

Two-particle model of anaerobic solid state fermentation

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Abstract A structured mathematical model of anaerobic solid state fermentation (ASSF) has been developed. Since a stable ASSF requires addition of significant quantities of methanogenic seed sludge and mass-transfer limitation becomes important, the model postulates the existence of two different types of particles inside the fermenting solid mass – so-called “seed” particles with low biodegradability and high methanogenic activity and so-called “waste” particles with high biodegradability and low methanogenic activity. Any particle is assumed to be a completely mixed reactor and mass transfer of solutes between the particles is brought about by diffusion. The model includes multiple-reaction stoichiometry, microbial growth kinetics, material balances, liquid-gas interactions and liquid phase equilibrium chemistry. The theoretical model agrees on the qualitative level with existing experimental studies of ASSF. Hypothetical computer simulations are presented to illustrate the influence of biodegradability and mass transfer intensity on the stability of ASSF. On this basis, possible measures are proposed to prevent accumulation of volatile fatty acids inside the “seed” particles beyond their assimilative methanogenic capacity.

Keywords Anaerobic solid state fermentation; biodegradability; diffusion; mathematical model

Introduction

Anaerobic solid state fermentation (ASSF) is now becoming economically attractive in comparison with the conventional practice of treatment of municipal solid waste (MSW) because it is substantially cheaper than incineration and landfilling and not more expensive than aerobic composting. Additional advantages of ASSF are generation of energy carrier (methane) and reduction of CO₂ emissions, which are responsible for global warming. From the mechanistic point of view, ASSF is an extremely complex multiple-stage process mediated by a variety of microorganisms where organic matter is finally mineralised. The remaining hardly biodegradable part of waste is stabilised and can be used as fertiliser or soil conditioner comparable with aerobic compost. In general, the overall anaerobic digestion of organic fraction of MSW can be roughly distinguished into four metabolic stages: *hydrolysis* (complex insoluble organic material is solubilized by enzymes excreted by hydrolytic microorganisms); *acidogenesis* (soluble organic components including the products of hydrolysis are converted into organic acids, alcohols, hydrogen and carbon dioxide); *acetogenesis* (the products of the acidogenesis are converted into acetic acid, hydrogen and carbon dioxide); *methanogenesis* (methane is produced from acetic acid, hydrogen and carbon dioxide as well as directly from other substrates such as formic acid, methanol and methylamines). In well-balanced anaerobic decomposition, all products of a previous metabolic stage are converted into the next one resulting in a nearly complete conversion of the anaerobically biodegradable organic material into end products (methane, carbon dioxide, hydrogen sulphide and ammonia) without significant accumulation of intermediary products. But the real practice of operation of ASSF reactors on source separated MSW (so-called biowaste) revealed some problems in maintaining a stable digestion process especially during the start up. The majority of these problems is related with a frequently occurring imbalance between acid production (more fast) and acid consumption (more slow) in the system. To mitigate these unwanted phenomena, several

approaches (addition of a sufficient amount of methanogenic seed material, addition of buffers, dilution of waste, aerobic pre-treatment, spatial separation of acid formation and methanogenesis combined with leachate recycling) were experimentally investigated (Ten Brummeler, 1993). Since the ASSF requires an accurate process control, a mathematical modelling is essentially needed. However, according to our knowledge, only few mathematical models were proposed till now devoted directly to ASSF. Thus, the objectives of this work were:

- (1) to develop a theoretical mathematical model of ASSF taking into account multiple-reaction stoichiometry and mass transfer inside the system;
- (2) to investigate with help of the model possible scenarios of process development under various conditions.

Computational methods

Simulations were performed on an IBM-compatible personal computer by numeric integration of the set of differential equations with an automatic selection of time step by a computer program based on a Runge-Kutta (4th order) technique. On each step of numeric integration, pH values were calculated using an iteration technique with automatic selection of the roots according to the physical sense. The computer program was written by authors in Turbo Pascal in a generalised form, where a variable number of steps, organisms, components, substrate and inoculum data could be specified. The program created an output data file in a format suitable for graphic processing.

