R\,T}{V_g}\left(\frac{N_m^{\alpha}}{16} - \frac{P_m}{P}F_t\right) \quad (42)$$

Total material balance

$$F_t = \frac{P}{P - P_w}\left(\frac{N_m^{\alpha}}{16} + \frac{N_c^{\alpha}}{44}\right) \quad (43)$$

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 α and β.

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 α.

7- Only the flow-through region was fed with the influent and the effluent streams.

8- The β liquid phase would exchange materials only with the α liquid phase.

9- The system pressure and reaction vo considered constant.

10- The energetic effects were not cons temperature was perfectly controlled.

11- At the operational temperature and p biogas was considered to be an ideal gas.

12- the biogas consisted of methane, CO_2 a

13- The water vapor in the biogas stream saturation state.

14- The CO_2 present in the α liquid ph thermodynamic equilibrium with the CO_2 phase and it obeyed Henry's law as follows:

$$[CO_2]^{\alpha} = \frac{C_c^{\alpha}/44}{1 + k_{a1}/[H^+] + k_{a1}k_{a2}/[H^+]^2} = \frac{}{}$$

15- The concentration of methane in th phase was assumed to be negligible, i. immediately transferred to the gas phase due solubility.

16- In the ionic charge balance (Equati algebraic sum of the concentrations of the compounds in the process, $[A^-C^+]$, was assu constant during the anaerobic digestion proce calculated from the initial pH of the system fo and β liquid phases.

$$[H^+] + [NH_4^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] +$$

$$[Ac^-] + [Pr^-] + [But^-] + [A^-C^+]$$

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 t to the two-region mixing model was t Levenspiel [15].

Computer simulations

The computer simulations were conducted evaluate the effect of the incomplete mixin anaerobic digestion performance of the ca through the changes on the characteris parameters a and b and also on the operating of the cyclic batch reactor. These simula performed by the numeric first order integra relevant equations with a fixed time step by

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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:

The ionic concentrations of different comp
function of its total concentration and pH:

$$\left[NH_4^+\right]=\frac{C_{am}/17}{1+k_{a6}/\left[H^+\right]}$$

$$\left[OH^-\right]=k_w/\left[H^+\right]$$

$$\left[HCO_3^-\right]=\frac{C_c/44}{1+\left[H^+\right]/k_{a1}+k_{a2}/\left[H^+\right]}$$

$$\left[CO_3^{2-}\right]=\frac{C_c/44}{1+\left[H^+\right]/k_{a2}+\left[H^+\right]^2/k_{a1}k_{a2}}$$

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

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

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

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

Parameter	K_{ss}	K_{spr}	K_{sbut}	K_{sac}	K_{iVFA}	K_{ipr}	K_{ibut}	K_{iam}	K
Unit	g/l	g/l	g/l	g/l	g/l	g/l	g/l	g/l	d
Value	0.5	0.259	0.176	0.12	0.33	0.96	0.72	0.26	1.
Parameter	μ_{maxA}	μ_{maxAP}	μ_{maxAB}	μ_{maxM}	y_e	n	m	pK_{hAP}	pK
Unit	d^{-1}	d^{-1}	d^{-1}	d^{-1}	---	---	---	---	--
Value	5.0	0.54	0.68	0.6	0.55	0.454	0.34	8.5	6.
Parameter	pK_{hAB}	pK_{lAB}	pK_{hM}	pK_{lM}					
Unit	---	---	---	---					
Value	8.5	6.0	8.5	6.0					

Table 2: Physio-chemical parameters at 35 °C [17]

Parameter	K_w	K_{a1}	K_{a2}	K_{a3}	K_{a4}
Unit	molar	molar	molar	molar	molar
Value	2.065×10^{-14}	4.909×10^{-7}	5.623×10^{-11}	1.73×10^{-5}	$1.445\times1($
Parameter	K_{a5}	K_{a6}	H_c		
Unit	molar	molar	atm.l/mol		
Value	1.445×10^{-5}	1.567×10^{-9}	37.67 [18]		

