THE <METHANE> SIMULATION MODEL AS THE FIRST GENERIC USER-FRIEND MODEL OF ANAEROBIC DIGESTION

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The examples of application of the generic <METHANE> simulation model to describe the kinetics of carbohydrate, protein and lipid bioconversion by the microbial community in anaerobic digesters and in various methanogenic environments are summarized. That model was written in a user-friend mode and it was originally oriented to a nonprofessional user. The new generation <METHANE> model is developed.

Introduction

Anaerobic bioconversion of organic waste is a multi-step process of series and parallel reactions in which several key groups of bacteria take part. To maintain an anaerobic treatment system that will stabilize organic waste efficiently, the non-methanogenic and methanogenic bacteria must be in a state of dynamic equilibrium. Anaerobic digestion systems are rather complex processes that unfortunately often suffer from instability. In order to be able to design and operate anaerobic digestion systems, appropriate mathematical models needs to be developed.

There are a number of the famous models of anaerobic digestion systems. However, these models were developing usually in a non-user-friend mode. So, the traditional users of the models have been the authors only. In 1993–94 the first publications of the <METHANE> simulation model have been appeared [1, 2]. The main objective of this paper was to summarize an application of the <METHANE> model for description a competition between methanogenic and sulfate reducing bacteria in anaerobic environment and a balance between polymer hydrolysis and methanogenesis during a solid waste degradation. It was discussed also a reduction of the <METHANE> model to the simplified kinetic equations treated by the non-linear regression to evaluate the kinetic parameter values.

Method

The new version of <METHANE> model presented here is based on the model developed earlier. It is assumed in the model that an initial complex substrate X_1 is a mixtures of proteins (P), lipids (L) and carbohydrates (C). Hydrolysis, acidogenesis, acetogenesis and methanogenesis induced by different groups of microorganisms were described. The following groups of variables and equations are included in the model:

1. Suspended solid concentrations (X_k, $k = 1, 2, 3$)

$$V\frac{dX_k}{dt} = q_f X_{Fk} - q_{BX} X_k + V\rho_{Xk}, \qquad (1)$$

where X_{Fk} are the influent concentrations of components of suspended solids; q_f is the feed flow rate; q_{BX} is the discharge rate of excess-suspended solids including biomass; ρ_{Xk} are the rates of transformation of the components of suspended solids, which were expressed as a product of the functions describing the temperature dependence, mechanism of substrate limitation and inhibition; V is the volume of liquid phase.

2. Active biomass concentrations (B_i, $i = 1, 2, \ldots, 10$)

$$V\frac{dB_i}{dt} = q_f B_{Fi} - q_{BX} B_i + V\rho_{Bi}, \qquad (2)$$

where B_{Fi} are the influent concentrations of active bacteria; ρ_{Bi} are the growth rates of various subpopulations.

3. Dissolved substrate concentrations (S_j, $j = 1, 2, \ldots, 13$)

$$V\frac{dS_j}{dt} = q_f\,(S_{Fj} - S_j) + V\rho_{Sj} + TRS_j, \qquad (3)$$

where S_{Fj} are the influent concentrations of soluble substrates; ρ_{Sj} are the rates of transformation of the components of soluble substrate; TRS_j are the rates of mass exchange between gaseous and liquid phases.

4. Partial gas pressures (p_l, $l = 1, \ldots, 5$)

$$\frac{dP_l}{dt} = \frac{RT}{V^g}\left[-\mathrm{TRS}_l + \sum_n \mathrm{TRS}_n \cdot \frac{P_l}{P_T}\right], \qquad (4)$$

where R is the universal gas constant; T is the temperature (K); V^g is the volume of gas phase; P_T is the total gas pressure.

Up to now the advantages of the detailed model for simulation of complex processes was described in a number of papers. The main feature of the <METHANE> model was a flexible way which allows to select initially the appropriate rate functions, temperature dependence and inhibition impact. Visual model calibration at which the differences between the values of observed and predicted variables were close to a minimum was used. Since 1993 the <METHANE> model was used as a tool for effective study of various key stages of anaerobic process. It helped to create the modifications of the model with additional facilities more convenient to a user. If the first version of the

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<METHANE> model was created in MS-DOS media, the new version, in which the additional groups of microorganisms (acetogenic bacteria) and the intermediate products (long-chain fatty acids—LCFA) were included, is created in WINDOWS media now. Variable total gaseous pressure was considered also.

A development of the generic model of anaerobic digestion is being developed now under Internatial Water Association [3].