Results and discussion

Model postulates and development

Development of the model is based on abundant experimental material and experience accumulated in the Department of Environmental Technology, Wageningen Agriculture University, the Netherlands during 15 years studies of ASSF of biowaste (Ten Brummeler, 1993; Veeken and Hamelers, 1999; Veeken *et al.*, 2000). These biowastes usually contain approximately 50% of organic material. The ASSF of biowaste has recently received a full-scale implementation in Lelystad (the Netherlands) due to the efforts of company Arcadis Heijdemij Realisatie (the corresponding technology is named BIOCEL, Figure 1).

Conceptual remarks and postulates:

1. Since stable ASSF of biowaste requires the addition of significant (approximately 50%) quantity of methanogenic seed sludge (Ten Brummeler, 1993), the model postulates the existence of two different types of particles inside the fermenting solid mass, so-called "seed" and "waste" particles (Figures 1 and 2). The first type of particles represents a digested solid material added as a seed with an already low biodegradability but a relatively high methanogenic activity. The second type of particles is fresh waste material added to the reactor to be digested with a high biodegradability and a low (if any) methanogenic activity.
2. Any particle is assumed to be completely mixed inside (concentration gradient of any component is absent along the particle length).
3. Both types of particles are tightly attached to each other (in other words, inter-particle distance is close to 0) and leachate recirculation is not applied. These assumptions were made to avoid an excessive complexity of the mathematical model, at least in the current stage of its development.
4. Exchange (mass transfer) of solutes between particles is brought about by diffusion.
5. There is no exchange of bacteria between particles.

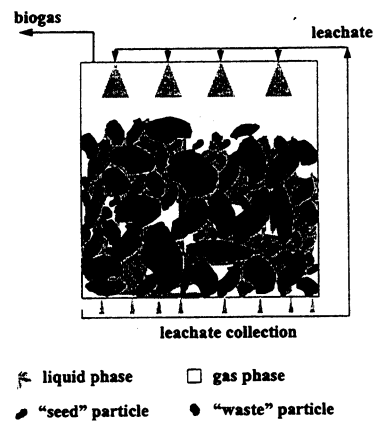


Figure 1 BIOCEL process

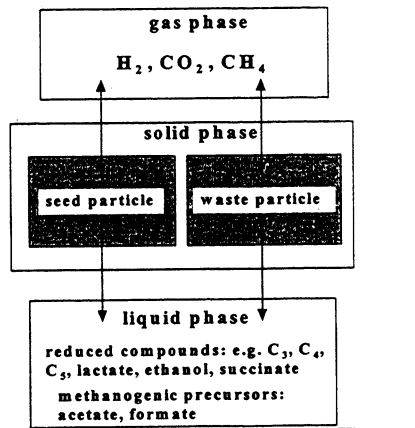
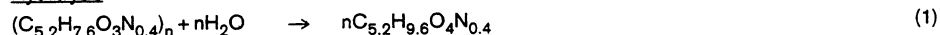
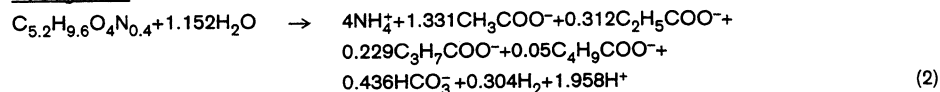
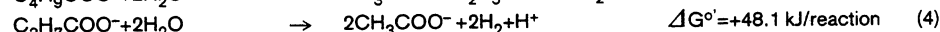
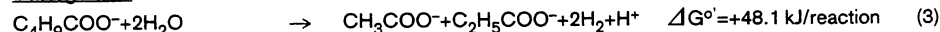
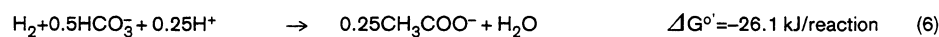


