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BATCH ANAEROBIC DIGESTION OF GLUCOSE AND ITS MATHEMATICAL MODELING. II. DESCRIPTION, VERIFICATION AND APPLICATION OF MODEL

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Abstract

A mathematical model of batch anaerobic digestion of glucose has been developed. The model includes five bacterial steps (acidogenesis, ethanol-degrading acetogenesis, butyrate-degrading acetogenesis, acetoclastic methanogenesis and hydrogenotrophic methanogenesis), bacterial decay, description of the reactor pH, and various inhibitions of the bacterial steps. The values of parameters of the model have been found, satisfactorily describing the experimental regularities. The numerical experiments have revealed and described the principle regulating factors of glucose methanogenesis. © 1997 Elsevier Science Ltd.

Key words: Mathematical model, kinetics, mass balance, inhibition, methanogenesis, glucose, ethanol, butyrate, acetate, hydrogen, pH.

NOMENCLATURE

Ac	acetate
b	bacterial decay rate constant (per h)
Bu	butyrate
Et	ethanol
f	conversion factor for substrate (mmol/g)
F	function
H	Henry's Law coefficient
I	inhibitor
K_I	inhibition constant (mM)
K_s	Monod saturation constant (mM)
pK_l	lower pH dropoff value, where the growth rates are 50% of the uninhibited rate [eqns (10) and (11)]
pK_u	upper pH dropoff value, where the growth rates are 50% of the uninhibited rate [eqns (10) and (11)]
S	substrate concentration (mM)
VSS	volatile suspended solids (g/l)
X	bacterial concentration (g/l)
Y	bacterial yield (g biomass/mmol substrate)
μ_m	maximum specific growth rate (per h)

Subscripts

i	substrate i
j	bacteria j
g	inhibition g
t	total

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INTRODUCTION

In Part I of this investigation (Kalyuzhnyi & Davlyatshina, 1997), the kinetics of batch anaerobic digestion of different mixtures of glucose and intermediates of its acidogenic degradation (ethanol, butyrate, propionate, and acetate) have been investigated, the process stoichiometry has been proposed, and some important inhibitions of the various bacterial steps involved have been noticed. This study served as a basis for developing the mathematical model described below.

Model description

General postulates

The model of batch anaerobic digestion of glucose developed by us is schematically shown in Fig. 1. The model involves five bacterial groups: glucose-fermenting acidogens, ethanol-degrading acetogens, butyrate-degrading acetogens, acetoclastic methanogens, and hydrogenotrophic methanogens. Stoichiometry as described in Part I of this investigation has been employed, although the propionate-degrading step has been grouped with butyrate-degrading step, taking into account the similar kinetic regularities of degradation of butyrate and propionate observed in our study (Kalyuzhnyi & Davlyatshina, 1997). Minor corrections to the corresponding stoichiometric coefficients have been made in order to balance the equations. All bacterial steps have been assumed pH-dependent in the model, consequently, the pH reactor equation derived from

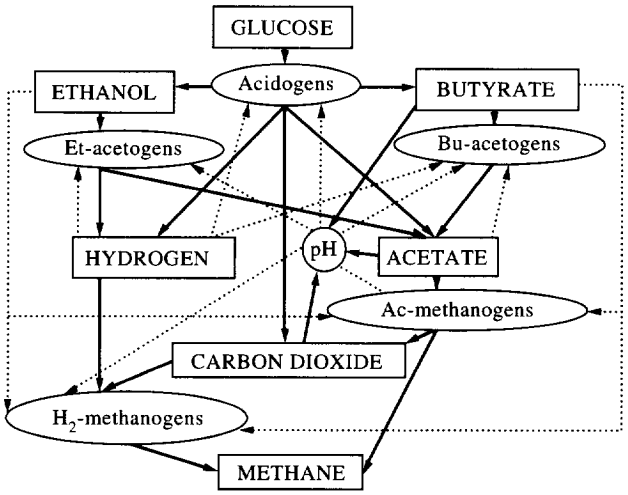


Fig. 1. Outline of methanogenesis model (——— material flow, · · · inhibition).

the ionic equilibrium of the components present in the liquid has also been included.

Hydrogen inhibition of the acidogenic step is considered in the model, because activity of the acidogenic bacteria, digesting glucose as a rule by the Embden–Meyerhoff pathway, strongly depends on the correlation of $NAD^+/NADH$ in their cells and the latter in turn is determined by concentration of hydrogen (Mosey, 1983). Also hydrogen inhibition of the acetogenic steps has been included to account for blockade of the reaction rates at high partial pressure of hydrogen (Kalyuzhnyi & Davlyatshina, 1997).

Acetate inhibition of the butyrate-degrading step, as has been shown in numerous studies (Kaspar & Wuhrman, 1978; Denac, 1986; Ahring & Westerman, 1988), as well as ethanol and butyrate inhibitions of both the methanogenic steps (Kalyuzhnyi & Davlyatshina, 1997) are also considered.

Finally, since the experiments proceeded during a long time (Kalyuzhnyi & Davlyatshina, 1997), bacterial decay has been accounted for in the model.

Stoichiometry

In the following bacterial steps cell mass is represented by the empirical formula $C_5H_9O_3N$ (Mosey, 1983).