Results and Discussion

Self-oscillating coexistance of methanogenic and sulfate reducing bacteria. In the anaerobic treatment of sulfate-containing wastewater, sulfate reduction interferes with methanogenesis [4]. Several mathematical models of sulfate fed reactors have been developed, mainly for continuous stirred tank reactor systems. They mainly focus on the interaction between sulfate reducing bacteria and methanogenic bacteria while accounting for sulfide toxicity [5]. The <METHANE> model was calibrated [6] on the experiments of Parkin and others [7] where anaerobic chemostats were operated at variation of COD (acetate) : S (sulfate) ratios from 60 : 1 to 2 : 1. The simulations showed that, when COD : S ratio was less than 10 : 1, both sulfate reduction and methanogenesis shut down, which agreed well with the experimental observation. The model revealed that free H_2S and pH inhibition were the main factors governing system failure. In addition, the former acted as a trigger stimulating a positive feedback loop between an increase in acetate and sulfate concentrations and a decrease in the pH level through microbial activity. Thus, an oscillating coexistance of methanogenic and sulfate reducing bacteria with a period of 5–20 days under conditions close to system failure could be modeled. This phenomenon emphasizes the high complexity of sulfate fed anaerobic systems.

The oscillating phenomenon was further investigated using a reduced model [8]. It was found that the self-oscillation mechanisms disappeared at strong venting rates with an inert gas as well as at increased buffer capacity. Actually, oscillating coexistance is a form of competition. During oscillations the inhibiting impact of H_2S on bacteria was reversible. The few fading oscillations were observed in Parkin's experiments directly. But nevertheless, the oscillation dynamics or the deterministic chaos may explain a rather large dispersion of experimental data in the steady-state under such conditions. O'Flaherty and Colleran [9] observed an oscillating pattern of inhibition and recovery of sulfate-reducing bacteria during volatile fatty acids degradation in sulfate fed stirred tank reactor. The addition of nitrogen gas scrubber, which appeared to prevent sulfide concentrations, stopped the oscillations.

To analyze an oscillating mechanism a special option was created in the <METHANE> model for comparison of dynamics of various microorganisms and factors, influencing on it: substrate limitation, biomass growth and death, inhibition and dilution. Having such an option, during simulations a user may easily determine in time a bottle-neck factor which is important for the total process of anaerobic conversion of complex material into methane.

Two-step kinetics of polymer hydrolysis. During anaerobic digestion a solid waste, a balance between the rates of polymer hydrolysis and methanogenesis is important. New version of the <METHANE> simulation model was used to describe the dynamic behavior of batch mesophilic degradation of solid poultry slaughterhouse (SSW) and source sorted household solid (SHW) wastes at the same organic loading, inoculum and temperature. SHW and SSW contain the different ratio of carbohydrates, proteins and lipids: carbohydrates are the main components in SHW, but proteins and lipids are the main components in SSW. Batch experimental data on volatile solids, ammonium, acetate, butyrate and propionate concentrations, pH-level, cumulative volume and methane partial pressure were used for model calibration and verification. The same model parameter values excepting a composition of solids and the hydrolysis rate coefficient were applied for description of the SSW and SHW wastes degradation. Simulation results for both solid wastes showed that a temporary inhibition of polymer hydrolysis by a high volatile fatty acids (VFA) concentrations as well as an inhibition of acetogenesis could be responsible for the two-step kinetics of polymer hydrolysis (Figs. 1 and 2).

The two-step kinetics of polymer hydrolysis of municipal solid waste was described earlier by Vavilin and others [10] assuming a temporarily polymer hydrolysis inhibition by VFA. However, Veeken and others [11] found that the hydrolysis rate constant was pH-dependent, but not related to the total VFA and undissociated VFA concentrations. In this study, for SHW during the initial step of polymer hydrolysis a VFA accumulation was accompanied by the pH drop from 7.0 to 6.0; but for SSW during that stage the pH value kept about 7.0 because of ammonium buffer. So, a direct inhibition by the pH value could not be responsible for the two-step kinetics of polymer hydrolysis in the case with SSW. Two alternative mechanisms of inhibition were considered in the model: an inhibition of acetogenesis and acetoclastic methanogenesis by LCFA, or by free ammonia. Both approaches were able to fit the experimental data rather closely, but assumption about LCFA inhibition seems to be more realistic. As it was shown earlier in the batch assays [12] with identical to SSW substrate a LCFA-inhibition was taken place during anaerobic digestion such a substrate. In this work we demonstrated that a stronger inhibition could be responsible for the lower rate of solids conversion into methane happened in the slaughterhouse waste reactor in comparison with the sorted household waste reactor. The upset of polymer hydrolysis followed the intensive methanogenesis with some delay in both digesters.

