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DYNAMIC MODELLING OF ANAEROBIC DIGESTION

R. MOLETTA*, D. VERRIER and G. ALBAGNAC
Station de Technologie Alimentaire, Institut National de la Recherche Agronomique, 369 rue J. Guesde, 59650 Villeneuve D'Ascq, France

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Abstract—The anaerobic digestion model presented here considers a two step process. First, acidogenic bacteria convert glucose into acetate then methanogenic bacteria convert this acid into methane and carbon dioxide. The biomass and metabolite production rates are described by distinct relations. Therefore, there is not a direct relationship between the growth and the energy production related to metabolite formation. The inhibitory effects of the unionized acid concentration on growth rate of both bacterial populations and the methane production from acetate were considered separately. The model was tested in batch cultures with two types of organic loads, i.e. pea bleaching wastewaters and a synthetic substrate containing sucrose and organic acid. The model allowed to simulate satisfactorily the methane production under very different operational conditions.

Key words—anaerobic digestion, modelization, wastewater treatment, acidogenesis, methanogenesis, inhibition, volatile fatty acids, maintenance energy

NOMENCLATURE

$\frac{dA}{dt}$ = variation rate of total acetic acid concentration ($kg\,m^{-3}\,day^{-1}$)
$\frac{dCH_4}{dt}$ = methane production rate ($kg\,m^{-3}\,day^{-1}$)
$\frac{dS}{dt}$ = variation rate of the concentration of acidogenic phase substrate (glucose) ($kg\,m^{-3}\,day^{-1}$)
$\frac{dX}{dt}$ = variation rate of microorganism concentration ($kg\,m^{-3}\,day^{-1}$)
A = total acetic acid concentration ($kg\,m^{-3}$)
AH = unionized acetic concentration ($kg\,m^{-3}$)
D = dilution rate (day^{-1})
H^+ = hydrogen ion concentration ($mol/10^{-3}\,m^3$)
K = constant
S = glucose equivalent concentration ($kg\,m^{-3}$)
SUB = acidogenic or methanogenic substrate concentration ($kg\,m^{-3}$)
V = specific production rate [$kg\,CH_4\,m^{-3}$ (digester) kg^{-1} (methanogenic bacteria)]
X = microorganism concentration ($kg\,m^{-3}$)
Y = yield ($kg\,kg^{-1}$)
μ = specific growth rate (day^{-1})
a = relative to acetic acid
d = relative to microorganism death
e = relative to acid dissociation
m = relative to methane
max = maximum
n = relative to maintenance energy
p = produced by microorganisms
s = relative to glucose
x = relative to microorganisms
0 = relative to influent
1 = relative to acidogenic phase
2 = relative to methanogenic phase.

*Present address: Station d'Oenologie et de Technologie Végétale, Institut National de la Recherche Agronomique, Boulevard Général de Gaulle, 11104 Narbonne Cedex, France.

INTRODUCTION

Anaerobic digestion of organic matters includes three biological steps performed by specific bacterial populations. Carbon and energy flows resulting from anaerobic digestion of domestic sludges have been described by McCarty (1981) and are summarized in Fig. 1.

Due to the complexity of the biological process it is difficult to develop a mathematical model reflecting the biological reality. Therefore, the models described in the literature are simplifications.

One of the first models developed (Andrews, 1969, 1971; Buhr and Andrews, 1977) took into account only the degradation rate of acetate to describe the overall rate of organic matter digestion. Hill and Barth (1977) included in their model the hydrolysis and acidogenesis steps to reflect the effect of organic overload and thus volatile fatty acid (VFA) accumulation on the methanization rate. These authors applied this model to the digestion of cattle manure. In this model unionized VFA inhibit the growth of both populations, while ammonia (unionized) only inhibit the methanogenic bacteria.

Sinechal *et al.* (1979) proposed a switch in the metabolism of acidogenic bacteria, when the residual acetate concentration was higher than $0.1\,g\,l^{-1}$. Beyond this concentration they considered that the acidogens produced a VFA mixture and that an inhibition constant (especially propionate) had to be introduced in the model.