Acidogenesis:

$$C_6H_{12}O_6+0.02H_2O\rightarrow 0.34C_2H_5OH+0.39C_3H_7COOH+1.31CH_3COOH+1.14CO_2+0.82H_2 \quad (1)$$

$$C_6H_{12}O_6+1.2NH_3\rightarrow 1.2C_5H_9O_3N+2.4H_2O \quad (2)$$

Ethanol acetogenesis:

$$C_2H_5OH+H_2O\rightarrow CH_3COOH+2H_2 \quad (3)$$

$$C_2H_5OH+0.2H_2O+0.4NH_3\rightarrow 0.4C_5H_9O_3N+2H_2 \quad (4)$$

Butyrate acetogenesis:

$$C_3H_7COOH+2H_2O\rightarrow 2CH_3COOH+2H_2 \quad (5)$$

$$C_3H_7COOH+0.4H_2O+0.8NH_3\rightarrow 0.8C_5H_9O_3N+2H_2 \quad (6)$$

Acetoclastic methanogenesis:

$$CH_3COOH\rightarrow CH_4+CO_2 \quad (7)$$

$$CH_3COOH+0.4NH_3\rightarrow 0.4C_5H_9O_3N+0.8H_2O \quad (8)$$

Hydrogenotrophic methanogenesis:

$$H_2+0.25CO_2\rightarrow 0.25CH_4+0.5H_2O \quad (9)$$

$$H_2+0.5CO_2+0.1NH_3\rightarrow 0.1C_5H_9O_3N+0.7H_2O \quad (10)$$

Growth kinetics and material balances

The growth kinetics are based on the following assumptions:

Growth of biomass proceeds according to Monod kinetics with simultaneous inhibition by some process components and pH modulation. Instead of using true Monod kinetics it is assumed that reaction kinetics for water and ammonium (reactions (1–6, 8, 10)) are of zero order in their concentrations. Because these substances are in excess in the reaction medium, this assumption is justified. Thus, a general equation for specific growth rates can be written as

$$\mu_j=\frac{\mu_{m,j}\cdot S_i}{F(I_g)\cdot(K_{s,j}\cdot F(I_{g'})+S_i)}\cdot F(\mathrm{pH}) \quad (11)$$

where $F(\mathrm{pH})$ is the pH modulation function; $F(I_g)$ and $F(I_{g'})$ are noncompetitive and competitive inhibition functions, respectively. A dual substrate form of Monod equation is postulated for hydrogenotrophic methanogens to account for their growth limitations caused by a deficiency of carbon dioxide in the reaction system under digestion of reduced substrates (ethanol, butyrate).

All product formations are directly coupled to biomass production due to the dissimilatory nature of anaerobic digestion.

Substrate consumption for maintenance is incorporated in the overall biomass yield.

Bacterial decay is described by first-order kinetics (Mosey, 1983; Bryers, 1985).

All reactions are effectively rate controlled, i.e. the effects of diffusional limitations of cells are constant and incorporated into the kinetic term. As was shown by Denac *et al.* (1988), diffusional gradients are not important in the calculation of the bulk concentrations of reactor components.

The effect of pH on the growth rates is described by a Michaelis pH function, normalized to give a

value of 1.0 as the center value (Angelidaki *et al.*, 1993):

$$F(\mathrm{pH}) = \frac{1+2\cdot 10^{0.5(pK_{l,j}-pK_{u,j})}}{1+10^{(\mathrm{pH}-pK_{u,j})}+10^{(pK_{l,j}-\mathrm{pH})}} \qquad (12)$$

Because not much exact quantitative information about pH modulation of different bacterial steps of anaerobic digestion is available, this is a reasonable first guess.

Acetate inhibition of the butyrate-degrading step is approximated by competitive inhibition function, as was shown by Denac (1986). All other inhibitions proceed according to noncompetitive kinetics (Mosey, 1983; Costello *et al.*, 1991; Kalyuzhnyi *et al.*, 1991). All inhibition functions have the form

$$F(I_g) = 1+I_g/K_{I,g} \qquad (13)$$

No temperature dependence of the kinetic parameters has been included in the model, because the experimental study (Kalyuzhnyi & Davlyatshina, 1997) used in the model validation was performed at the fixed temperature (35°C).

With the assumptions formulated above, the growth rate expressions and the resulting material balances are summarized in the Appendix. Conversion factors used are given in Table 1.

The pH calculation

For calculation of changing pH values during the process we used the approaches proposed previously (Kalyuzhnyi *et al.*, 1986; Angelidaki *et al.*, 1993). In summary, the pH value was determined in our case (high capacity of phosphate buffer, range of pH used of 5.5–8.0) by the ionic equilibrium of the following components present in the liquid: CO_2, CH_3COOH, C_3H_7COOH, $H_2PO_4^-$, H_2O, and C^+, A^-, which represent cations and anions, respectively (the impact of NH_3 and CO_3^{2-} was negligible in these conditions). Each component was ionized to a degree determined by the pH, i.e.

$$CO_2+H_2O \leftrightarrows HCO_3+H^+ \quad K_{a1,CO_2}$$

$$CH_3+COOH \leftrightarrows CH_3COO^-+H^+ \quad K_{a,CH_3COOH}$$

$$C_3H_7+COOH \leftrightarrows C_3H_7COO^- + H^+ \quad K_{a,C_3H_7COOH}$$

$$H_2PO_4^- \leftrightarrows HPO_4^{2-} + H^+ \quad K_{a2,H_3PO_4}$$

$$H_2O \leftrightarrows OH^- + H^+ \quad K_w$$

The resulting equilibrium pH was determined by the charge balance equation:

$$[H^+]+[C^+] = [OH^-]+[HCO_3^-] + [CH_3COO^-]+[C_3H_7COO^-]+[H_2PO_4^-] + 2\cdot[HPO_4^{2-}]+[A^-]$$

The transformation of this equation with elimination of negligible items ($[H^+],[OH^-] < [C^+],[A^-]$) leads to an algebraic equation of high degree on $[H^+]$:

$$[H^+] = f([CH_3COOH]_t, [C_3H_7COOH]_t, [CO_2]_t) \qquad (14)$$

where subscript t means total concentration (sum of ionized, unionized and gaseous forms) of given component. The solution of eqn (14) was done by standard computer iteration with selection of the roots according to the physical sense. The values of the physico-chemical parameters used are provided in Table 2.