Kinetic analysis of low temperature methanogenesis. The detailes of the low temperature degradation pathways of diverse substrates and the composition of the microbial communities in various methanogenic environments are still largerly unknown. Simulation modelling of methanogenesis during anaerobic conversion of complex organic matter at low temperatures by microbial consortia was performed by Vavilin and others [13, 14]. A simple

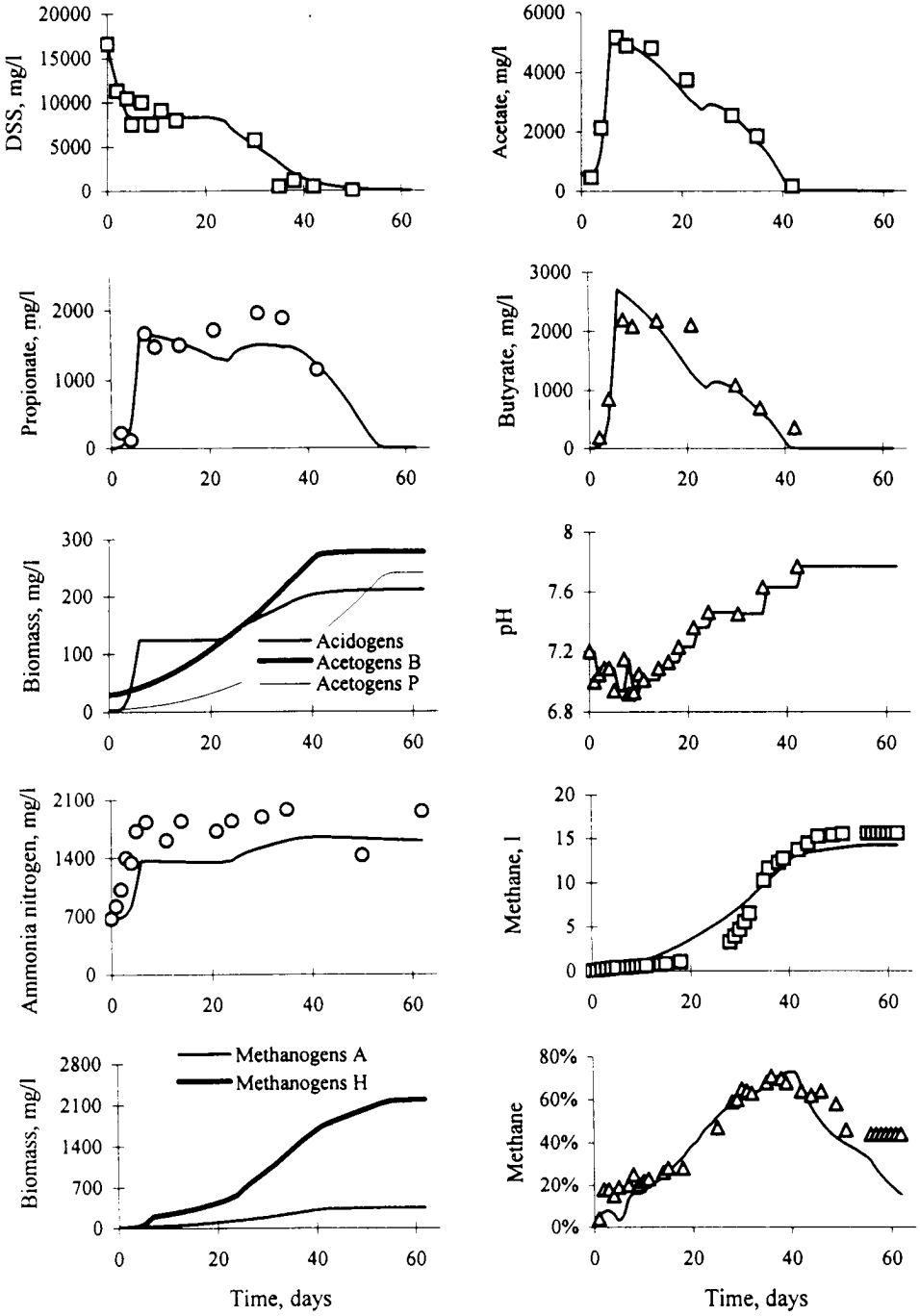

Fig. 1. Time profiles of main model variables in digester with SSW. Symbols: experimental data (presented by E. Salminen and J. Rintala); lines: model predictions (DSS degradable suspended solids, B butyrate, P propionate, A aceticlastic, H hydrogenotrophic).

method originated from a generic model of anaerobic digestion discussed above was developed to analize the kinetics of low temperature substrate degradation by microbial consortia of forest, tundra, or prarie soils, leaf litter and pond silt [15]. Non-linear regression was a tool for estimation not only of the values of kinetic coefficients but of their standard deviations too. However, this technique was restricted to rather simple case studies with: (i) series reactions when the feed-back loops including pH influence were neglected; (ii) use of the exponential equations for the rates of intermediate stages if the current substrate concentrations was considered to be substantially higher than the half-saturation substrate coefficients; (iii) neglection of the biomass decay processes in the biomass rate functions.