Mosey (1982) supposed that the $NADH/NAD^+$ ratio regulates the synthesis of various VFA. His model considers the metabolic formation and degradation pathways of individual VFA.

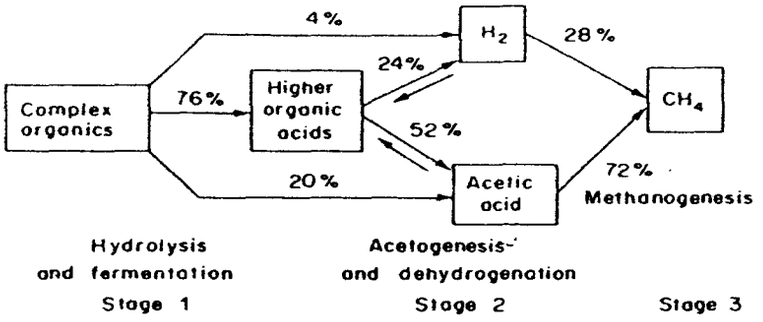

Fig. 1. The three stages of methane fermentation and the percentage flow of the energy content of complex organic materials through each stage into methane as represented by the chemical oxygen demand (McCarty, 1981).

DESCRIPTION OF THE MODEL

The model presented here simulates the mesophilic anaerobic digestion of easily fermentable substrates in a completely stirred tank reactor.

The two steps considered are the substrate (glucose) conversion into acetate and then the production of methane and carbon dioxide from this acid.

In this model, we separated the expressions of growth and metabolite production rates in order to represent the metabolite production by resting cells. The latter parameter may be related to the substrate consumption for maintenance energy production (Moletta and Albagnac, 1984). The introduction of the interstitial pH of the sludge as a parameter allows the calculation of the unionized VFA concentration. The inhibitory effect of acids on growth of acidogenic and methanogenic bacteria and on methane production rate were considered.

Obviously, this simplified scheme does not include acetogenesis reactions from individual VFA and thus the inhibition of propionate degradation rate by hydrogen and acetate (Kaspar and Wuhrman, 1978).

MATHEMATICAL DEVELOPMENT

Microbial growth

Mass balances. The variations of acidogenis and methanogenis biomass were expressed by the following relations:

$$\left(\frac{dX}{dt}\right) = D(X_0 - X) - K_d X + \mu X. \qquad (1)$$

Expression of rates. The specific growth rates of acidogenic and methanogenic bacteria were calculated from the equation used by Andrews (1969) and Hill and Barth (1977). In this relation the inhibition by VFA is expressed as follows:

$$\mu = \mu_{max} \frac{1}{1 + \frac{K}{(SUB)} + \frac{(AH)}{K_i}}. \qquad (2)$$

The substrate (SUB) is expressed as glucose or acetate equivalent respectively during the steps of acidogenesis and methanogenesis.

Substrate consumption

Mass balances. Mass balances during acidification and methanization were expressed by the following relation:

Acidogenesis:

$$\left(\frac{dS}{dt}\right) = D(S_0 - S) - \left(\frac{dS}{dt}\right)_{x_1} - \left(\frac{dS}{dt}\right)_e. \qquad (3)$$

Methanogenesis:

$$\left(\frac{dA}{dt}\right) = D(A_0 - A) + \left(\frac{dA}{dt}\right)_p - \left(\frac{dA}{dt}\right)_{x_2} - \left(\frac{dA}{dt}\right)_m. \qquad (4)$$

Expression of rates

Acidogenesis:

Conversion rates of substrate (glucose) to acidogenic biomass and acetic acid are expressed as follows:

$$\left(\frac{dS}{dt}\right)_{x_1} = \frac{\mu_1 X_1}{Y_{x_1 s}} \qquad (5)$$

$$\left(\frac{dS}{dt}\right)_e = K_{sx_1} \cdot X_1 + K_{mx_1} \cdot X_1 \frac{S}{K_m + S}. \qquad (6)$$

The latter equation reflects the energy conservation during substrate catabolism. It includes two terms corresponding to an energy consumption for growth and for maintenance. So the rate of acetate production is:

$$\left(\frac{dA}{dt}\right)_p = Y_{ac_1} \left(\frac{dS}{dt}\right)_e \qquad (7)$$