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Table 3: Characteristics of the feed

Characteristic	Value
Insoluble substrate	30.4 (g/l)
Soluble substrate	5.4 (g/l)
Total acetate	4.5 (g/l)
Total propionate	2.3 (g/l)
Total butyrate	0.2 (g/l)
Total ammonia	3.0357 (gNH_3/l)
Total carbon dioxide	0.0 (g/l)
Total microbial biomass	0.2 (g/l)
Fraction of acidogens	0.65
Fraction of propionate acetogens	0.025
Fraction of butyrate acetogens	0.025
Fraction of methanogens	0.30
pH	7.0

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_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 t_r = 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 concentrat the α and β liquid phases become entirely sim other. The resulting homogeneous and non-hc medium concentrations throughout the total the reactor due to the high and low interchang in tested ranges, shows that the two-region m used to simulate anaerobic reactors with the ic non-ideal mixing conditions.

The effects of the mixing parameters a a methane yield and the CO_2 composition in the shown in Figures 4 and 5. As can be seen, t yield shows high fluctuations as function of t the mixing parameters a and b equal to 0 respectively. However these variations are s less frequent for the other mixing group consi observation could be accounted for the cc profile of the different components in the r methane yield increased with increasing parameter b from 0.5 to 5.0 so that the metha the steady-state conditions for (a = 0.3 and b (a = 0.3 and b = 5.0) were equal to 165, and respectively. Also the methane production s for the latter mixing parameters group with b of mixing than in the case of the form parameters group. On the other hand, as Figure5, 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 r production with lower CO_2 percent whic having lower biogas refinery cost.

The steady-state methane yield as a f feeding period (t_r) is shown in Figure 6 for tl batch reactors with HRTs of 12, 18, and respectively. The mixing parameters a and simulations were chosen 0.3 and 0.5, respectiv be seen, there is an optimum t_r correspon maximum methane yield for all three cases. Tl t_r value increases with the increase in HRT HRTs of 12, 18, and 24 days, the optimum and 5 days, respectively. This means that for systems a ratio 3/12, 4/18, and 5/24 of reacto replaced with entering new raw materials wl the reactors. Also, the ratio of t_r/(a.HRT), the flow-through region volume that is replaced for these three cases are equal to 0.83, 0.7

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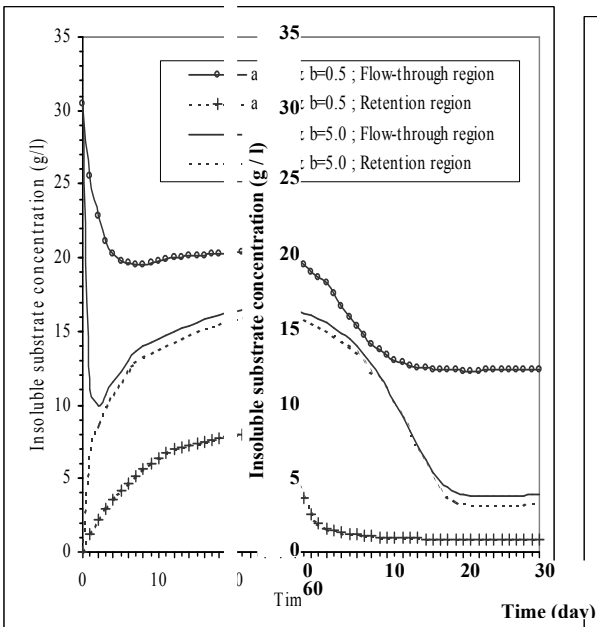

Figure 2. Dynamic
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Fig. 2: Dynamic simulation of the ana cattle manure in a daily cyclic batch days and the different degrees of mixin the insoluble substrate concentration.