Figure 2 Schematic representation of two-particle model of ASSF

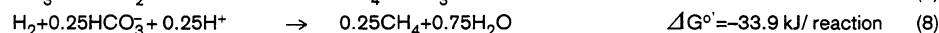
Stoichiometry. Since carbohydrates (cellulose, hemicellulose) and proteins are the main biodegradable components of the biowaste (Ten Brummeler, 1993), it was estimated that the biodegradable part roughly consists of 60% carbohydrates (representative formula – $C_6H_{12}O_6$) and 40% proteins (representative formula – C_4H_6ON) (Pavlostathis and Giraldo-Gomez, 1991). Combining these two formulas, the stoichiometric formula of hypothetical monomer of particulate biodegradable matter can be expressed as $C_{5.2}H_{9.6}O_4N_{0.4}$. During fermentation of monomer, C_2 – C_5 VFA were detected as major products in the liquid medium (Veeken *et al.*, 2000). Their ratio was estimated as acetate:propionate:butyrate:valerate (expressed in g COD/l)=0.51:0.21:0.22:0.06 (Veeken *et al.*, 2000) and this ratio was used below under postulation of stoichiometry of acidogenic step. All other fermentation products detected in minor quantities (lactate, ethanol, methanol, formate etc.) were neglected in the model to avoid its excessive complexity. The stoichiometry of acetogenic and methanogenic steps is quite trivial though a homoacetogenic step was introduced into the model to take into account consumption of hydrogen under suppressed methanogenesis.

The general reaction sequence by which the hypothetical polymer is transformed by the different groups of anaerobic bacteria can be presented (on molar basis) as:

Hydrolysis**Acidogenesis****Acetogenesis**

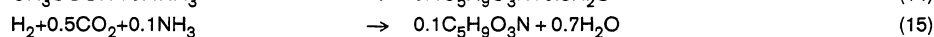
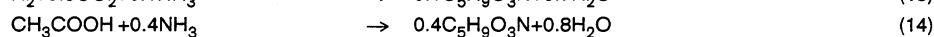
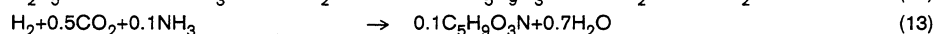
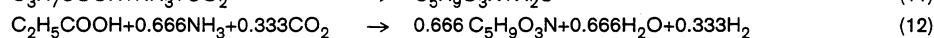
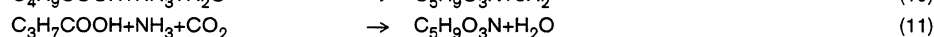
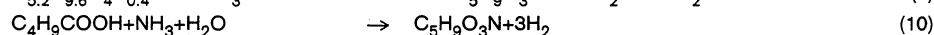
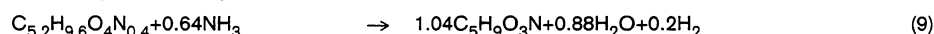


Methanogenesis

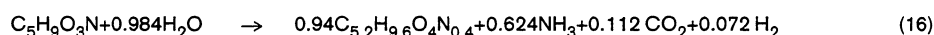


According to the stoichiometric scheme (1–8), the conversion process consists of 1 enzymatic step (reaction 1) and 7 bacterial steps (reactions 2–8). The latter steps are carried out by 6 groups of bacteria: the group X_1 contains all fermentative bacteria and is responsible for reaction (2); X_2 , all valerate- and butyrate-degrading acetogenic bacteria (AB) and reactions (3–4); X_3 , all propionate-degrading AB and reaction (5); X_4 , all homoacetogenic bacteria (HAB) and reaction (6); X_5 , all acetotrophic methanogenic bacteria (MB) and reaction (7); X_6 , all hydrogenotrophic MB and reaction (8).

The empirical formula $\text{C}_5\text{H}_9\text{O}_3\text{N}$ was chosen to represent anaerobic bacterial mass (Kalyuzhnyi, 1997). Thus, the corresponding stoichiometric equation for biomass formation can be written as:



Finally, to keep thoroughly a mass balance in the system, especially on carbon and nitrogen, the dead biomass was assumed to be a subject of hydrolysis with simultaneous production of the monomer according to the following equation:



Kinetics. The kinetics is based on the following assumptions and postulates.

1. Hydrolysis steps proceed according to the first order kinetics and the hydrolysis constant k is expressed by the equation adapted from Veeken *et al.* (2000) for ASSF of biowaste:

$$k [\text{day}^{-1}] = 0.012 \cdot \text{pH} - 0.042 \quad (17)$$

2. For all bacterial steps, reaction kinetics for carbon dioxide, ammonia and water is of zero order in their concentrations because they are present in saturated concentrations in the reactor medium.
3. Growth of biomass proceeds according to so called equilibrium-based kinetics (Hoh and Cord-Ruwish, 1996) with pH modulation:

$$\mu_j = \mu_{m,j} \left(\frac{S_i - I_i}{K_i + S_i + I_i} \right) F_j(\text{pH}), \quad (18)$$

where $\mu_{(m),j}$ – (maximum) specific growth rate of bacteria j ; S_i – concentration of substrate i ; K_i – Monod saturation constant for substrate i .