Methanogenesis:

The rates of acetate consumption for methanogenic biomass production $(dA/dt)_{x_2}$ and decarboxylation into methane and carbon dioxide, $(dA/dt)_m$, were respectively:

$$\left(\frac{dA}{dt}\right)_{x_2} = \frac{\mu_2 X_2}{Y_{x_2 ac}} \qquad (8)$$

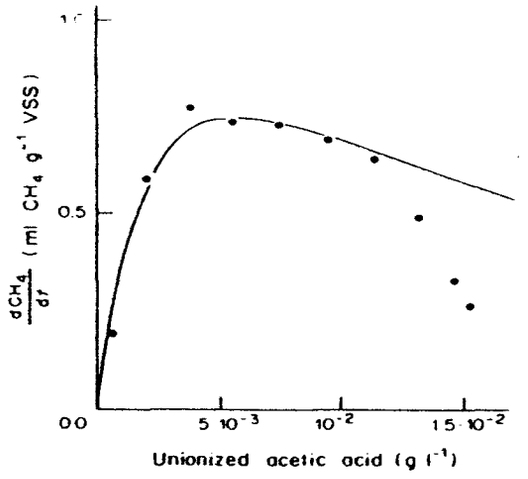

Fig. 2. Simulation of the variation of the methane production rate with acetic acid concentration by expression (12). The values for calculation were: $K'_m = K'_{ms} = 5.72\ 10^{-3}$ g l^{-1}; $V_m^{max} = 29.4$ ml CH_4 g^{-1} VSS.

and

$$\left(\frac{dA}{dt}\right)_m = \left(\frac{dCH_4}{dt}\right)\frac{1}{Y_{ma}}. \quad (9)$$

The unionized acid concentration is calculated from the total acetate acid dissociation concentration, as follows:

$$(AH) = \frac{(A)}{1 + \frac{K_e}{(H^+)}}. \quad (10)$$

Methane production

The rate of methane production is described by an equation derived from that of Yarovenko and Nakhmanovich (1973), i.e.

$$\left(\frac{dCH_4}{dt}\right) = V_m^{max} \cdot X_2 \cdot \frac{AH}{AH + K_m} \cdot \frac{K_{im}}{K_{im} + AH}. \quad (11)$$

An example of modelling by this equation is given in Fig. 2. The batch cultures of 50 mM acetate were run with industrial anaerobic sludges adapted to vegetable canning effluents. After an adaptation period characterized by a rapid increase in the methane production rate, the model simulates properly the effect of acetate concentration.

SCHEME OF THE MATHEMATICAL STEPS DURING TIME INCREMENT

Figure 3 shows the different steps of the calculation.

DETERMINATION OF MODEL PARAMETERS

Model constants were obtained either by simulation, by stoichiometric reactions, or from the literature. Table 1 reports these values and their signification. The methods used for determining them are described below.

Determination of the maximum growth yields: Y_{x_1s}, Y_{x_2a}

These yield values were determined assuming the formula $C_5H_7O_2N$ as microorganism composition. It was known that these elements represent 92% of the total dry cell weight. Thus, the equations of substrate conversion (glucose or acetic acid) into microorganisms are respectively:

Acidogens:

$$C_6H_{12}O_6 + 1.2\ NH_3 \rightarrow 1.2\ C_5H_7O_2N + 3.6\ H_2O \quad (12)$$

Methanogens:

$$C_2H_4O_2 + 0.4\ NH_3 \rightarrow 0.4\ C_5H_7O_2N + 1.2\ H_2O. \quad (13)$$

Equations (12) and (13) give identical results for Y_{x_1s} and Y_{x_2a}: 0.82 g g^{-1}.

Growth energy yield of acidogenic microorganisms K_{sx_1}

The value of K_{sx_1} is the amount of substrate transformed into product to supply the energy required for production of 1 g of dry cell. We considered that a glucose molecule yielded 3 acetates and produced simultaneously 6 ATP. The maximum energy yield for cell production was chosen equal to 32 g of cells per mol of ATP (Stouthamer, 1976). Accordingly, 0.93 g of glucose are required to produce the energy used for the synthesis of 1 g of cells.

