

IMPLEMENTATION OF ADM 1 MODEL IN AQUASIM BIOFILM REACTOR COMPARTMENT

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Abstract

A simulator based on Anaerobic Digestion Model no.1 (ADM 1) and the AQUASIM Biofilm Reactor Compartment is built. It is observed that in order to use the AQUASIM Biofilm Reactor Compartment without numerical errors, the ADM 1 model has to be implemented solely as a set of differential equations (DE); quite different to the conventional approach of differential algebraic equation format (DAE). The simulator is then used to analyze the behavioral deviations of a completely mixed bioreactor due to the formation of biofilms on the reactor surfaces. Simulations show that a thin biofilm formation does not really instigate a major digression in the reactor performance; however it does have a propensity to increase the stability of the bioreactor primarily through the increased biomass concentration and the reduced accumulation of intermediates. A detailed sensitivity analysis is also carried out to identify the affects due to uncertainty of additional mass transfer (and other) parameters used in the biofilm model. The analysis shows that the uncertainties due to these extra parameters do not lead to significant deviations in the majority of the simulation outputs apart from the case of biofilm thickness.

Keywords: ADM 1, biofilm, modeling, simulation

1 Introduction

The main scope of this study is to develop an anaerobic biofilm reactor model based on the generic Anaerobic Digestion Model no. 1 structure [1] together with AQUASIM "Biofilm Reactor Compartment" [2] to simulate anaerobic digestion processes with both suspended and attached (biofilm) biomass. The model is to be used to analyze the effects of biofilm formation in a completely mixed anaerobic digester under different operating conditions. A completely mixed bio-reactor with biofilms, often unintentional and unavoidable, may probably lead to deviated behavior from so called

ideal CSTR. In addition to the biofilm formation, several other factors like the presence of agglomerated bio particles, poor mixing and the formation of dead volumes can also lead to a system with significant concentration gradients and increased sludge retention times, closely resembling a biofilm reactor rather than an ideal CSTR. Hence the approach can also benefit modeling other common bio-reactor types which can be modeled as combinations of ideal and non-ideal CSTRs; for example an Upflow Anaerobic Sludge Blanket (UASB) reactor may be approximated with two non ideal CSTRs. The current text is primarily aimed at recognizing and implementing the necessary structural changes required for using ADM 1 together with AQUASIM Biofilm Reactor Compartment.

It has been suggested that full execution of the ADM 1 model in a biofilm configuration would result a unified model structure for anaerobic biofilm reactors [3]. However according to the authors' previous experience [4] full implementation of the ADM 1 model in "AQUASIM Biofilm Reactor Compartment" cannot be done by exactly following the way it has been implemented for a CSTR. This is primarily due to the difference in the way of representing physico-chemical processes (mainly acid-base dissociation reactions) in the two different cases, in order to acquire a numerically solvable equation system. Acid-base reactions in the ADM 1 model can either be implemented as a combination of differential and algebraic sets of equations (DAE) or a set of differential equations (DE). The standard (commonly available) ADM 1 simulators implemented for a CSTR (using AQUASIM), use the DAE approach. This is possibly due to the fact that DE approach can result in a stiffer equation system with higher level of numerical inaccuracies.

2 Methodology

When implementing the model in the AQUASIM Biofilm Reactor Compartment (BRC), the DAE approach cannot be used, because the solver used in

the BRC model can not numerically handle the resulting differential algebraic equation system. Thus, a direct conversion of the existing CSTR based ADM 1 simulator into a biofilm simulator is not possible without sufficient changes in the program structure. The required structural changes have basically to do with removing the acid-base equilibrium processes from the program and re-defining them as dynamic processes together with the additional rate terms for the generation of free forms of the acids from their respective ionic forms. This process is illustrated next (sections 2.1 and 2.2) by taking the inorganic carbon $\text{CO}_2/\text{HCO}_3^-$ pair as example.

2.1 DAE Implementation

Under this scheme, the total inorganic carbon (IC) concentration is defined as a dynamic state variable and included in the mass balance analysis (Eq. 1),

$$\frac{dS_{IC}}{dt} = \frac{q}{V}(S_{IC,in} - S_{IC}) + \sum R_j - R_{T,CO_2} \quad (1)$$

$\sum R_j$ represents the summation of generation rates according to the ADM1 stoichiometric matrix. R_{T,CO_2} is the additional CO_2 loss rate due to dynamic gas transfer from liquid phase to headspace (gas and liquid phases in the digester are not considered to be in equilibrium). The concentrations of CO_2 and HCO_3^- are related by the Inorganic carbon (IC) balance (Eq. 2) and equilibrium relation [5] between CO_2 and HCO_3^- (Eq. 3).