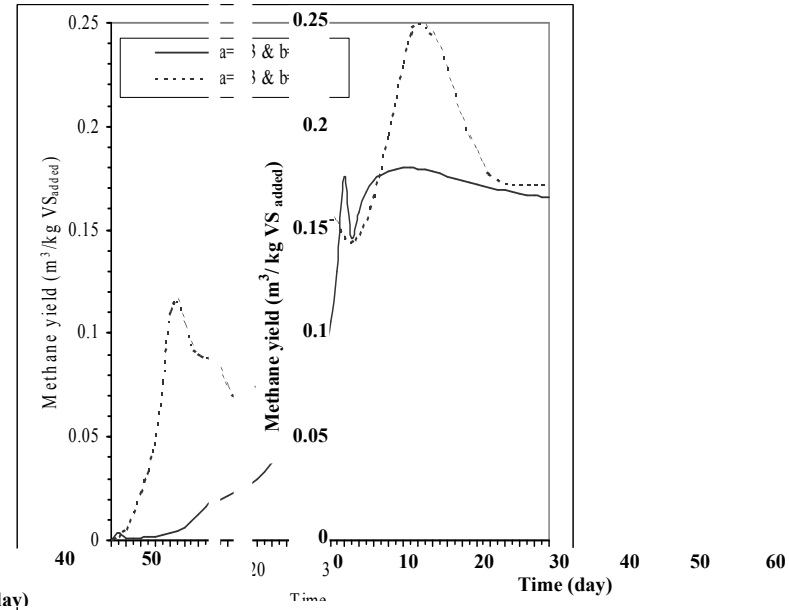

Figure 4. Dynamic
of the cattle manur
HRT=12 days and t

Fig. 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.

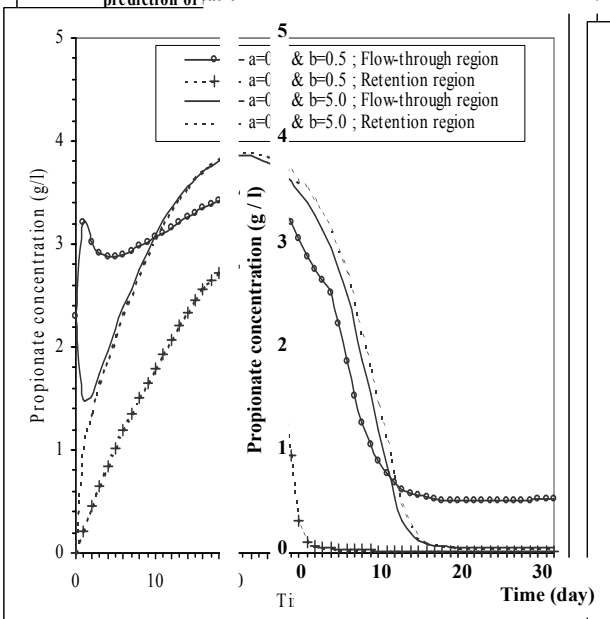

Figure 3. Dynami
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Fig. 3: Dynamic simulation of the an cattle manure in a daily cyclic batch re and the different degrees of mixing fo propionate concentration.