Maintenance energy yield of acidogenic microorganisms K_{mx_1}

For the acidogenic microorganisms, the energy maintenance coefficient was chosen equal to 0.0169 mol ATP g^{-1} cell h^{-1} (Moletta and Albagnac, 1984). Considering that when one acetate is produced, 2 ATP are synthetized and that one glucose produces 3 acetates, the amount of glucose consumed for maintenance energy corresponds to 12.1 g g^{-1} cell per day.

Decay constants K_{d_1} and K_{d_2}

The decay constants were chosen equal to zero for the following reasons: first, the batch experiments were done within a very short time and the effect of microorganism death could be considered as negligible; second, in our opinion, this constant should be very low. Indeed, anaerobic digesters start rapidly after several month shut-down, which could not be compatible with K_d values close to 0.02 day $^{-1}$. Hill *et al.* (1983) assumed that the microbial death was a function of VFA concentration.

Maximum yield for glucose conversion to acid (Y_{as})

The stoichiometric yield of glucose conversion to acetic acid is 1 g acetic per g of glucose. In fact, acidogenic substrate is not only glucose and acid produced is not only acetic acid, this involves that the

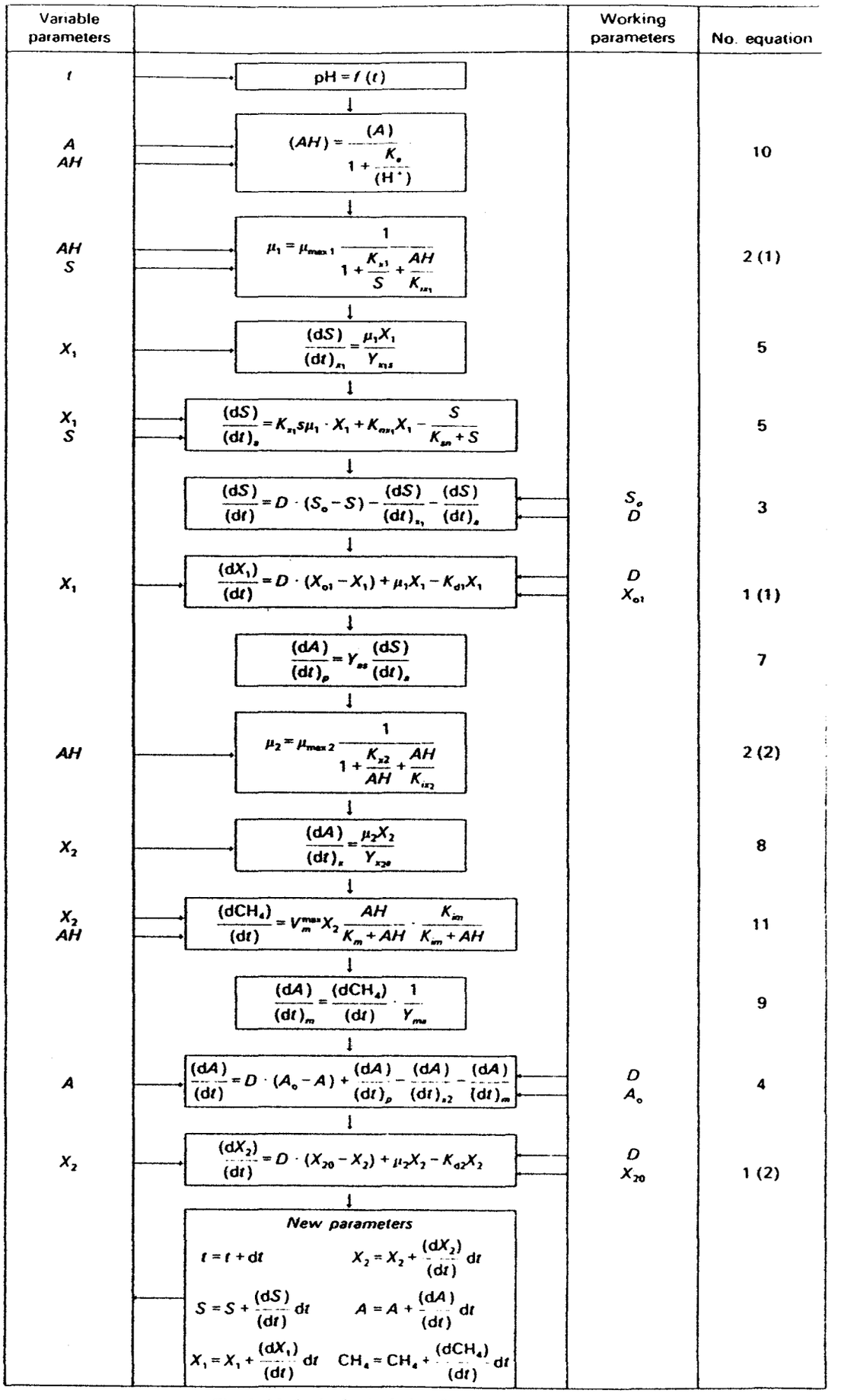

Fig. 3. Method of calculation for one time increment.

Table 1. Signification and values of parameters used in the model

Parameters	Values unit	Signification	Equation
K_a	$1.728\ 10^{-5}$	Dissociation constant for acetic acid at 35°C	10
K_{im}	$0.059\ g\ l^{-1}$	Inhibition constant of acetic acid (expressed as unionized acid) on methane production	11
K_{i1}	$0.02\ g\ l^{-1}$	Inhibition constant of acidogenic bacteria growth (expressed as unionized acetic acid)	2(1)
K_{i2}	$0.04\ g\ l^{-1}$	Inhibition constant of methanogenic bacteria growth (expressed as unionized acetic acid)	2(2)
K_m	$0.0208\ g\ l^{-1}$	Saturation constant of methane production (expressed as unionized acetic acid)	11