$$S_{IC} = S_{CO_2} + S_{HCO_3} \quad (2)$$

$$S_{HCO_3} = \frac{K_{a,CO_2} S_{IC}}{(K_{a,CO_2} + S_{H^+})} \quad (3)$$

2.2 DE Implementation

Under DE implementation, the total IC, is no longer considered. Instead the both components (free component CO_2 and ionic component HCO_3^-) are represented in two different mass balance equations (Eq. 4 & Eq. 5).

$$\frac{dS_{CO_2}}{dt} = \frac{q}{V}(S_{CO_2,in} - S_{CO_2}) + \sum R_j - R_{T,CO_2} + R_{A/BCO_2} \quad (4)$$

$$\frac{dS_{HCO_3}}{dt} = -\frac{q}{V} S_{HCO_3} - R_{A/BCO_2} \quad (5)$$

Equilibrium relation is also no longer used. However an additional rate equation is required to accommodate the dynamic generation of free form (CO_2) from its ionic form (HCO_3^-), (Eq. 6)

$$R_{A/BCO_2} = K_{A/BCO_2}(S_{HCO_3} \cdot S_{H^+} - K_{a,CO_2} \cdot S_{CO_2}) \quad (6)$$

Here K_{A/BCO_2} is the rate coefficient of the base to acid reaction. It is observed that the convergence of the solution is very sensitive to the order of the value of this coefficient.

The same procedure described above is repeated for Inorganic Nitrogen (IN) system ($\text{NH}_3/\text{NH}_4^+$), and volatile fatty acids (VFA) systems (Free acid/ ionic form systems for Acetic, Propionic, Butyric and Valeric). One more (algebraic) equation for ionic charge balance combined with water dissociation is required to close the equation system (Eq. 7).

$$S_{H^+} + S_{NH_4^+} + S_{Cat^+} - S_{HCO_3^-} - S_{OH^-} - \frac{S_{Ac^-}}{64} - \frac{S_{Pr^-}}{112} - \frac{S_{Bu^-}}{160} - \frac{S_{Va^-}}{208} - S_{An^-} = 0 \quad (7)$$

Here S_{Cat^+} and S_{An^-} represent the other cations and anions in the system which are not considered relevant to any processes but should have to be considered to close the charge neutrality of the solution. The values in the denominators of VFAs are the COD equivalents of one mole of respective acid. These values are there just for the sake of converting their concentrations into Kmol/m^3 . This is required because the concentrations of VFAs are defined as Kg COD/m^3 in the ADM1 model (while other ions are defined in Kmol/m^3).

2.3 Simulator Development

An AQUASIM program file was constructed with ADM 1 model using the Biofilm Reactor Compartment as the reactor configuration. The standard DAE format was initially used. Upon recognizing the incompatibility of this format with the Biofilm Reactor Compartment, the program structure was changed from DAE to DE format (as explained in section 2.2). During that process, "Total concentration" variables were replaced with "Free concentration" variables adding six new dynamic processes to represent the "ionic" to "free" conversion reactions. (4 processes for VFAs and two for IC and IN) in place of their equilibrium processes defined under DAE format. The charge balance and the water dissociation were combined together to form one single equilibrium expression under the DE implementation. Also relevant acid/base concentration variables were changed from their originally defined "equilibrium state variable" condition to "dynamic volume state variable" condition. Quite different to the DAE mode, the convergence of the solution is detected to be extra sensitive to some of the kinetic constants when the DE approach is adopted.

It is also found that the solution will not converge for some higher values of boundary layer mass transfer

resistances. Thus the correct selection of diffusion coefficients is observed to be crucial for a convergent solution. Very low diffusion coefficients will, for example, lead to high boundary layer resistances and the model will not yield a converging solution. Note that for the ideal CSTR case, mass transfer is not included; but for the biofilm (and in most “real processes”), mass transfer limitation can become a significant phenomenon.

The diffusion coefficients of the components in the biofilm were taken as their “effective” values, approximately taken as 0.6 times the diffusion coefficients of them through pure water [6]. Diffusion coefficients of components in water were taken from Cunningham (2001) [6]. For the components where diffusion coefficients were not found, a general average value of $0.004147 \text{ m}^2/\text{d}$ was used. (Sensitivity analysis revealed that these values have a low sensitivity to the final simulation results; see section 3).

The biofilm is modeled as a film growing on a cylindrical surface inside a cylindrical reactor. This makes the biofilm surface area vary with the growth of the film and is introduced in the form,

$$A = 2\pi(L + l_o)(r - z) \quad (8)$$

Where A is the biofilm surface area and L and r are the wetted length of the cylindrical reactor and the radius of the reactor respectively. z denotes the space coordinate perpendicular to the biofilm substratum (surface of the cylinder). Additional biofilm area due to reactor bottom, mixer, etc. can be introduced as an additional wetted length l_o for the sake of simplicity. This is possible since the reactor volume and the biofilm surface area are introduced independently into the program.