Equilibrium-based growth equation was used to correctly predict growth rates of AB when they should be zero due to the free energy change being zero. The general form of inhibition term I in eq. (18) is derived from mass-action ratio and for a unique growth limiting substrate has a form:

$$I = \frac{P_1 \cdot P_2 \cdot \dots \cdot P_n}{K_e}, \quad (19)$$

where $K_e = \exp(-\Delta G^0/RT)$,

4. The effect of pH on the growth rates is described by a second degree Michaelis pH function, normalised to give a value of 1.0 as the centre value (Kalyuzhnyi, 1997):

$$F(\text{pH}) = \frac{1 + 2 \cdot 10^{0.5(\text{pK}_l - \text{pH})}}{1 + 10^{(\text{pH} - \text{pK}_l)} + 10^{(\text{pK}_u - \text{pH})}}, \quad (20)$$

where pK_l and pK_u – lower and upper pH drop-off values for growth rate, respectively.

5. All product formations are directly coupled to biomass production due to the dissimilatory nature of anaerobic digestion.
6. Bacterial decay is described by first order kinetics.
7. Substrate consumption for maintenance is incorporated in the overall biomass yield.

Liquid phase equilibrium chemistry. For calculation of pH values and concentrations of (un)dissociated species forms inside the both particles during the process, we used the approach described previously (Kalyuzhnyi, 1997). In short, the pH value is calculated from the ionic balance equation, which includes all the ionised compounds in the liquid phase of each particle.

Mass transfer between particles. According to our assumption, mass transfer of solutes between particles is brought about by diffusion. In a simplified way, the rate of this transport M_i can be represented as:

$$M_i = \frac{2D_i(S_{i,s} - S_{i,w})}{L_s^2 + L_w^2}, \quad (21)$$

where D_i – diffusion coefficient for substrate i in particle medium, L_s and L_w – lengths of “seed” (subscript s) and “waste” (subscript w) particles, respectively.

Material balances. Based on assumptions about a complete mixing inside both particles, a general material balance for any non-gaseous component in the liquid phase for batch reactor can be written as:

$$dS_{i,s(w)}/dt = r_{i,s(w)} + M_i \quad (22)$$

For liquid concentrations of gaseous compounds GS_i (hydrogen, methane carbon dioxide) certainly, Eq. (22) should contain an additional term describing a mass-transfer t_i into the gas phase, i.e.

$$\frac{dGS_{i,s(w)}}{dt} = r_{i,s(w)} + M_i - t_{i,s(w)}, \quad (23)$$

where

$$t_{i,s(w)} = k_L a (GS_{i,s(w)} - p_i / H_{e_i}), \quad (24)$$

where $k_L a$ – mass transfer coefficient from the liquid into the gas phase; H_{e_i} and p_i – Henry coefficient and partial pressure in the gas phase for i -gaseous substrate.

The partial pressure p_i in the gas volume is calculated by a component balance around the gas phase (total pressure in the reactor headspace was accepted to be equal to 1 atm):

$$\frac{dp_i}{dt} = \frac{t_i V_i V_L - G p_i}{V_g}, \quad (25)$$

where V_i – specific volume of i -gaseous substrate; V_L and V_g – volumes of reactor liquid and gas phases, respectively.

A total balance gives the gas volumetric flow rate G from the reactor:

$$G = V_1 \cdot \sum(t_i \cdot V_i) \quad (26)$$

Model parameters. The physico-chemical model parameters were directly taken from the literature (Kalyuzhnyi, 1997). Bacterial model parameters (Table 1) were adapted from the previous model (Veeken *et al.*, 2000) or taken to be consistent with the literature data (Pavlostathis and Giraldo-Gomez, 1991). Diffusion coefficient for hydrogen was taken as $6.5 \cdot 10^{-6}$ cm²/s, for all other solutes – as $2.0 \cdot 10^{-6}$ cm²/s. For simplicity, L_s and L_w were accepted to be the same (0.5 cm).