Computational methods

Simulations were performed by numeric integration of the relevant equations with a fixed time step by a computer program based on a Runge–Kutta (second-order) technique (Cameron, 1983). The program was written in Fortran in a generalized form, where a variable number of steps, organisms, components, substrate and inoculum data could be specified through an input file. The program created an output data file in a format suitable for graphic processing.

Model parameters

A lot of preliminary simulations were undertaken to determine the most appropriate set of model parameters. The methodology of these investigations is discussed in more detail in the Results and Discussion. After all, the values of model parameters have been chosen in a range consistent with our own experimental work (Kalyuzhnyi & Davlyatshina, 1995) or values reported in the literature. The kinetic parameters used in the model are presented in Tables 3 and 4.

Table 1. Conversion factors used in the model

Conversion factor	Value, mmol/g	Basis
f_1	5.56	$C_6H_{12}O_6$
f_2	21.7	C_2H_5OH
f_3	11.4	C_3H_7COOH
f_4	26.7	CH_3COOH
f_5	500.0	H_2

Table 2. Physico-chemical model parameters at 35°C (Weast & Astle, 1981)

Parameter	Value
K_{a1,CO_2}	4.9×10^{-4} mM
K_{a,CH_3COOCH}	1.728×10^{-4} mM
K_{a,C_3H_7COOH}	1.439×10^{-4} mM
K_{a2,H_3PO_4}	1.4×10^{-4} mM
H_{CO2}	0.0376 atm/mM

Since all the kinetic data (Kalyuzhnyi & Davlyatshina, 1997) used in the model validation were obtained at the same initial concentrations of biomass (approximately 0.3 g VSS/l), the initial state of the modeling biosystem was fixed as follows:

$$X_1^0 = 0.058 \text{ g/l}; X_2^0 = 0.011 \text{ g/l};$$

$$X_3^0 = 0.017 \text{ g/l}; X_4^0 = 0.025 \text{ g/l};$$

$$X_5^0 = 0.039 \text{ g/l}$$

These values were chosen to be consistent with the experiments mentioned above. Some incongruity between sum of these biomass concentrations and the VSS concentration can be attributed to the presence of other bacteria in the inoculum and the biological inactivity of some part of the VSS.

Table 3. Growth parameters

Bacterial groups	μ_m, per h	K_s, mM	Y, g/mmol	b, per h	Reference
Acidogens	1.79	0.128	0.0288	0.0008	Mosey, 1983
	0.25	0.115	0.0069	0.0010	Bryers, 1985
	0.05	0.729	0.0069	0.017	Denac *et al.*, 1988
	—	0.128	—	0.004	Costello *et al.*, 1991
	0.4	0.042	0.0053	0.0004	Ryhiner *et al.*, 1993
	0.208	2.778	—	—	Angelidaki *et al.*, 1993
	0.175	0.128	0.0220	0.00125	Used here
Et-degrading acetogens	0.42 (chemostat)	0.0003 (chemostat)	—	—	Chartrain *et al.*, 1987
	0.28	0.06	0.002	0.00125	Used here
Bu-degrading acetogens	0.029	0.083	0.02	0.0004	Mosey, 1983
	0.015	0.083	0.0098	0.0001	Gujer & Zehnder, 1983
	0.010	3.125	0.0046	0.0004	Bryers, 1985
	0.015	3.125	0.0046	0.0011	Denac *et al.*, 1988
	0.081	0.083	0.0075	0.004	Costello *et al.*, 1991
	0.011	0.008	0.0059	0.0004	Ryhiner *et al.*, 1993
	0.028	2.0	—	—	Angelidaki *et al.*, 1993
	0.011	1.1	0.0045	0.00125	Used here
Acetoclastic methanogens	0.019	2.78	0.0025	0.0004	Mosey, 1983
	0.014	2.58	0.0033	0.0006	Gujer & Zehnder, 1983
	0.014	7.81	0.0019	0.001	Bryers, 1985
	0.014	3.70	0.0019	0.0006	Denac *et al.*, 1988
	0.019	2.57	0.0025	0.0013	Costello *et al.*, 1991
	0.008	0.1	0.0030	0.0004	Ryhiner *et al.*, 1993
	0.025	2.0	—	—	Angelidaki *et al.*, 1993
	0.015	2.3	0.0025	0.00083	Used here
H_2 utilizing methanogens	0.173	0.001[a]	0.0025[a]	0.0004	Mosey, 1983
	0.058	0.038[a]	0.0008[a]	0.0006	Gujer & Zehnder, 1983
	0.058	0.038[a]	0.0005[a]	0.0004	Bryers, 1985
	0.058	0.038[a]	0.0005[a]	0.0042	Denac *et al.*, 1988
	0.163	0.001[a]	0.0025[a]	0.0038	Costello *et al.*, 1991
	0.058	0.001[a]	0.0008[a]	0.0004	Ryhiner *et al.*, 1993
	0.058	0.008[a] 0.01[b]	0.0004[a]	0.00125	Used here Used here

[a]For hydrogen.
[b]For carbon dioxide.