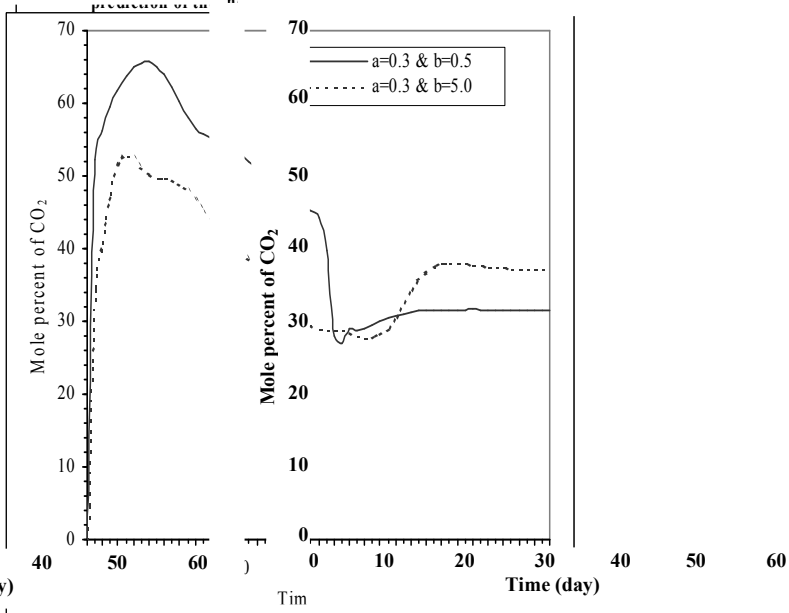

Figure 5. Dynamic
of the cattle manu
prediction of the C

Fig. 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.

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respectively. It is seen that the methane yield at the optimum conditions for the system with the ratio of t_r/(a.HRT) equal to 0.69 is higher than two other systems. Therefore, it can be concluded that there is an optimum ratio of t_r/(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=0.3and b =0.5,t $_r$=1 day) and an approximately non-ideally mixed continuous flow reactor (a=0.3 and b=0.5,t $_r$=0.1day). 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 t_r/(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 t_r/(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_r of 2 days and an HRT of 24 days, and in the second and third systems, an approximately continuous flow reactor (t_r = 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 degre on the methane yield becomes less imp unexpected decrease in the methane yiel increase in the mixing parameter a for reactor can be explained, as mentioned ea change in the value of t_r/(a.HRT). When parameter a increases from 0.3 to 0.6, th t_r/(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 pa equal to 0.3 is illustrated in Figure 9 fo different systems. In the first system, a reactor with a t_r of 2 days and an HRT of 1 ratio of t_r/(a.HRT) being equal to 0.55) and in and third systems, an approximately conti reactor (t_r = 0.1) with an HRT of 12 and 24 been simulated. As is seen, the methane yie 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, t the degree of mixing becomes less imp increased retention time of the materials in the

To evaluate the applicability of t preliminary simulations were compared to experimental runs [19] measuring methan various organic loading rate for an HRT o determine the most appropriate set of mi 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 and 4.0, respectively. Steady-state methane y HRT of 6 days were then predicted for diffe 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 digesti is dependent on the degree of mixing achie reactors. However, it is difficult and expensive

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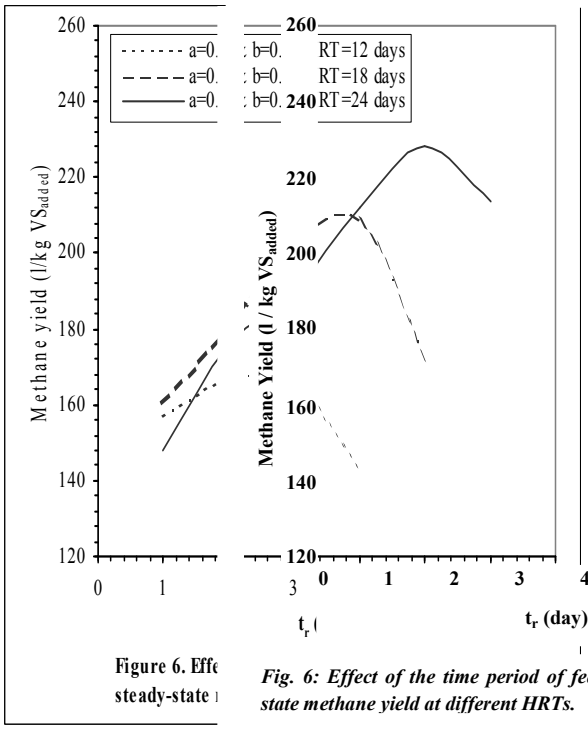

Figure 6. Effe
steady-state

Fig. 6: Effect of the time period of feedin state methane yield at different HRTs.