K_{s1}	$12.1\ g\ g^{-1}\ l^{-1}$	Quantity of substrate transformed to acetic acid which gives the energy used for maintenance per 1 g of acidogenic microorganism per day	6
K_m	$0.26\ g\ l^{-1}$	Saturation constant in the expression of glucose consumption for maintenance energy	6
K_{s2}	$0.93\ g\ l^{-1}$	Quantity of substrate (glucose) converted to acid which gives the energy used for the production of 1 g of acidogenic microorganisms	6
K_{s1}	$0.26\ g\ l^{-1}$	Saturation constant in the expression of acidogenic bacteria growth	2(1)
K_{s2}	$0.003\ g\ l^{-1}$	Saturation constant for the methanogenic bacteria growth (expressed as unionized acetic acid)	2(2)
V_m^{max}	$0.5\ g\ g^{-1}\ day^{-1}$	Maximal production rate of methane (expressed in g) per 1 g of methanogenic bacteria per day	11
Y_{as}	$0.83\ g\ g^{-1}$	Maximum yield of glucose conversion to acid	7
Y_{ma}	$0.26\ g\ g^{-1}$	Methane production yield from acetic acid	9
Y_{s1}	$0.82\ g\ g^{-1}$	Maximum growth yield of acidogenic bacteria on glucose	5
Y_{s2a}	$0.82\ g\ g^{-1}$	Maximum growth yield of methanogenic bacteria on acetic acid	8
μ_{max1}	$1.5\ day^{-1}$	Maximum specific growth rate of acidogenic bacteria	2(1)
μ_{max2}	$0.138\ day^{-1}$	Maximum specific growth rate of methanogenic bacteria	2(1)

maximum yield should be lower. We found that a value of 0.83 g equivalent acetate g^{-1} equivalent glucose is a good approximation for Y_{as}.

EXPRESSION OF COMPLEX EFFLUENTS

The composition of complex effluents was expressed as glucose or acetic acid equivalent.

Organic acid and alcohol concentrations were determined and expressed as acetate equivalent according to the stoichiometric equations reported in Table 2. The value obtained represents the substrate (acetic acid) directly fed to methanogens. The COD corresponding to alcohol and organic acids was subtracted from total COD of the wastewater and the result was converted into glucose equivalent taking into account that 1 g of glucose has a COD of 1.066 g O_2.