2.4 Simulation

Simulations were carried out using two AQUASIM programs developed with identical operational conditions and parametric values. One is for simulating an ideal CSTR configuration (completely mixed reactor compartment without biofilm) and the other program simulating a completely mixed bulk liquid compartment interacting with a biofilm matrix growing on available surfaces, implemented in AQUASIMs “Biofilm reactor compartment” (as explained in section 2.3). The simulation profiles for the ideal CSTR and the biofilm bulk zone were then compared against each other. The common operational inputs used in simulations are tabulated below (Table 1). These specific values were selected to closely resemble a laboratory scale reactor in operation at Telemark University College. In addition to these operational conditions, all the other parameters and constants (kinetic and other) were given the typical values listed under ADM 1.

Table 1: Main operational parameters

Parameter	Value
Reactor volume	0.01 m^3
Headspace volume	0.00595 m^3
Feed flow rate	$0.0005 \text{ m}^3/\text{day}$
Feed composition (Kg COD/ m^3)	Proteins: 6 Carbohydrates: 4 Lipids: 0 Sugar (monosaccharides): 0

The biofilm compartment was configured as a “confined” reactor with a rigid structure with no suspended solids in the pore volume. Surface detachment is taken equal to 0.63 times the growth velocity of the biofilm (when growth velocity is positive; otherwise, zero detachment).

3 Results and Discussion

Figure 1 and Figure 2 shows the simulation profiles for the Biofilm reactor configuration and the ideal CSTR configuration, respectively. The CSTR case was simulated for 100 days while the biofilm reactor was simulated for 200 days to achieve (pseudo) steady states. The biofilm thickness did not reach a steady level even within 200 days (Fig. 1a) and simulation shows that at least a 400 + days duration is required for the biofilm thickness to show any sign of a level off under the currently selected conditions. The program started to become numerically unstable at higher simulation times (after 418 days duration). The increasing biofilm thickness simulated towards the end of the simulations did not influence the other simulated parameters, that remained at stable levels, implying a pseudo steady state. Some parameters did not stabilize within the simulation time shown for the ideal CSTR either, as discussed below.

The biofilm is grown to a thickness of 0.04 mm during the 200 days simulation time. This is comparatively a thin biofilm and is expected to represent biofilm formation in a laboratory scale rigorously stirred reactor with high fluid shear stresses.

3.1 Ideal CSTR Vs Biofilm

Comparing the methane generation, it is decided to compare the liquid phase methane concentrations at steady state as a direct and simple way of comparison. By this mean, additional uncertainties involved in liquid-gas transfer were avoided. The ideal CSTR configuration produced $0.0393 \text{ Kg COD}/\text{m}^3$ at steady state while the CSTR with Biofilm produced a slightly lower value of $0.0348 \text{ Kg COD}/\text{m}^3$ (Fig. 1b and Fig. 2a). This difference is shown to be numerically

significant even when the uncertainties due to different model parameters are considered (see section 3.2). However the approximately close methane generation by the two models is an expectable observation under the conditions of simulation (exactly similar operating conditions, similar kinetics and a very thin biofilm formation). Besides the uncertainty caused by additional model parameters used in the biofilm model, there can also be an added uncertainty caused by the model structures themselves and is not quantified here. Hence the small difference in methane productions of the two model configurations is not really considered to be significant although they are in fact numerically distinguishable over parameter uncertainties.

The biofilm reactor has obtained a total biomass concentration of 4.63 Kg COD /m³ at the end of the 200 day simulation period; while the ideal CSTR configuration yields a significantly lower total biomass concentration of 1.17 Kg COD/m³ (Fig 1c-1 , Fig. 1c-2 and Fig 2b). This is a realistic simulation that illustrates the main reason why operators and designers try to obtain biofilm (or other types of aggregates) growth. Higher retention of biomass due to biofilm formation can increase the overall biomass concentration. This in fact will increase the reactor reserve capacity leading to a more stable reactor under external disturbances and implying that more compact reactors can be designed. Additionally, Fig. 1d illustrates the biomass profiles (volume fractions of biomass) in the biofilm matrix zone at about the 200th day simulation time. It can be noticed that there are no steep spatial gradients of the biomass profiles inside the biofilm; an expected result for a thin biofilm. Also certain species selected by their higher growth rates dominate the biofilm. The even distribution of the bacterial species involved can be of advantage for the process, making the exchange of the intermediate products between the species more efficient.