Lokshina and others [16] used the integrated Monod and Haldane models that combine acetate consumption, methane production and biomass growth equations for evaluation of kinetic coefficients of acetoclastic methanogenesis from acetate consumption or methane production data. The linear and exponential approximations and the limitations of their applicability were deduced from the integrated models. The Monod and Haldane models yield a sigmoidal S-shaped methane accumulation and acetate depletion curves. Roughly, these curves may be divided

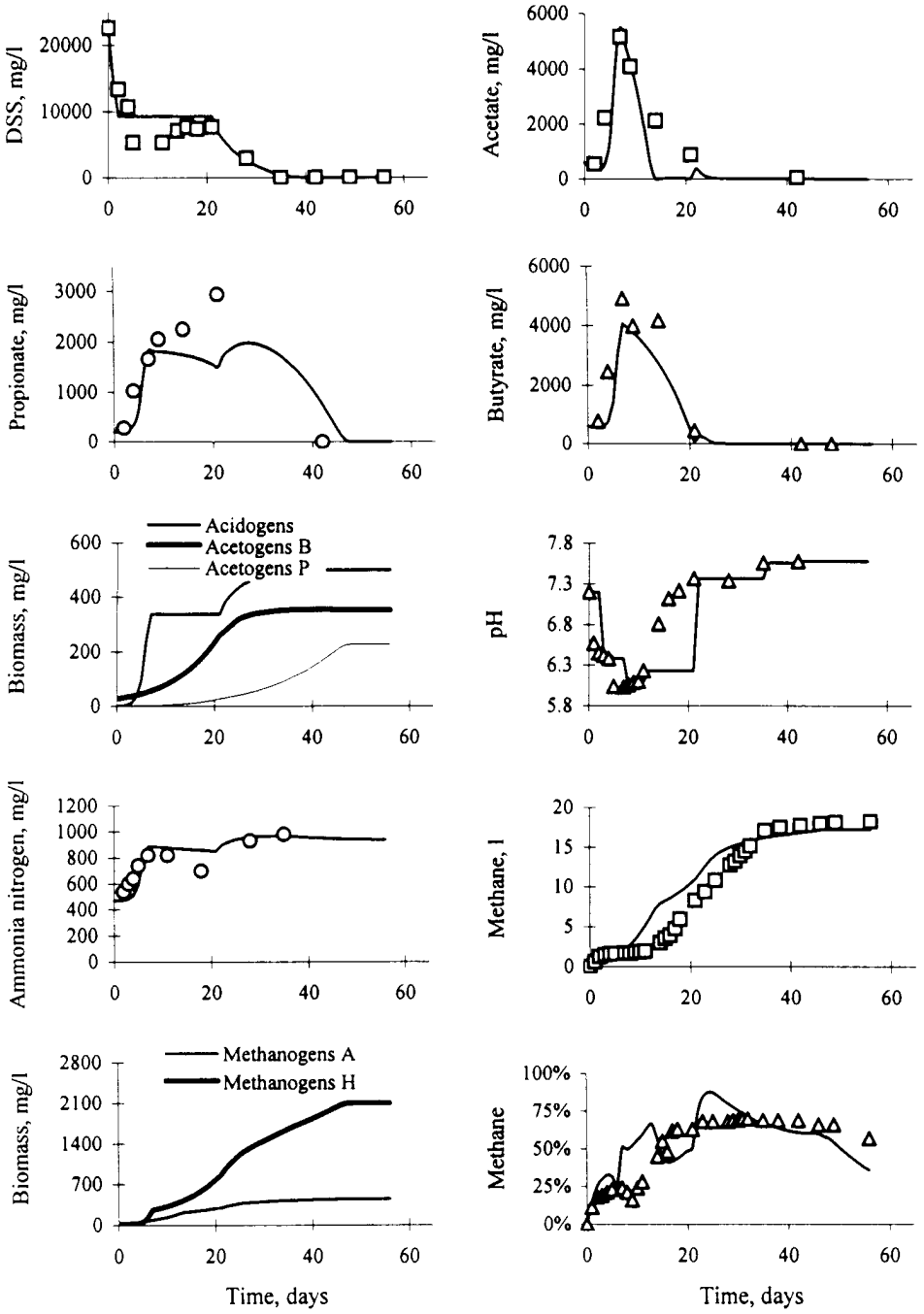

Fig. 2. Time profiles of main model variables in digester with SHW. Symbols: experimental data (presented by E. Salminen and J. Rintala); lines: model predictions.