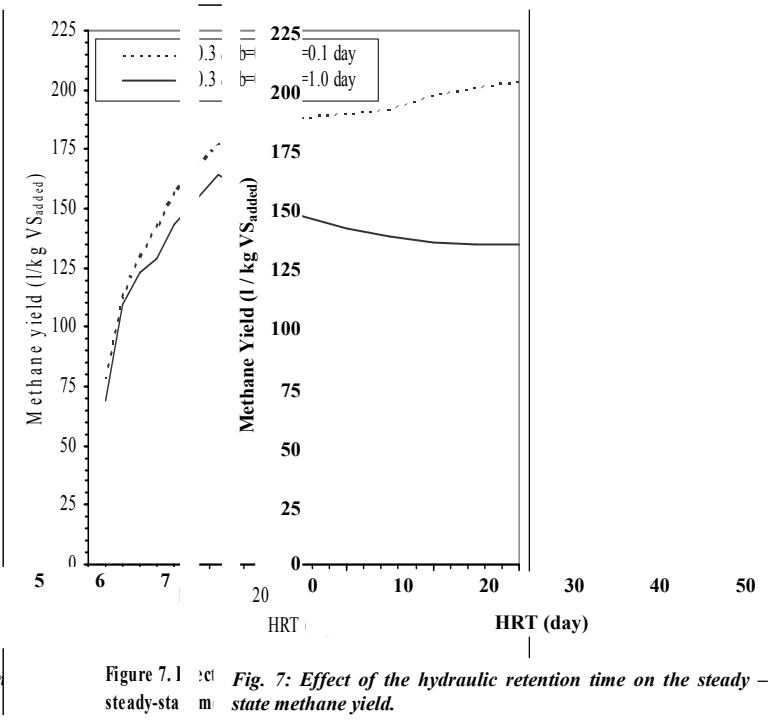

Figure 7. I
steady-sta

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

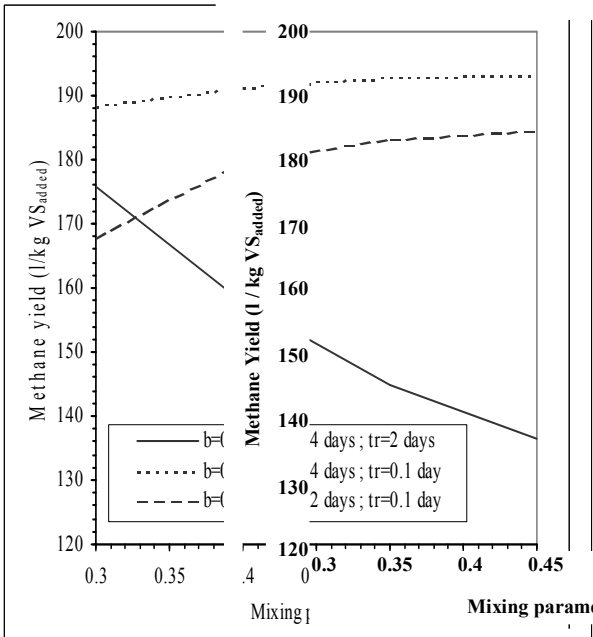

Figure 8. Effec
through region
different HRT's

Fig. 8: Effect of the relative volume region (a) on the steady – state meth HRts.