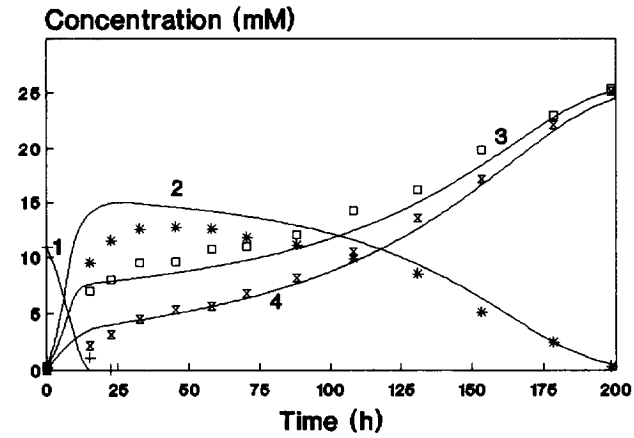
Table 4. The pH modulation and inhibition parameters

Bacterial groups	pK_l	pK_u	K_{I,H_2}, atm[a]	$K_{I,Ac}$, mM	$K_{I,Et}$, mM	$K_{I,Bu}$, mM	
Acidogens			0.0005[b]				
	5.0	8.0	0.0005				Used here
Et-degrading acetogens	6.05	7.95	0.005				Used here
Bu-degrading acetogens	6.0[c]	8.5[c]	0.0005[b]	30			
	6.05	7.95	0.0001	10			Used here
Acetoclastic methanogens	6.0[c]	8.5b					
	6.2	7.8			35	21	Used here
H_2-utilizing methanogens	6.0[c]	8.5[c]					
	6.2	7.8			29	16	Used here

[a]Conversion factor factor from atm to mM for our reactors is 0.0156 atm/mM.
[b]Costello *et al.* (1991).
[c]Angelidaki *et al.* (1993).

RESULTS AND DISCUSSION

The modeling data of the basic variable (glucose) clearly demonstrate (Fig. 2) the multi-stage nature of the anaerobic digestion process: the acidogenic step is practically completed within 20 h, the ethanol-degrading one proceeds during 45 h, butyrate-degrading and methanogenic ones proceed in about 200 h that corresponds well with the experimental data. The model slightly overestimates the acetate and butyrate concentrations during the first 100 h due to the model's simplistic assumption that lactate or other oxyacids are not revealed in the kinetics of glucose decomposition (Kalyuzhnyi & Davlyatshina, 1997). Additional stoichiometric equations would be required to accurately estimate the



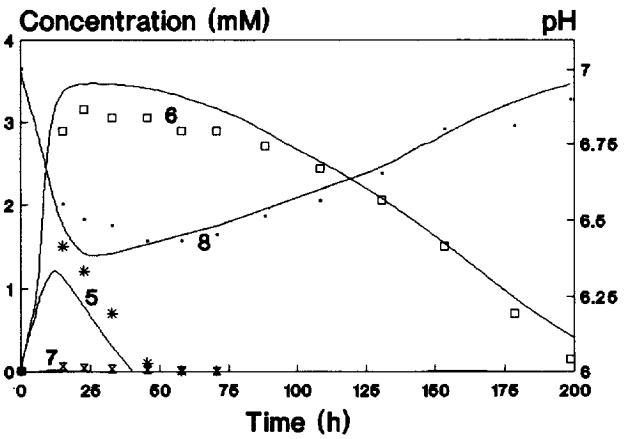
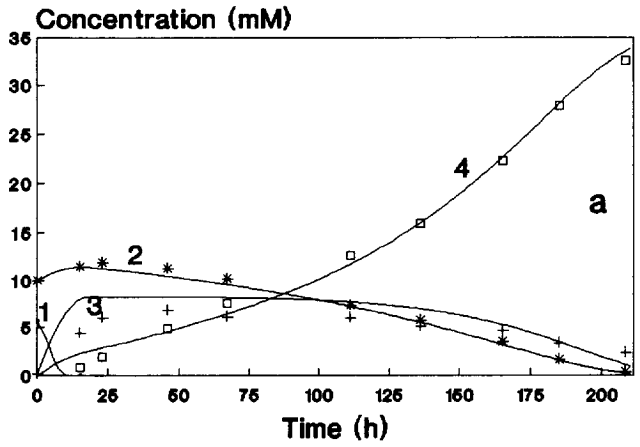


Fig. 2. Model prediction (lines) versus observation (points) of batch anaerobic digestion of glucose (Kalyuzhnyi & Davlyatshina, 1997): 1—glucose, 2—acetate, 3—carbon dioxide, 4—methane, 5—ethanol, 6—butyrate, 7—hydrogen, 8—pH.



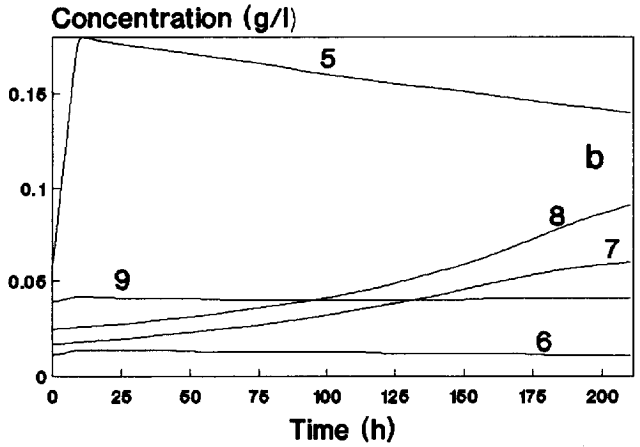
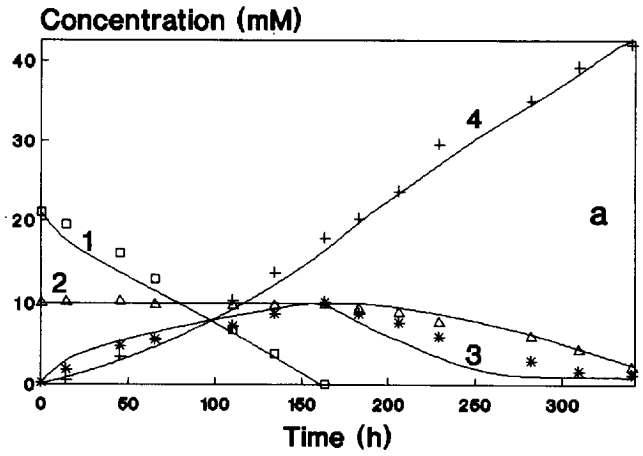
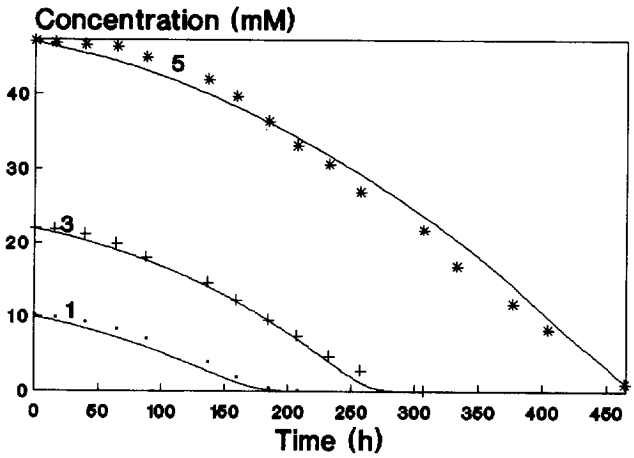