MODEL VERIFICATION

To test our model, batch assays of anaerobic digestion of pea bleaching effluents and of sucrose–organic acid mixture were performed at 35°C. Experimental methane productions were compared with simulation results.

Experimental procedure

Cultures were made in batches in 500 ml flask reactors with agitation. The sludges used were collected from an industrial digester treating canning waste waters (Verrier *et al.*, 1983). Table 3 indicates the characteristics of these sludges.

The pea bleaching effluent was mixed with the anaerobic sludges in the following proportions: 12, 20 and 50%.

Table 2. Expression of the conversion of intermediary metabolite acetate equivalent

			Theoretical yields
Dihydrogen	$4H_2 + 2HCO_3^- + H^+$	$\rightarrow CH_3-COO^- + 4H_2O$	1/4 mol acetate mol H_2^{-1}
Propionate	$CH_3-CH_2-COO^- + 3H_2O$	$\rightarrow HCO_3^- + CH_3-COO^- + H^+ + 3H_2$	1.75 mol acetate mol propionate^{-1}
Butyrate	$CH_3-CH_2-CH_2-COO^- + 2H_2O$	$\rightarrow 2CH_3-COO^- + H^+ + 2H_2$	2.5 mol acetate mol butyrate^{-1}
Valerate	$CH_3-CH_2-CH_2-CH_2-COO^- + 2H_2O$	$\rightarrow CH_3COO^- + CH_3-CH_2-COO^- + H^+ + 2H_2$	3.25 mol acetate mol valerate^{-1}
Lactate	$3CH_3-CHOH-COO^-$	$\rightarrow 2CH_3-CH_2-COO^- + CH_3-COO^- + HCO_3^- + H^+$	1.5 mol acetate mol lactate^{-1}
Ethanol	$CH_3-CH_2OH + H_2O$	$\rightarrow CH_3-COO^- + H^+ + 2H_2$	1.5 mol acetate mol ethanol^{-1}

Table 3. Physicochemical characteristics of sludge and wastewater

	Soluble COD (g l^{-1})	Total COD (g l^{-1})	S/S* (g l^{-1})	VSS† (g l^{-1})	pH
Sludge	0.392	10.87	12.8	8.6	7
Wastewater	16.7	21.5	4.6	4.5	3.93

*SS = suspended solid.
†VSS = volatile suspended solids.

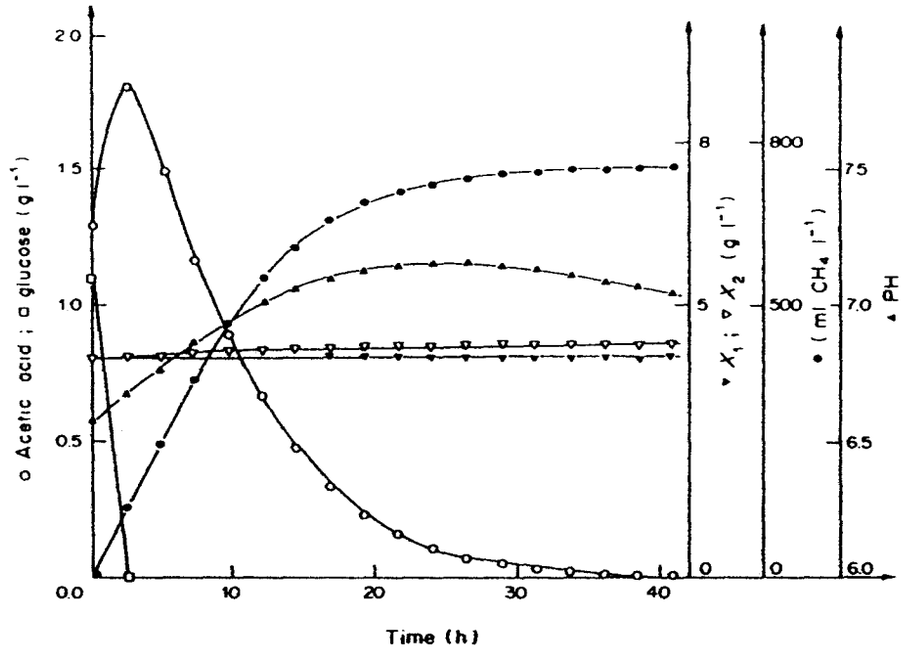

Fig. 4. Simulation of digester response to pea bleaching wastewater treatment by batch reaction (calculated for 12% wastewater and 88% sludge).