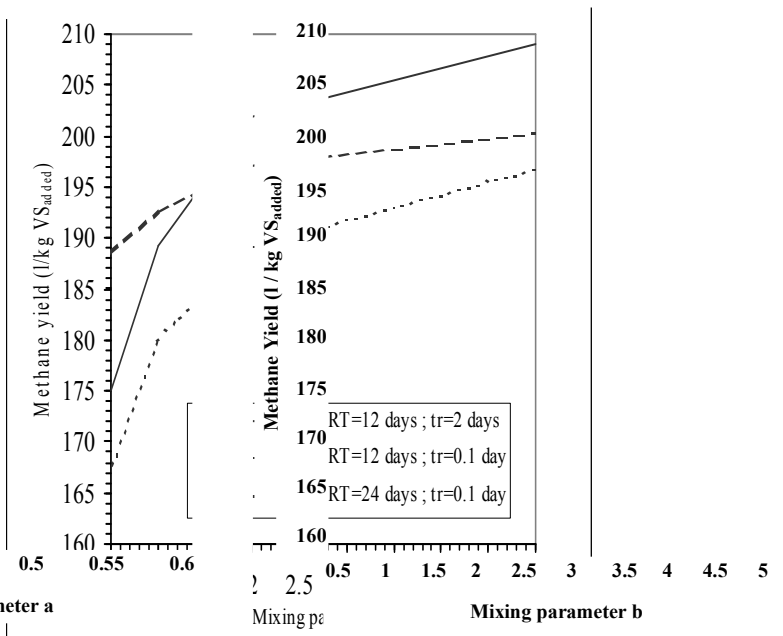

Figure 9. Effe
the feed flow
yield at differ

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.

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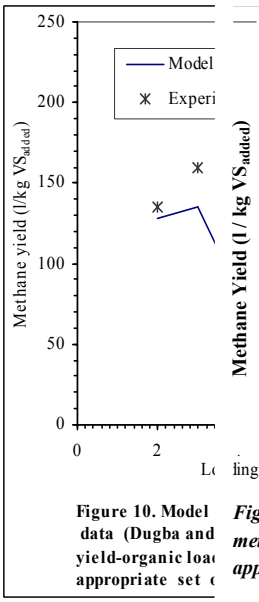

Figure 10. Model data (Dugba and yield-organic loa appropriate set

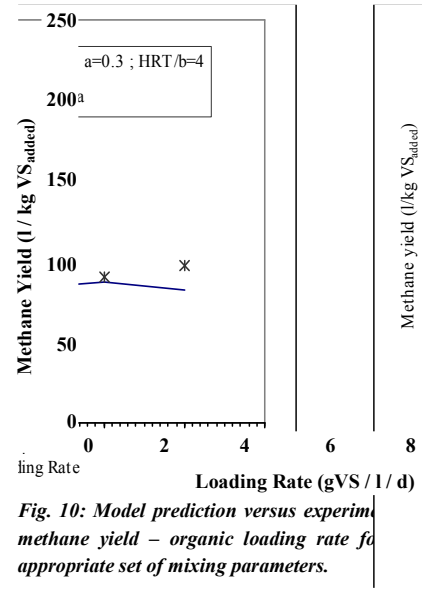

Fig. 10: Model prediction versus experim methane yield – organic loading rate fo appropriate set of mixing parameters.

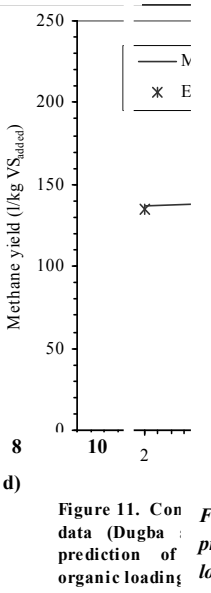

Figure 11. Con data (Dugba prediction of organic loading

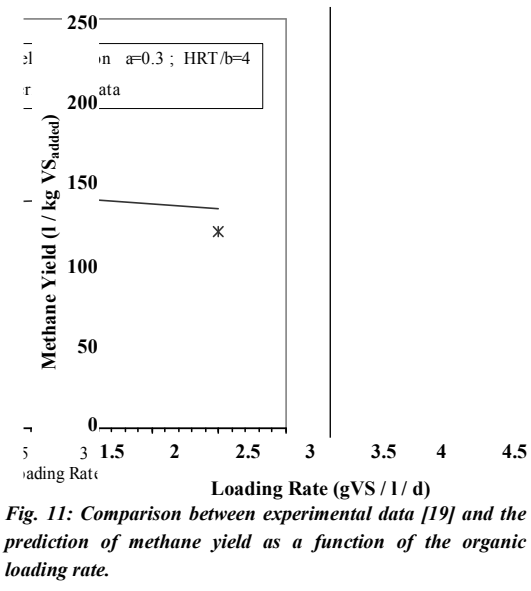

Fig. 11: Comparison between experimental data [19] and the prediction of methane yield as a function of the organic loading rate.