Fig. 3. Model prediction (lines) versus observation (points) of batch anaerobic digestion of mixture of glucose and butyrate (Kalyuzhnyi & Davlyatshina, 1997): 1—glucose, 2—butyrate (sum of butyrate and propionate for observation), 3—acetate, 4—methane, 5—bacteria X_1, 6—bacteria X_2, 7—bacterial X_3, 8—bacterial X_4, 9—bacterial X_5.

acidogenic step. From Fig. 2 the regulation of the methanogenic system by hydrogen is clearly seen: there is a lag period (approximately 45 h) on the curve of consumption of butyrate followed by its conversion only after decreasing the hydrogen concentration in the reactor.

Figure 3 presents the modeling data for the conversion of the glucose–butyrate mixture. In full accordance with experiments (Kalyuzhnyi & Davlyatshina, 1997), the model clearly shows the initial increase of butyrate concentration, its slow consumption, relatively slow conversion of acetate and slightly diauxic shape of the methane curve [Fig. 3(a)]. Also, the model reveals the growth kinetics of each bacterial group in this system during the process (it is practically impossible to do that in the experiment). From Fig. 3(b), it is seen that the fast growth of acidogens X_1 and ethanol-degrading acetogens X_2, leading to complete glucose and ethanol exhaustion, is then followed by their lysis. Butyrate-degrading acetogens X_3 are under strong inhibition by hydrogen and partially by acetate, the concentration changes of which determine the shape of their growth curve. The growth curve of acetoclastic methanogens X_4 has a smooth exponential type because their limiting substrate (acetate) is constantly present in the system in a sufficient concentration and the inhibition of their growth by butyrate is not practically displayed under a given concentration of the latter. Finally, the shape of the growth curve of H_2-utilizing methanogens X_5 is also determined by the presence of their limiting substrate (hydrogen) in the system. A starting increase of growth of these bacteria during the period of fermentation of easily digested hydrogenic substrates (glucose and ethanol) soon after their exhaustion is followed by the delay, caused by slight input of hydrogen into the system (low rate of butyrate conversion). The activation of the latter process, following then in accordance with the principle of the feedback relation, gives an initial new increase of the growth of bacteria X_5.





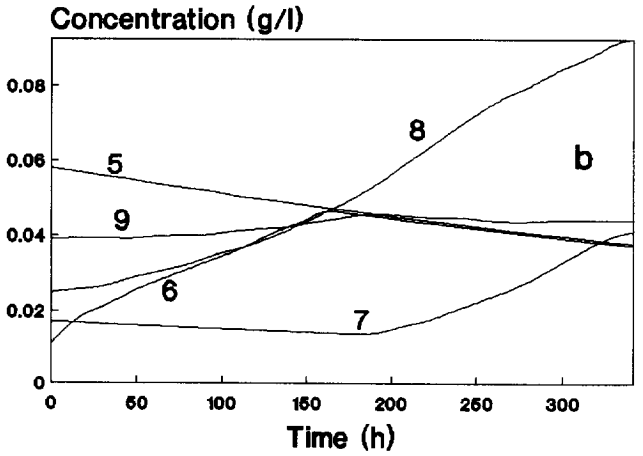


Fig. 4. Model prediction (lines) versus observation (points) of batch anaerobic digestion of mixture of ethanol and butyrate (Kalyuzhnyi & Davlyatshina, 1997): 1—ethanol, 2—butyrate, 3—acetate, 4—methane, 5—bacteria X_1, 6—bacteria X_2, 7—bacteria X_3, 8—bacteria X_4, 9—bacteria X_5.