Table 1 Bacterial parameters used in the model

Bacterial groups	μ_m , day ⁻¹	K_s , mM	Y , g VSS/mol	b , day ⁻¹	pK_1	pK_u
FB (X_1)	1.125	0.128	7.5	0.2	5.2	8.0
(Va+Bu)-AB (X_2)	1.65	0.283	7.5	0.03	6.2	8.0
Pr-AB (X_3)	0.8	0.53	5.0	0.01	6.2	8.0
HAB (X_4)	4.25	5.0	2.5	0.2	5.2	8.0
Ac-MB (X_5)	0.5	2.57	2.5	0.02	6.2	8.0
H ₂ -MB (X_6)	2.65	1.0	2.5	0.09	6.2	8.0

Simulation results

Typical results of computer simulations on the basis of the developed two-particle model are presented in Figure 3. It is seen that although a stable (in general) digestion process is met, big concentration differences are observed in “seed” and “waste” compartments of the BIOCEL reactor with regard to main variables of the process. During the first 8 days, a significant accumulation of VFA (more than 40 mM) occurred inside “waste” particles (Figure 3a) resulting in a sharp decrease of pH (Figure 3b). It is obvious that such low pH values completely suppressed methanogenic and acetogenic activities in these

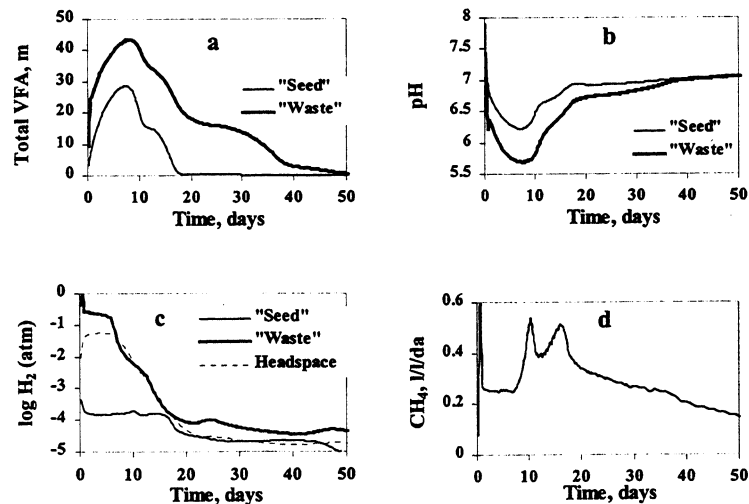


Figure 3 Simulation of “healthy” case of ASSF of biowaste: dynamics of VFA (a), pH (b), H₂ (c) inside the “seed” and “waste” particles and methane production rate (d)

compartments. The latter is supported by high hydrogen concentrations (Figure 3c) inside “waste” particles during the first week of the process. However, due to existence of mass-transfer limitations between the particles, an accumulation of VFA inside “seed” particles (Figure 3a) was relatively moderate (less than 30 mM) and drop in pH values was not so pronounced (Figure 3b). Such conditions allow the “seed” microflora to perform VFA consumption which can be seen from low concentrations of hydrogen inside “seed” environments (Figure 3c) and stable specific rate of methane production (0.25 l/l/day, Figure 3d) during this period. Further on (days 10–20), the “seed” microflora actively consumed accumulated VFA (Figure 3a) leading to restoration of pH values not only inside the “seed” but also the “waste” compartments (Figure 3b). This resulted in increased specific rate of methane production in the reactor (>0.4 l/l/day, Figure 3d). In the late stage of the run (days 20–50), the specific rate of methane production began to decrease (Figure 3d) due to exhaustion of biodegradable matter in the system. The limiting step of methane production in this period was mainly a transfer of VFA from “waste” to “seed” particles though VFA-consuming and methanogenic activities of “waste” microflora also increased substantially. Finally, the former “waste” particles became new “seed” particles with regard to their biodegradability and methanogenic activity.