The total volume (sludges and wastewaters) was 250 ml. The effluent was at pH 3.4 and it mainly contained lactic acid (7.45 g l^{-1}). Table 3 indicates the COD and suspended solids; they are expressed as acetic acid and glucose equivalent which are 11.18 and 8.6 g l^{-1} respectively.

Two other assays of anaerobic digestion were made in the same conditions. In the first one, 1.5 g l^{-1} of sucrose and 0.75 g l^{-1} of acetic acid were added to 250 ml of sludges and in the second, the load was 4 g l^{-1} of sucrose and 1 g l^{-1} of acetic acid.

All these experiments were run in parallel. The initial gas phase was N_2/CO_2 (85/15). The gas flow rates were measured by gas meters (Moletta and Albagnac, 1982) and the composition was determined by gas chromatography according to Van Huystens (1967) with a thermal conductivity detector. Corrections necessary to express the volume of methane produced per liter of sludge were made. The volume of methane produced was expressed at 35 C and 1 ATM. Samples of 3 ml were collected for pH determination. pH variations with time were expressed as a polynomial equation. This is necessary for the expression of unionized acid concentrations used in the present model.

Results

Anaerobic digestion of pea bleaching wastewaters. Figure 4 gives an example of simulation applied to a mixture including 12% wastewater and 88% sludge. Figures 5, 6 and 7 compare the simulation and experimental results of methane production from pea bleaching wastewaters.

The experimental pH values and methane production rates for the different assays were rather different. Our model allowed us to simulate properly methane productions.

Anaerobic digestion of a synthetic substrate. Like in previous experiments, anaerobic digestion of the sucrose-acetic acid mixture was simulated satisfactorily on batch cultures (Figs 8 and 9), though large pH variations were observed during the digestion of 4 g l^{-1} of sucrose and 1 g l^{-1} of acetic acid.

CONCLUSION

The present model considers two steps, i.e. acidogenesis corresponding to the conversion of easily fermentable sugar to acetic acid and methanogenesis corresponding to the decarboxylation of this acid into methane and carbon dioxide. The metabolite