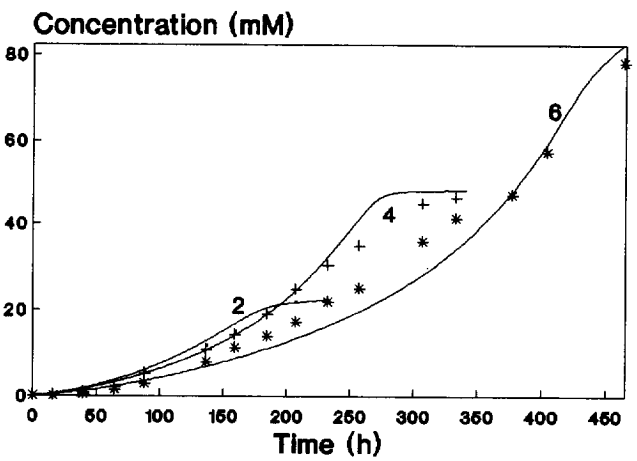
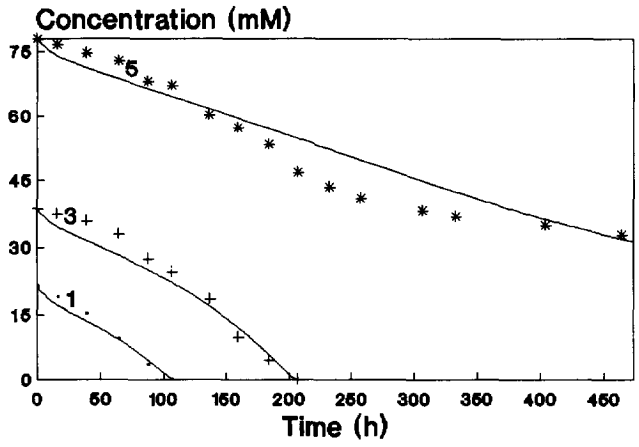


Fig. 5. Model prediction (lines) versus observation (points) of batch anaerobic digestion of butyrate at various initial concentrations (Kalyuzhnyi & Davlyatshina, 1997): 10 mM (1—butyrate, 2—methane); 22 mM (3—butyrate, 4—methane); 47 mM (5—butyrate, 6—methane).



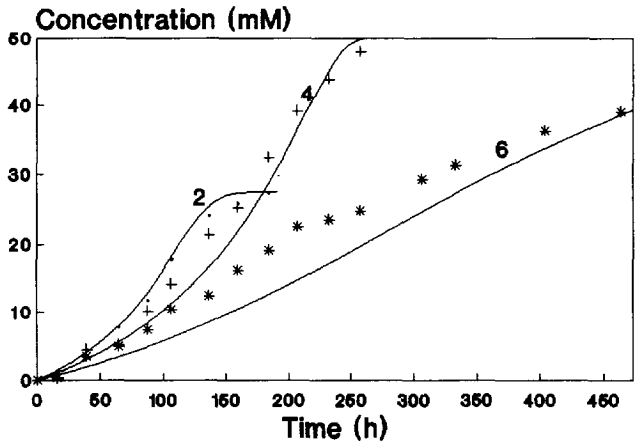


Fig. 6. Model prediction (lines) versus observation (points) of batch anaerobic digestion of ethanol at various initial concentrations (Kalyuzhnyi & Davlyatshina, 1997): 21.1 mM (1—ethanol, 2—methane); 38.5 mM (3—ethanol, 4—methane); 77.8 mM (5—ethanol, 6—methane).

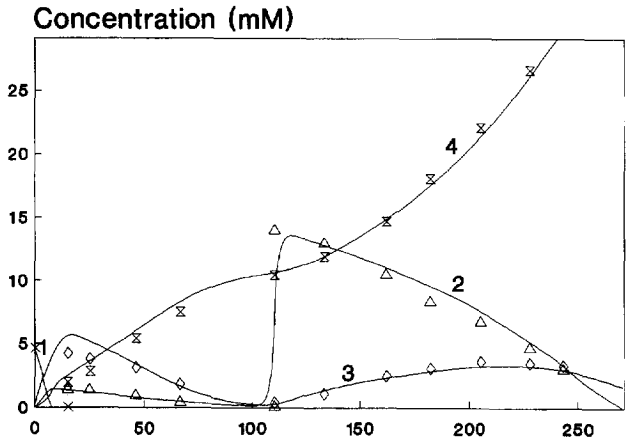


Fig. 7. Model prediction (lines) versus observation (points) for successive digestion of glucose and butyrate (Davlyatshina, 1993): 1—glucose, 2—butyrate, 3—acetate, 4—methane.

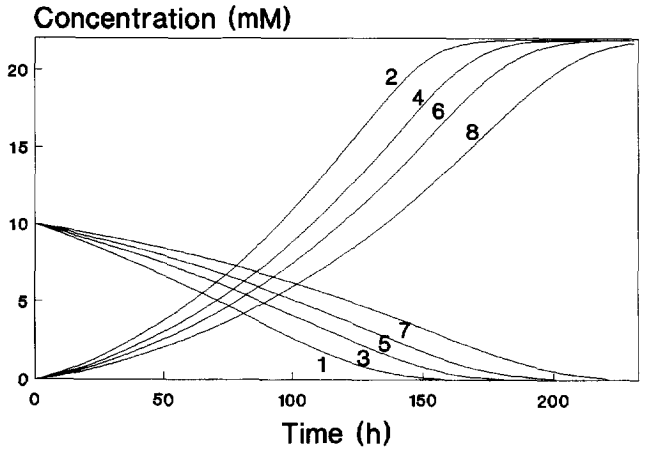


Fig. 8. Modeling results of batch anaerobic digestion of butyrate (initial pH 7.0) at various initial concentrations of bacteria X_3: 0.027 g/l (1—butyrate, 2—methane); 0.02 g/l (3—butyrate, 4—methane); 0.016 g/l (5—butyrate, 6—methane); 0.012 g/l (7—butyrate, 8—methane).

The modeling data for the conversion of another interesting mixture of the intermediates (ethanol+ butyrate) are presented in Fig. 4. It is seen that, in general, predictions agree well with the experimental data (Kalyuzhnyi & Davlyatshina, 1997), indicating, for example, complete delay in the butyrate degradation until the ethanol level was exhausted [Fig. 4(a)]. This is caused by the inhibition of butyrate-degrading acetogens X_3 [curve 7, Fig. 4(b)] by hydrogen generated during ethanol degradation. Also the time of complete exhaustion of ethanol, as well as the localization of the maximum in the acetate curve obtained with the help of the model, exactly coincide with those found in the experiment [Fig. 4(a)]. At the same time the model underestimates the ethanol concentrations during the first 100 h and the acetate concentrations during active butyrate degradation. Both these latter discrepancies can be attributed to a more complex mechanism of inhibition of the process than was assumed in the model.