Table 4: Operating parameters of the reactor

Operational parameters	Values
Total volume	15 liters
Temperature	35 °C
pH	Controlled at 6.7-7.3
Mixing of reactor	1 minute every hour
VS loading rate for HRT=3 days	2,3,4,6,8 gVS/l/day
VS loading rate for HRT=6 days	2,3,4 gVS/l/day

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 ma as depicted by the two-region model, the degr mixing affects the residence time distributic distribution of components in the reactor. Co the kinetic rates of the anaerobic digesti are influenced. Also it is observed that of feeding as well as the mixing paramete distribution of components in the reactor. there is an optimum ratio of t_r/(a.HRT) for reactors resulting in the maximum methane simulation results shows that the reactor per improved when the period of feeding appr continuous flow regime. The obtained result importance of mixing consideration when sin anaerobic digestion process and consec designing the reactor. The two-region mixing be used for the simulation of the anaerob whose mixing patterns resemble such a mix The characteristic mixing parameters of the mixing model can be calculated from the e tracer-response curves and by fitting the e data to the model by using the least-square me

Acknowledgment

The authors would like to express their a

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for the financial support provided by Center of Renewable Energies for Research and Application and Dr. M. Khalagi Asadi, the head of the center.

Nomenclature

a	mixing parameter
b	mixing parameter
C	liquid concentration (g/l)
$[CO_2]$	free CO_2 in liquid concentration (mol/l)
d	day
f_{pr}	mass conversion factor of propionate to acetate=0.8108
f_{but}	mass conversion factor of butyrate to acetate=0.6818
F_t	biogas transfer rate (mol/d)
F(pH)	pH function
H	Henry's constant (atm.l/mol)
HRT	hydraulic retention time
K	hydrolysis rate constant (d^{-1})
K_0	non-inhibited hydrolysis rate constant (d^{-1})
K_{a1}	first dissociation constant of carbonic acid
K_{a2}	second dissociation constant of carbonic acid
K_{a3}	dissociation constant of acetic acid
K_{a4}	dissociation constant of propionic acid
K_{a5}	dissociation constant of butyric acid
K_w	dissociation constant of water
K_d	bacterial decay rate constant (d^{-1})
K_i	inhibition constant (g/l)
K_s	Monod saturation constant (g/l)
m	feed constant used in Equation 1
n	feed constant used in Equation 1
N	gas transfer rate (g/d)
$[NH_3]$	free NH_3 in liquid concentration (mol/l)
P	pressure (atm)
pK_h	constant used in Equation 16
pK_l	constant used in Equation 16
Q	volumetric flow rate (l/d)
r_d	bacterial decay rate (g/l.d)
r_h	hydrolysis reaction rate (g/l.d)
r_s	substrate consumption rate (g/l.d)
r_x	bacterial growth rate (g/l.d)
R	gas constant (atm.l/mol.K)
R	recycle flow ratio defined in Equation 18
t	time (d)
T	temperature (˚K)
V_g	gas volume of reactor (l)
V_l	liquid volume of reactor (l)
VFA	volatile fatty acids
X	microorganisms concentration
y_e	yield factor used in Equation
$Y_{s/x}$	yield factor of biomass Equation 10
A	flow-through region
β	retention region
θ	hydraulic retention time (d)
μ	specific growth rate (d^{-1})
μ_{max}	maximum specific growth rat

Subscripts

ac	acetate
am	ammonia
A	cidogenic bacteria
AB	butyric degrading acetogenic
AP	propionate degrading acetoge
but	butyrate
c	carbon dioxide
e	exchange between zones
f	feed
i	component i
i	initial conditions
is	insoluble substrate
m	methane
M	methanogenic bacteria
pr	propionate
r	effluent flow
s	soluble substrate
w	water

Received: 21st October 2001 ; Accepted: 25th

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