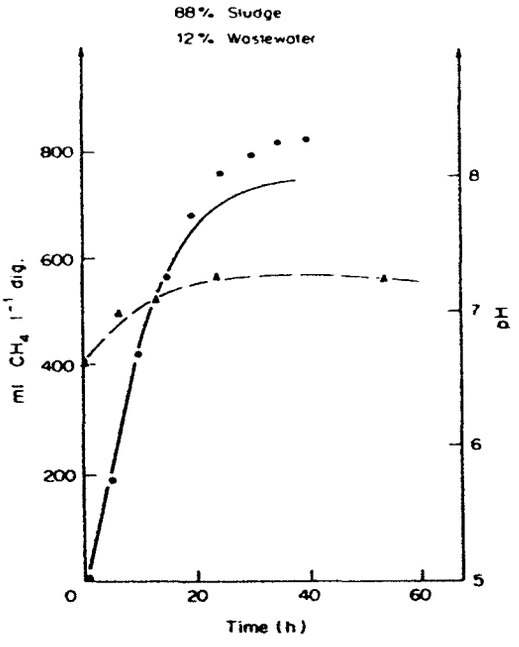

Fig. 5

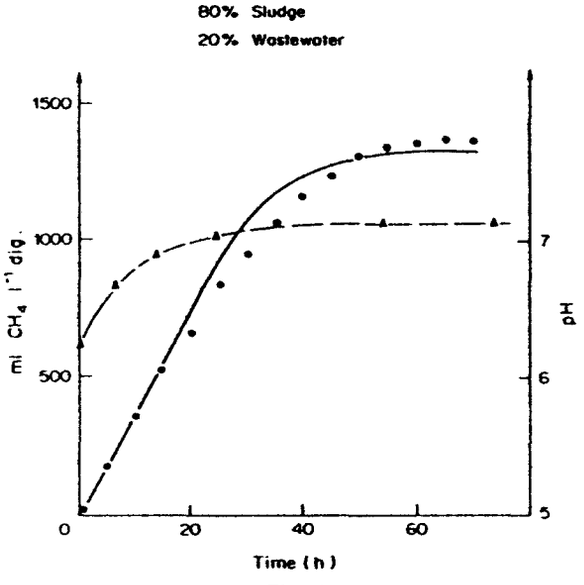

Fig. 6

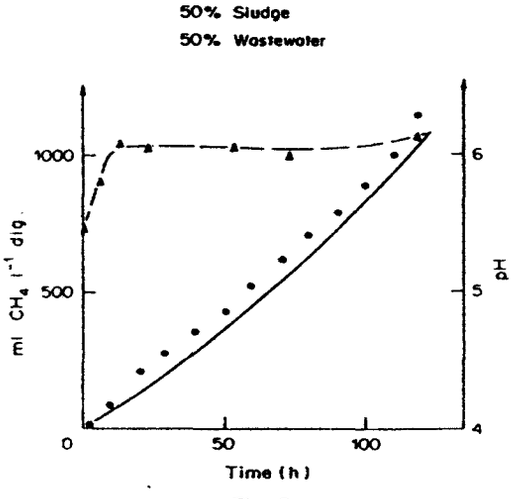

Fig. 7

Figs 5, 6 and 7. Comparison of model predictions (——) with experimental result (●) for methane production from pea bleaching wastewater. Experimental pH is reported (▲).

productions (acid or methane) are not considered as proportional to the respective production of biomass and each kinetic is represented by a different equation.

The unionized acid concentration inhibits the microorganism growth (acidogenic and methanogenic) and the production rate of methane.

This model was tested in batch cultures for the simulation of anaerobic digestion of synthetic substrate (sucrose and acetic acid) and of pea bleaching wastewaters. It represented satisfactorily methane production under very different physicochemical conditions. Our future purpose is to test this model on continuous fermentation with pH simulation.

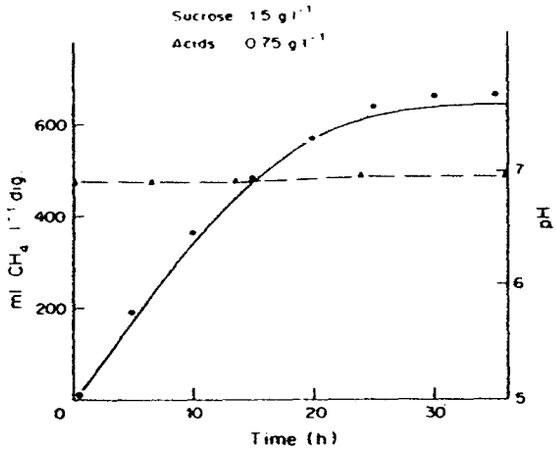

Fig. 8

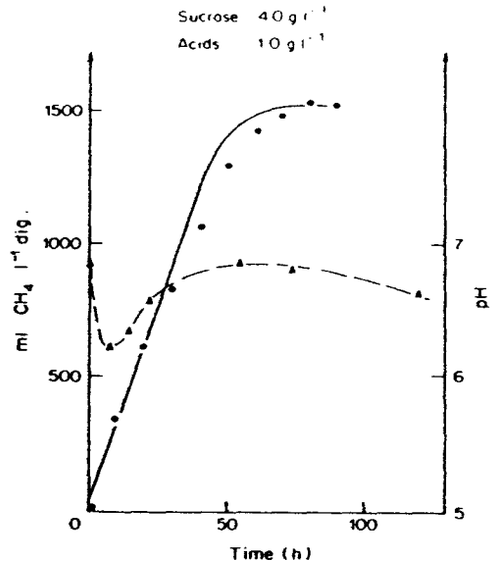

Fig. 9

Figs 8 and 9. Comparison of model predictions (——) with experimental result (●) for methane production from sucrose and acid mixture. Experimental pH is reported (▲).

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