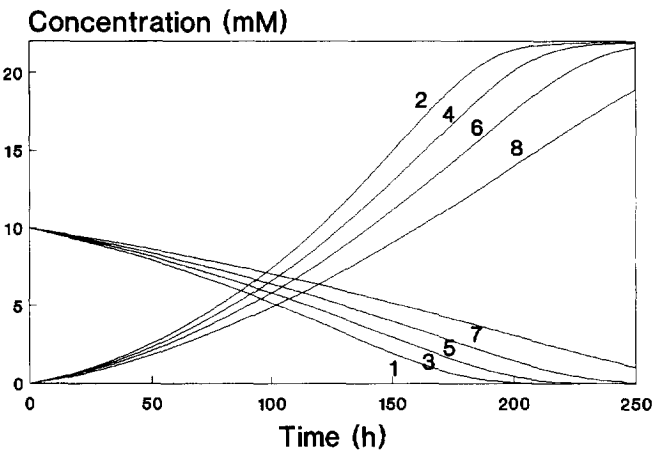


Fig. 9. Modeling results of batch anaerobic digestion of butyrate (initial pH 7.0) at variation of parameter $K_{I,4}$, mM: 0.004 (1—butyrate, 2—methane); 0.001 (3—butyrate, 4—methane); 0.0005 (5—butyrate, 6—methane); 0.00025 (7—butyrate, 8—methane).

Let us discuss some numerous experiments based on variation of initial concentrations of the glucose decomposition intermediates which were actively used by us under selection of the model parameter values. Figure 5 presents the modeling results obtained for various initial butyrate concentrations. The comparison with the experiment (Kalyuzhnyi & Davlyatshina, 1997) shows that the model exactly predicts key properties of this system: weak inhibition of methane formation by butyrate and times of complete consumption of the latter.

The modeling results obtained by varying the initial ethanol concentration are presented in Fig. 6. It is seen that, as in the experiment (Kalyuzhnyi & Davlyatshina, 1997), ethanol inhibits the rate of methane formation. An increase in its concentration more than 70 mM leads to a significant decrease of the medium pH (at the expense of acetate accumulation), followed by a delay in the conversion processes. In general, the case with the initial ethanol concentration of 78 mM is not very well described by the present model, probably, due to a more complex inhibition influence of high ethanol concentrations on the conversion process than was postulated in the model.

Analogous numerous experiments based on the variation of initial concentrations have also been done with other intermediates of acidogenic glucose decomposition, that enabled us to choose the most appropriate set of model parameter values (Tables 3 and 4), giving a satisfactory agreement between predictions and observations.

As an illustration of the last statement (besides the results given above), let us attract attention to the modeling data of cases with successive inputs of substrates to the reaction medium. Figure 7 presents only one example of such experiments. Namely, the system, initially digesting glucose, was disturbed by addition of butyrate at 110 h. Such disturbance did not lead to a stressed state of the methanogenic system. On the contrary, it had utilized the new added butyrate more quickly than in the case of simple butyrate conversion (Fig. 5, curve 1). As the modeling results show, it is related with the fact that at the disturbance moment, the concentrations of bacteria X_3–X_5, taking part in butyrate conversion, were higher than those in the initial inoculum due to their preceding growth on glucose decomposition intermediates. Thus, the microbial system in the latter case is more ready and balanced for butyrate utilization than the initial inoculum. On the whole, the model gives a satisfactory description of this experiment (Fig. 7).

Under detailed investigation of the developed model, we have discovered its interesting feature, which seems to reflect an important property of the methanogenic biosystem. Specifically, the model demonstrates a relatively weak response on variation (in limits of half order) of the initial concentration of all five bacterial groups postulated in it. For example, a more than two-fold decrease of the concentration of acetogenic bacteria X_3, which are key ones for butyrate conversion, in the inoculum leads only to a 22% increase of time of complete consumption of butyrate, and a moderate delay in the formation of methane (Fig. 8). It demonstrates a high degree of self-regulation of the methanogenic microbial community, which is relatively quickly able to form the balanced bacterial content necessary for realization of the anaerobic conversion process from that or another initial state. Also, a weak dependence of the process kinetics on the initial bacterial concentration allows the model to describe methanogenesis in the systems where the starting microbial content is determined approximately, or is estimated from indirect data.

Finally, an example showing how the model can elucidate and characterize the key factors influencing the methanogenesis process follows. The above-mentioned high sensitivity of kinetics of butyrate conversion to the level of hydrogen in the system can be illustrated in numerous experiments with a help of parameter $K_{I,4}$ included in eqn (A3). Varying this parameter we model the response of the system to different hydrogen levels. From Fig. 9 it is noted that an decrease of $K_{I,4}$ leads to a decrease of the activity of bacteria X_3, causing the delay of butyrate conversion and subsequent methane formation. Since the parameter $K_{I,4}$ determines the time of complete butyrate conversion, the comparison of these times with experimental times allows one to select its appropriate value, which is listed in Table 4. By analogy, the selection of values of other parameters and coordination of them has been realized.

CONCLUSIONS

Thus, the mathematical model of methanogenesis from glucose developed by us adequately describes the experimental data and can be used both for further investigation of anaerobic digestion in nature and in kinetic description and optimization of performance of anaerobic reactors.