Long chain fatty acids (LCFA) accumulation profiles are quite different in the two reactor configurations. In the biofilm bulk phase, LCFA concentration reaches a peak at 0.36 Kg COD/m³ on around 60th day and then it reduces quite rapidly (Fig. 1e). In the case of the ideal CSTR, LCFA concentration continues to rise (Fig. 2c). Finally it stabilizes approximately at 0.1 Kg COD/m³ after more than 300 days (simulation profile not shown here). LCFA accumulation in anaerobic digesters can inhibit all microbial species and probably acetoclastic methanogens are more heavily inhibited. The lower average LCFA accumulation level in the biofilm configuration further increases the stability of this bio-reaction system, reducing its susceptibility to LCFA inhibition. Such inhibition is, however, not currently included in the ADM 1 model in its standard form and is thus not included in the simulations performed in this study.

Simulation results for VFAs for the two different models are illustrated in Fig. 1f, Fig. 1g and Fig. 2d. The concentrations of free VFAs diminish after about 100 days in the biofilm mode and it is the ionic forms that are prevalent. For the CSTR case it is observed that ionic forms are in negligible concentrations (results not shown here) and VFAs basically exist in free form. The total VFA concentrations are, however, higher for the biofilm case. Note that a major model structure change has been done in the way of implementing these ionic dissociation reactions when we modify the model structure to accommodate biofilm phenomena. Hence it is expected that there could be a relatively high uncertainty caused by the model structure itself on the outputs of VFA variables. However in general it can be expressed that the lower amounts of free acids (compared to ionic form) lead to a less inhibition on organisms. Lower free VFA accumulation is a sign of a more stable digester with higher reserve capacity to handle shock loads or other disturbances, again favoring the biofilm mode reactors.

Several other variables behave in a somewhat similar manner in the two models. Inhibition factors, feed particulates (lipids, proteins and particulate carbohydrates), inorganic carbon and soluble COD are such variables with resembling profiles in the two model configurations (see Fig. 1 and Fig. 2).

Fig.1 (a),(b), (c1), (c2), (e), (f),(g), (h), (i),(j),(k) : Simulation profiles for the bulk liquid zone in BRC