In general, Figure 3 represents a so-called “healthy” case of ASSF of biowaste when VFA accumulation inside the “seed” particles is beyond their assimilative methanogenic capacity. A variety of other computer simulations has been undertaken to determine the main factors influencing the stability of the process. Figure 4 demonstrates an impact of the two most important – biodegradability of biowaste and intensity of transport of solutes between the particles. It is seen that increase of both parameters after a certain limit led to the development of “unhealthy” scenarios of ASSF of biowaste, i.e. complete acidification of not only the “waste” but also the “seed” compartments (Figures 4a and 4c). As a result, specific rate of methane production decreased to the end of the run (Figures 4b and 4d).

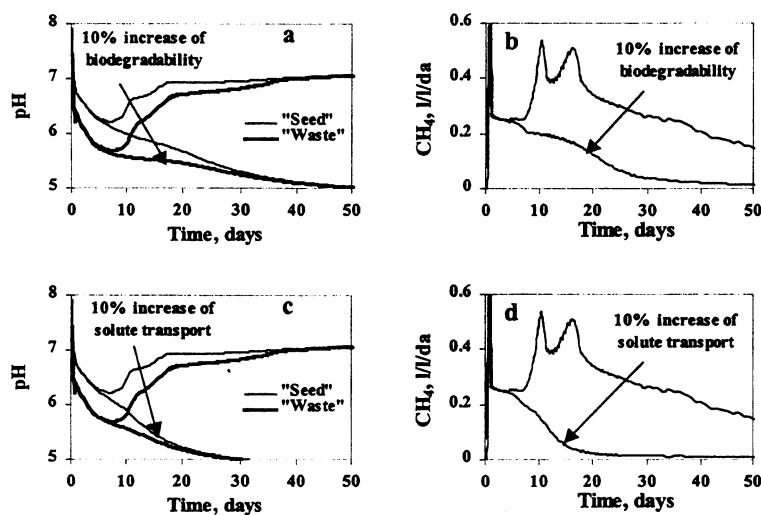


Figure 4 Impact of waste biodegradability and intensity of solute transport on stability of ASSF according to the model

Conclusions

The developed theoretical two-particle model gives mathematical expression to the innovative concept of the mechanism of material metabolism in ASSF and agrees on the qualitative level with existing experimental studies of this process. According to the model, the crucial point in reaching a “healthy” ASSF in a one-stage batch process consists of prevention of VFA accumulation inside the “seed” particles beyond their assimilative methanogenic capacity. Possible measures can include the following:

- to reduce the biodegradability of waste (e.g., by dilution with poorly degradable materials);
- to slow down the transport of solute (mainly VFA) from “waste” to “seed” particles (e.g., space separation of both types of particles).
- plug-flow reactor with semi-continuous feeding.

Though we could not find yet a proper set of experimental data to validate the model quantitatively, the first step has been already undertaken in this direction. On the basis of the two-particle model, Veeken and Hamelers (2000) have developed the reactor model to interpret their experiments on ASSF of biowaste with leachate recirculation. Further development of practical experiments is expected to confirm the declared approach.

Acknowledgement

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References

- Hoh, C.Y. and Cord-Ruwish, R. (1996). A practical kinetic model that considers end product inhibition in anaerobic digestion processes by including the equilibrium constant. *Biotechnol. Bioeng.*, **51**, 597–604.
- Kalyuzhnyi, S.V. (1997). Batch anaerobic digestion of glucose and its mathematical modeling. II. Description, verification and application of model. *Biores. Technol.*, **59**, 249–256.
- Pavlostathis, S.G. and Giraldo-Gomez, E. (1991). Kinetics of anaerobic treatment: a critical review. *Crit. Rev. Environ. Control*, **21**, 411–490.
- Ten Brummeler, E. (1993). Dry anaerobic digestion of organic fraction of municipal solid waste. Ph.D. Thesis. Wageningen Agriculture University. The Netherlands.
- Veeken, A. and Hamelers, B. (1999). Effect of temperature on hydrolysis rate of selected biowaste components. *Biores. Technol.*, **69**, 249–254.
- Veeken, A. and Hamelers, B. (2000). Effect of substrate-seed mixing and leachate recirculation on solid state digestion of biowaste. *Wat. Sci. Tech.*, **41**(3), 255–262 (this issue).
- Veeken, A., Kalyuzhnyi, S., Scharff, H. and Hamelers, B. (2000). Inhibition of anaerobic hydrolysis of biowaste by pH and VFA: experimental observations and simulations. *J. Environ. Engin.* (submitted for publication).