on three parts: exponential growth, linear and declining growth phases. However, the specific methanogenic activity or acetoclastic methanogenic activity of biomass are calculated usually from the steepest linear part in the methane accumulation or acetate depletion curves, which follows an exponential phase of biomass growth.

We showed that the Haldane model is more adequate to describe experimental data on methane production by samples of biomass taken from the upflow sludge blanket reactor (UASB) and lake sediments over a wide range of initial acetate concentrations. The maximum growth rate of biomass (μ_m) values increased at increasing temperatures (the lake sediments at 6, 15 and 30°C: 0.046 ± 0.007, 0.075 ± 0.007, 0.196 ± 0.011 day^{-1}, respectively; the UASB biomass at 11 and 22°C: 0.04 ± 0.01, 0.19 ± 0.07 day^{-1}, respectively). For the lake sediments the values of half-saturation coefficients increased but the values of inhibition coefficients (K_I) decreased at decreasing temperatures at 6, 15 and 30°C. The rather low characteristic values of the K_I value about 8–10 mM was found at psyhcrophilic conditions. At the highest temperature of 30°C no difference was found between the Haldane and Monod models.

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References

1. Vasiliev, V.B., Vavilin, V.A., Rytov, S.V., and Ponomarev, A.V. (1993) *Wat. Resources*, **20**, 633–643.
2. Vavilin, V.A., Vasiliev, V.B., Ponomarev, A.V., and Rytov, S.V. (1994a) *Biores. Technol.*, **48**, 1–8.
3. Newletter (1999) *IAWQ Specialist Group on Anaerobic Digestion. International Association on Water Quality.* No 5. January 1999, pp. 5–7.
4. Elfernik, S.O., Visser, A., Hulshoff, Pol L., and Stams, A.J.M. (1994) *FEMS Microbiological Reviews*, **15**, 119–136.
5. Kalyuzhnyi, S.V., Fedorovich, V.V., Lens, P., Hulshoff, Pol L., and Lettinga, G. (1998) *Biodegradation*, **9**(3–4), 187–199.
6. Vavilin, V.A., Vasiliev, V.B., Rytov, S.V., and Ponomarev, A.V. (1994b) *Biores. Technol.*, **49**, 105–119.
7. Parkin, G.F., Lynch, N.A., Kuo, W.-C., Van Keuren, E.L., and Bhattacharya, S.K. (1990) *J. WPCF*, **62**, 780–788.
8. Fomichev, A.V. and Vavilin, V.A. (1997) *Ecol. Modelling*, **95**, 133–144.
9. O'Flaherty, V. and Colleran, E. (1999) *Biores. Technol.*, **68**, 101–107.
10. Vavilin, V.A., Rytov, S.V., Lokshina, L.Ya., and Rintala, J.A. (1999) *In: Proc. II Intern. Sympos. On Anaerobic Digestion of Solid Wastes (Barcelona, 15–17 June, 1999)*, part II, pp. 1–4.
11. Veeken, A., Kalyuzhnyi, S., Scharff, H., and Hamelers, B. J. (2000) *Environ. Engineering*, **126**, No. 12, 1100–1111.
12. Salminen, E., Rintala, J.A., Lokshina, L.Ya., and Vavilin, V.A. (2000) *Wat. Sci. Tech.*, **36**, No. 6–7, 531–538.
13. Vavilin, V.A., Rytov, S.V., Lokshina, L.Ya., Kotsyurbenko, O.R., Nozhevnikova, A.N., and Parshina, S.N. (1997). *Wat. Sci. Tech.*, **36**, No. 6–7, 531–538.
14. Vavilin, V.A., Lokshina, L.Ya., Rytov, S.V., Kotsyubenko, O.R., and Nozhevnikova, A.N. (2000). *Biores. Techn.*, **71**, 195–209.
15. Lokshina, L.Ya., and Vavilin, V.A (1999) *Ecol. Modelling*, **117**, 285–303.
16. Lokshina, L.Ya., Vavilin, V.A., Kettunen, R.H., Holliger, Ch., and Nozhevnikova, A.N. (submitted) *Wat. Res.*