Fig. 1(d): Biomass profile in biofilm solid matrix in BRC at day 200

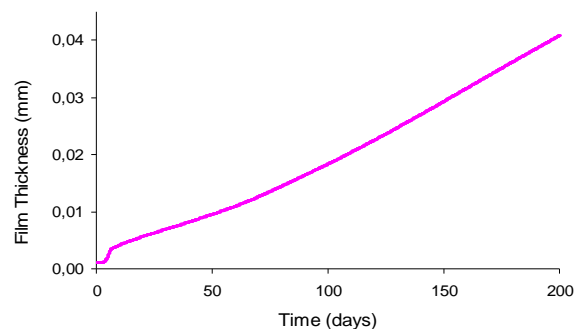


Fig.1(a) : Development of biofilm thickness

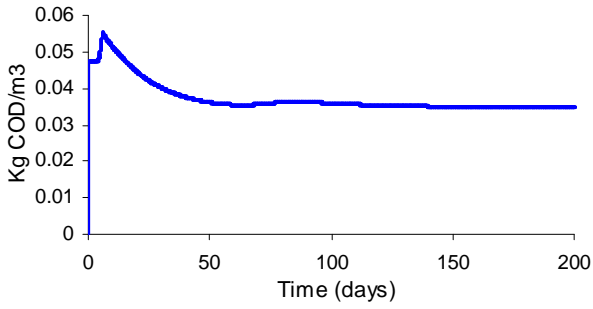


Fig.1(b) : Reactor CH₄ concentration

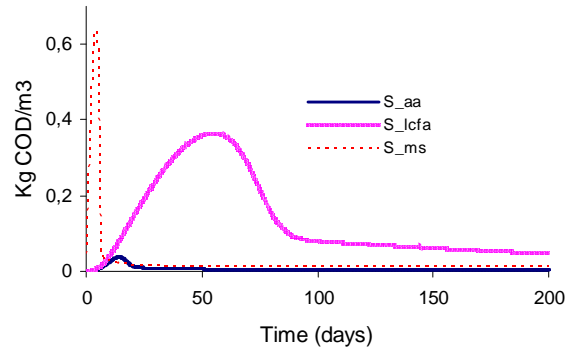


Fig.1(e) : Soluble intermediates

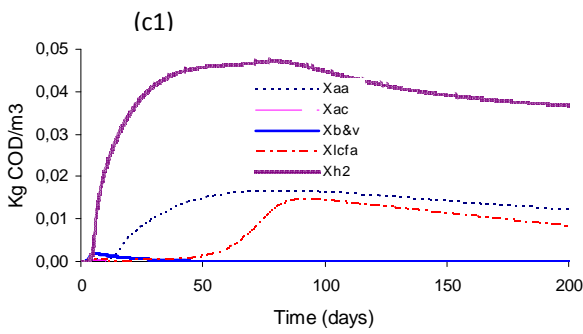


Fig.1-(c1) & (c2) : Biomass concentrations

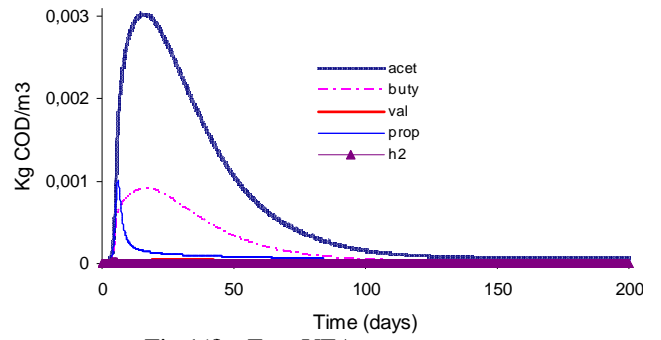


Fig.1(f) : Free VFAs

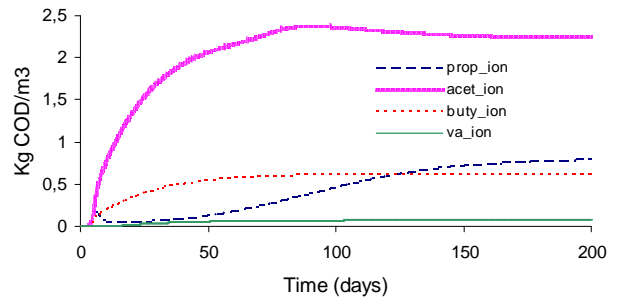
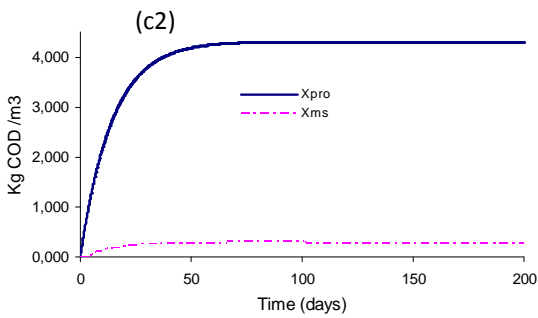