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APPENDIX

Growth rate expressions

Specific growth rate of acidogens, X_1:

$$\mu_1 = \frac{\mu_{m,1} \cdot S_1}{K_{s,1}+S_1} \cdot \frac{1}{1+S_5/K_{I,1}} \cdot \frac{1+2\cdot 10^{0.5(pK_{l,1}-pK_{u,1})}}{1+10^{(pH-pK_{u,1})}+10^{(pK_{l,1}-pH)}} \tag{A1}$$

Specific growth rate of ethanol-degrading acetogens, X_2:

$$\mu_2 = \frac{\mu_{m,2} \cdot S_2}{K_{s,2}+S_2} \cdot \frac{1}{1+S_5/K_{I,2}} \cdot \frac{1+2\cdot 10^{0.5(pK_{l,2}-pK_{u,2})}}{1+10^{(pH-pK_{u,2})}+10^{(pK_{l,2}-pH)}} \tag{A2}$$

Specific growth rate of butyrate-degrading acetogens, X_3:

$$\mu_3 = \frac{\mu_{m,3} \cdot S_3}{K_{s,3}+(1+S_4/K_{I,3})+S_3} \cdot \frac{1}{1+S_5/K_{I,4}} \cdot \frac{1+2\cdot 10^{0.5(pK_{l,3}-pK_{u,3})}}{1+10^{(pH-pK_{u,3})}+10^{(pK_{l,3}-pH)}} \tag{A3}$$

Specific growth rate of acetoclastic methanogens, X_4:

$$\mu_4 = \frac{\mu_{m,4} \cdot S_4}{K_{s,4}+S_4} \cdot \frac{1}{1+S_2/K_{I,5}} \cdot \frac{1}{1+S_3/K_{I,6}} \cdot \frac{1+2\cdot 10^{0.5(pK_{l,4}-pK_{u,4})}}{1+10^{(pH-pK_{u,4})}+10^{(pK_{l,4}-pH)}} \tag{A4}$$

Specific growth rate of hydrogenotrophic methanogens, X_5:

$$\mu_5 = \frac{\mu_{m,5} \cdot S_5 \cdot S_6}{(K_{s,5}+S_5)(K_{s,6}+S_6)} \cdot \frac{1}{1+S_2/K_{I,7}} \cdot \frac{1}{1+S_3/K_{I,8}} \cdot \frac{1+2\cdot 10^{0.5(pK_{l,5}-pK_{u,5})}}{1+10^{(pH-pK_{u,5})}+10^{(pK_{l,5}-pH)}} \tag{A5}$$

Material balances

Acidogens, X_1:

$$\frac{dX_1}{dt} = \mu_1 \cdot X_1 - b_1 \cdot X_1 \tag{A6}$$

Ethanol-degrading acetogens, X_2:

$$\frac{dX_2}{dt} = \mu_2 \cdot X_2 - b_2 \cdot X_2 \tag{A7}$$

Butyrate-degrading acetogens, X_3:

$$\frac{dX_3}{dt} = \mu_3 \cdot X_3 - b_3 \cdot X_3 \tag{A8}$$

Acetoclastic methanogens, X_4:

$$\frac{dX_4}{dt} = \mu_4 \cdot X_4 - b_4 \cdot X_4 \tag{A9}$$

Hydrogenotrophic methanogens, X_5:

$$\frac{dX_5}{dt} = \mu_5 \cdot X_5 - b_5 \cdot X_5 \tag{A10}$$

Glucose, S_1:

$$\frac{dS_1}{dt} = -\frac{\mu_1}{Y_1} \cdot X_1 \tag{A11}$$

Ethanol, S_2:

$$\frac{dS_2}{dt} = 0.34 \cdot (1 - f_1 Y_1) \cdot \frac{\mu_1}{Y_1} \cdot X_1 - \frac{\mu_2}{Y_2} \cdot X_2 \tag{A12}$$

Butyrate, S_3:

$$\frac{dS_3}{dt} = 0.39 \cdot (1 - f_1 Y_1) \cdot \frac{\mu_1}{Y_1} \cdot X_1 - \frac{\mu_3}{Y_3} \cdot X_3 \tag{A13}$$

Acetate, S_4:

$$\frac{dS_4}{dt} = 1.31 \cdot (1 - f_1 Y_1) \cdot \frac{\mu_1}{Y_1} \cdot X_1 + (1 - f_2 Y_2) \cdot \frac{\mu_2}{Y_2} \cdot X_2 + 2 \cdot (1 - f_3 Y_3) \cdot \frac{\mu_3}{Y_3} \cdot X_3 - \frac{\mu_4}{Y_4} \cdot X_4 \tag{A14}$$

Hydrogen, S_5:

$$\frac{dS_4}{dt} = 0.82 \cdot (1 - f_1 Y_1) \cdot \frac{\mu_1}{Y_1} \cdot X_1 + 2 \cdot (1 - f_2 Y_2) \frac{\mu_2}{Y_2} \cdot X_2 + 2 \cdot (1 - f_3 Y_3) \frac{\mu_3}{Y_3} \cdot X_3 - \frac{\mu_5}{Y_5} \cdot X_5 \tag{A15}$$

Carbon dioxide, S_6:

$$\frac{dS_6}{dt} = 0.82 \cdot (1 - f_1 Y_1) \cdot \frac{\mu_1}{Y_1} \cdot X_1 + (1 - f_4 Y_4) \cdot \frac{\mu_4}{Y_4} \cdot X_4 - 0.25 \cdot (1 - f_5 Y_5) \cdot \frac{\mu_5}{Y_5} \cdot X_5 - 0.5 \cdot f_5 \cdot \mu_5 \cdot X_5 \tag{A16}$$

Methane, S_7:

$$\frac{dS_7}{dt} = (1 - f_4 Y_4) \cdot \frac{\mu_4}{Y_4} \cdot X_4 + 0.25 \cdot (1 - f_5 Y_5) \cdot \frac{\mu_5}{Y_5} \cdot X_5 \tag{A17}$$