Fig. 1(g): Dissociated VFAs

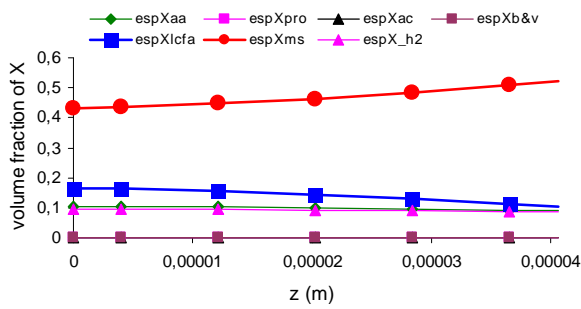


Fig. 1(d): Volume fractions of biomass in biofilm matrix

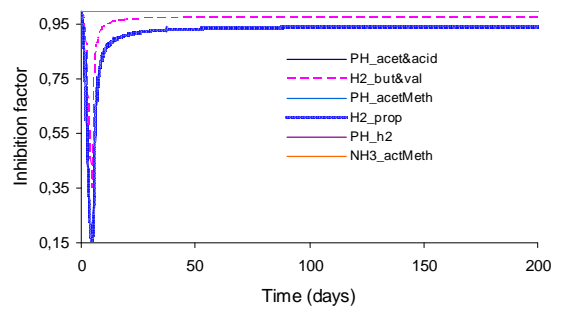


Fig.1(h) : Inhibition factors

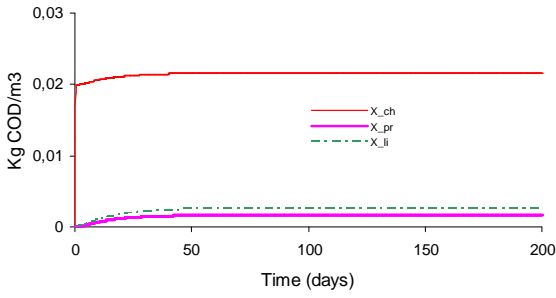


Fig.1(i) : Particulate substrates

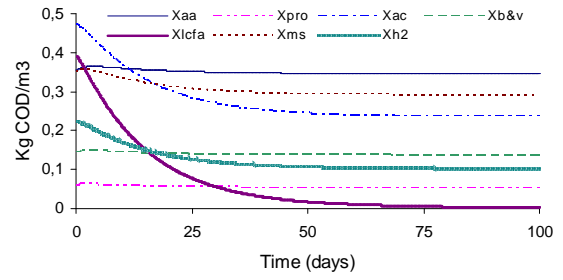


Fig. 2(b): Biomass concentrations

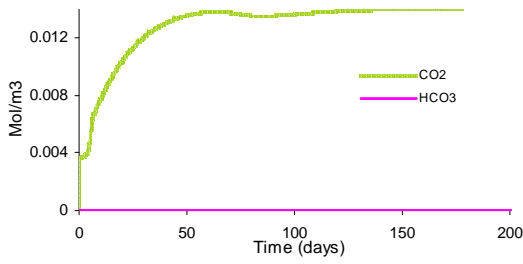


Fig.1(j) : Inorganic carbon

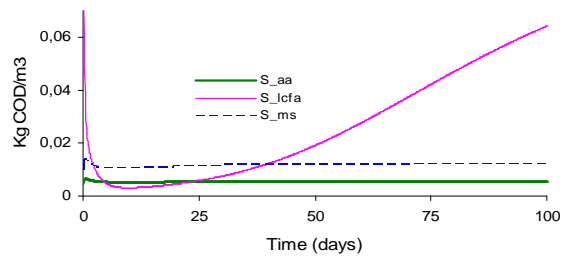


Fig. 2 (c) : Soluble Intermediates

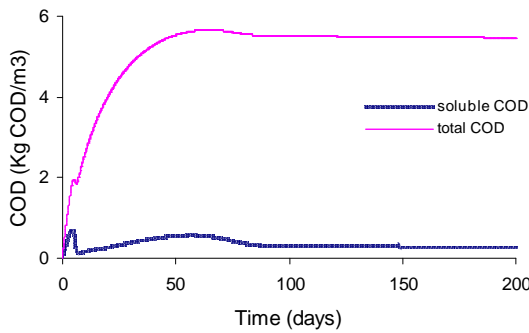


Fig.1(k) : Chemical oxygen demand

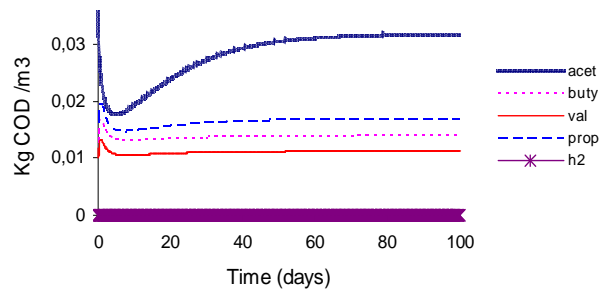


Fig. 2(d): Total VFAs

Fig. 2(a) to Fig 2 (h): Simulation profiles for the ideal CSTR configuration

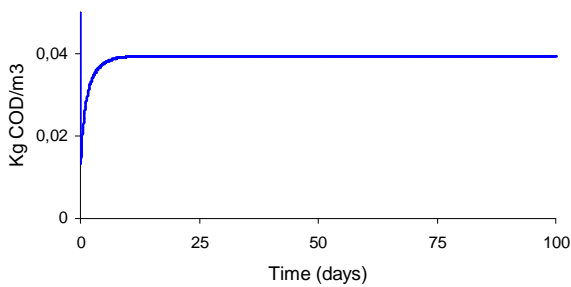


Fig. 2(a): Reactor CH₄ concentration

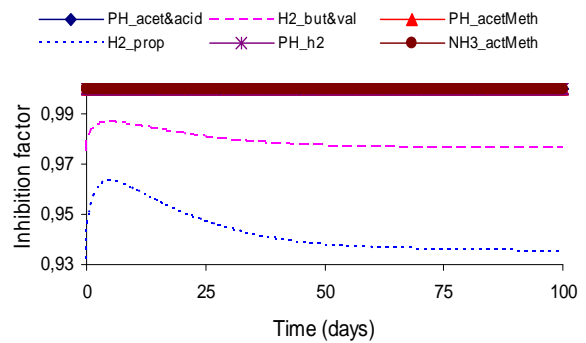


Fig. 2(e) : Inhibition factors

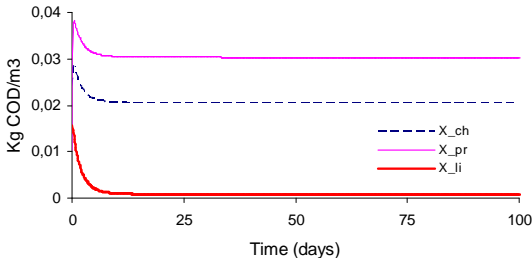


Fig. 2(f): Particulate substrates

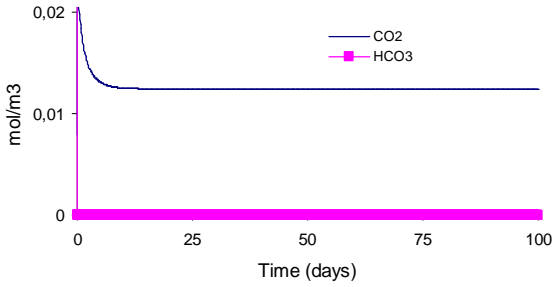


Fig. 2(g): Inorganic carbon

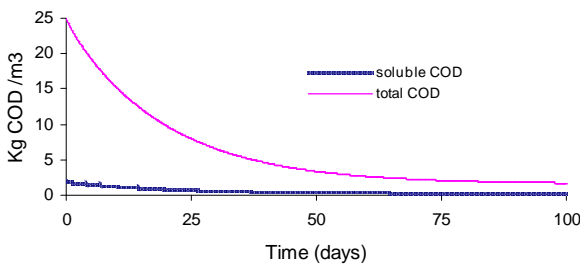


Fig. 2(h): Chemical oxygen demand

3.2 Uncertainty and Sensitivity Analysis

In addition to the difference in reactor configurations in the two cases tested, it is plausible that the additional parameters used in the biofilm model can lead to an additional uncertainty in the model results. Thus this additional uncertainty must be tested to differentiate it from the real difference in the results of the two models. The eleven (11) different diffusion coefficient parameters used in the biofilm model are directly selected for a sensitivity analysis. In addition, kinetic constant for CO₂-HCO₃⁻ acid-base reaction (*K_{ab_co2}*), volume-specific liquid-gas transfer coefficient (*k_{la}*), boundary layer thickness (*LL*), maximum bacterial density in the biofilm (*rho*) are also selected for sensitivity analysis due to either their highly variant/uncertain nature or the known high sensitivity towards the model results. In AQUASIM, the uncertainty is determined by using the following error propagation formula which is based on the

linearized propagation of standard deviations of the parameters of interest.

$$\sigma_y = \sqrt{\sum_{i=1}^m \left(\frac{\partial y}{\partial p_i} \right)^2 \sigma_{p_i}^2} \tag{9}$$

Here *p_i* are the uncertain parameters of interest and σ_{p_i} represents their standard deviations. Then σ_y is the (approximately) estimated standard deviation of the model output *y* at any given point of space and time. Figure 3 illustrates the result of the development of biofilm thickness with time. The upper and lower error bounds generated by the uncertainty of the parameters clearly show that the expected error would increase with time evolution. Biofilm thickness is recognized to be the most uncertain model result according to the analysis performed. Fortunately most of the other model outputs (other than the biofilm thickness) do not show this higher level of uncertainty. For example, the result for CH₄ generation (as bulk liquid phase concentration) from the two models can simply be numerically distinguished after taking care of the uncertainty. Figure 4 shows the CH₄ generation from the two models with respective error bounds.

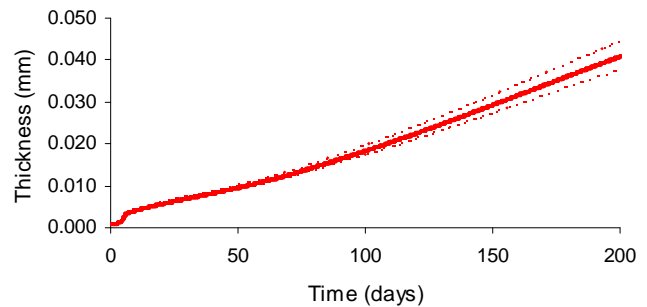


Fig.3: Development of biofilm thickness with respective error bounds

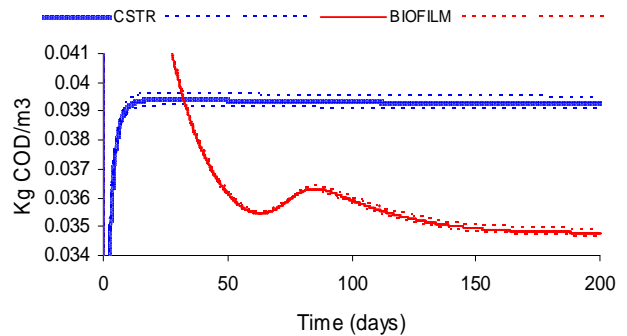


Fig. 4: Comparison of CH₄ generation according to the two models with their error bounds

3.2.1 Sensitivity Ranking

After performing the sensitivity analysis, a sensitivity ranking was carried out to recognize the most important parameters influencing different state variables at different compartments of the biofilm. However this sensitivity ranking process was very computational intensive and took more than 12 hours on a PC (Pentium D, 2.8 GHz CPU; 1.0 GB ram; Windows XP OP sys.) to complete only the bulk volume and biofilm matrix compartments (excluding the pore volume). Table 2 demonstrates the recognized ranking of the parameters of interest influencing the output variable s_{ch4} ; CH_4 concentration in the bulk volume compartment. It tabulates the selected parameters of interest according to the descending order of the average absolute value of the “absolute relative” sensitivity function (Eq. 10), and the error contribution of each parameter (Eq. 11),

$$\delta_{y,p}^{a,r} = p \frac{\partial y}{\partial p} \quad (10) \quad \delta_{y,p}^{err} = \frac{\partial y}{\partial p} \sigma_p \quad (11)$$

Where, y is the model output variable and p represents any parameter of interest (in AQUASIM, p must be defined as a constant variable or a real list variable).

σ_p is the standard deviation of p . The absolute relative sensitivity function $\delta_{y,p}^{a,r}$ gives the absolute change in y per 100% change in parameter p . Although several other types of sensitivity functions can be defined, for comparison of the effect of different parameters on a common model output, “absolute relative” sensitivity function is considered to be the most suitable. This is because the units of the parameter p do not affect the unit of the sensitivity value.

Table 2: Sensitivity ranking of the selected parameters on CH_4 concentration in biofilm bulk zone

Rank	Parameter	Sensitivity AR (kg COD.m-3)	Error contribution (kg COD.m-3)
1	rho	0.0007918	7.918e-005
2	kAB_co2	0.0003995	3.995e-005
3	kLa	0.0002485	2.485e-005
4	DSms	4.597e-005	4.597e-006
5	LL	2.196e-005	2.196e-006
6	DSvfa	7.755e-006	7.755e-007
7	DSlcf	6.412e-006	6.412e-007
8	DSaa	2.373e-006	2.373e-007
9	DX	1.657e-006	1.657e-007
10	DXcbh	1.63e-006	1.63e-007
11	DXlip	1.491e-006	1.491e-007
12	DXpro	1.471e-006	1.471e-007
13	DSact	1.14e-006	1.14e-007
14	DSh2	1.122e-006	1.122e-007
15	DSch4	5.507e-010	5.507e-011

According to the Table 2, bacterial density, CO_2-HCO_3 kinetic coefficient, liquid gas transfer coefficient and boundary layer thickness are among the most sensitive parameters affecting the model output S_{ch4} . The diffusion coefficients show a relatively lesser sensitivity. Even though this order may change upon the considered variable, it is observed that “rho” and Kab_{co2} are the most sensitive parameters for the majority of the variables in bulk liquid compartment of the biofilm.

3.4 Further Improvements

The two models must be further compared against each other on the performance under various disturbances. For example, it can be tested on the behavior under an aerobic invasion or a shock loading.

The current simulation was carried out with a thin biofilm layer formation (resembling a typical lab scale CSTR reactor in operation). It is also interesting to observe the outcome when the biofilm is allowed to grow thicker and possesses a more significant volume fraction from the total reactor volume. Moreover, the program structure must have to be improved further to handle numerical instabilities occurring at higher simulation times.

It is our experience that the prediction of pH is observed to be unsatisfactory in the standard ADM1 model for many cases. The same drawback was noted here and is basically due to the difficult guess-estimation of various ionic species including other cations and anions not involved in the reactions of interest. Anyway no attempt was made here to optimize the pH predictions, as the main objective of this study was quite different.

4 Conclusions

Implementation of the ADM1 model based on a “Differential Equation- DE” approach was found to facilitate the use of “AQUASIM biofilm reactor compartment” to develop an anaerobic digestion simulator to account for reactions occurring in both the dispersed bulk liquid and in microbial aggregates.

Simulations of a completely mixed bioreactor with biofilm formation on surfaces and an ideal CSTR model having no biofilm effect both gave realistic and roughly similar results.

The methane generation rate was similar but numerically significantly different in the two cases. The simulations show that the biofilm tend to increase the digester stability through increased total reactor biomass and reduced level of accumulation of inhibitory intermediates.

A sensitivity analysis was performed to recognize the additional uncertainty induced by the extra parameters used in the biofilm model. Error bounds generated by the uncertainty of the selected parameters are small, except for the case of biofilm thickness.

5 General Nomenclature

DS / DX – diffusion coefficients

S – concentration / soluble substrate concentration

X – biomass / particulate substrate concentration

aa – amino acids

ac/act/acet – acetic acid or acetates

b&v – butyrate and valerate

bu/buty – butyric acid or butyrates

ch /cbh – carbohydrates

esp – volume fractions of biomass

h₂- hydrogen

in – inlet (concentration)

K_{a,co2} –equilibrium coefficient of CO₂(aq)/ HCO₃⁻ pair

lcfa – long chain fatty acids

li /lip – lipids

ms – monosaccharides

pro /pr – protein

prop – propionic acid /propionates

q – volumetric flow rate

R – rate of generation

t – time

V – reactor volume

va/val – valeric acid or valerates

vfa – volatile fatty acids

6 References

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