

# Mathematical modeling of primary sludge anaerobic hydrolysis

Efstathiou E.<sup>1</sup>, Mamais D.<sup>2\*</sup>, Tsourtis S.<sup>2</sup> and Tridimas P.<sup>2</sup>

<sup>1</sup>Athens Water and Sewerage Company S.A (E.Y.D.A.P.), Oropou 156, 11146, Galatsi, Athens, Greece

<sup>2</sup>Sanitary Engineering Laboratory, Department of Water Resources and Environmental Engineering, School of Civil Engineering, National Technical University of Athens, Iroon Polytechniou 9, Zografou 157 80, Athens, Greece

Received: 10/05/2017, Accepted: 15/05/2019, Available online: 15/05/2019

\*to whom all correspondence should be addressed: e-mail: mamais@central.ntua.gr

<https://doi.org/10.30955/gnj.002343>

## Abstract

The aim of this work was the application and evaluation of a mathematical model for the simulation of anaerobic hydrolysis and acid production processes. For the description of the processes involved, the Anaerobic Digestion Model ADM1 was employed. The ADM1 implementation in prefermenters is relatively easy, but the estimation of its components concentrations, kinetic parameters and stoichiometric coefficients, remains a problem to be solved. This study provides useful results for the ADM1 implementation in acid digesters design and operation. Model calibration and verification was performed using experimental data from two bench scale acid digesters operating at different temperatures (12, 20, 27 and 34 °C) and retention times (1,2, 4 and 6 days). Model sensitivity analysis illustrated that the values of pH, disintegration kinetic parameter and acetoclastic methanogenesis specific rate, as well as biomass and inert soluble COD concentrations in the primary sludge exert a significant influence on soluble COD production. Model parameters (disintegration and hydrolysis kinetic parameters and specific rate of methane production) as well as the temperature dependency of these parameters are given in this paper.

**Keywords:** Anaerobic sludge hydrolysis, mathematical modelling, prefermenter, temperature effect.

## 1. Introduction

Anaerobic biodegradation processes may be divided to at least three stages: hydrolysis, acid/acetogenesis and methanogenesis. These processes are normally catalyzed by intracellular or extracellular enzymes and act on the pool of available organic material. Disintegration of composites (such as dead biomass) to particulate constituents and their subsequent enzymatic hydrolysis to soluble monomers are extracellular processes. Digestion of soluble materials mediated by organisms is intracellular process and results in biomass growth and decay (IWA, 2002).

In the hydrolysis phase, the volatile suspended solids, mainly consisting of proteins (approx. 30%), carbohydrates (approx. 40%) and lipids (approx. 30%), are

hydrolyzed by means of extracellular enzymes to aminoacids, sugars and long chain fatty acids (LCFA) respectively. In acidogenesis phase the products from the hydrolysis are fermented into volatile acids and in subsequent acetogenesis phase LCFA as well as volatile fatty acids (VFA) except acetate are decomposed through  $\beta$ -oxidation (Brinch *et al.*, 1994). Finally, methane is produced in the last phase by means of two groups of methanogen bacteria: a) hydrogenotrophic methanogens, and b) acetoclastic or acetotrophic bacteria.

Acid phase digestion may be employed to produce soluble organic carbon suitable for use as energy substrate for two-stage biological denitrification or biological phosphorus removal (BNR), (Pitman *et al.*, 1992). Maximum production of soluble organic carbon can be achieved only when methane production has been effectively suppressed. The minimum cell residence time for methane production from lipids and volatile acids at mesophilic temperatures and normal pH values of 6.8 to 7.5 is approximately 2.5 to 4 days. However some methane is produced at much shorter detention times due to utilization of hydrogen produced during fermentation of carbohydrates and proteins to volatile acids. Minimum cell residence time for hydrogen utilizing bacteria at 37°C is 19 hours. Methane production also can be suppressed by reduction of pH below the normal range of 6.8 to 7.5 required by the methanogenic phase (Eastman and Ferguson, 1981).

*Guerrero et al.* (1999), reported that during primary sludge digestion an initial period between 1-10 days could be observed where hydrolysis – acidification were the controlling processes and very low methane production occurred. Following this initial period, VFA accumulation decreases and methane production becomes more important.

The Anaerobic Digestion model No. 1 (ADM1) (IWA, 2002), is a structured model with disintegration and hydrolysis, acidogenesis, acetogenesis and methanogenesis steps. Extracellular solubilisation steps are divided into disintegration and hydrolysis, of which the first is a largely non-biological step and converts composite particulate substrate to inerts, particulate carbohydrates,

proteins and lipids. The second is enzymatic hydrolysis of particulate carbohydrates, proteins and lipids to monosaccharides, aminoacids and long chain fatty acids (LCFA), respectively. Disintegration is mainly included to describe degradation of composite particulate material such as primary or waste activated sludge. The hydrolysis steps are to describe the degradation of well defined macromolecule substrates to each soluble monomer. All disintegration and hydrolysis kinetics are represented by first order kinetics. Two separate groups of acidogens degrade monosaccharide and aminoacids to organic acids, hydrogen and carbon dioxide. The organic acids are subsequently converted to acetate, hydrogen and carbon dioxide by acetogenic groups that utilize LCFA, butyrate and valerate (one microorganism group for both substrates), and propionate. The hydrogen produced by these organisms is consumed by a hydrogen-utilizing methanogenic group, and the acetate by an aceticlastic methanogenic group. Substrate based Monod-type kinetics (slightly different from ASM Monod growth-based kinetics) are used as the basis for all intracellular biochemical reactions. Death of biomass is represented by first order kinetics, and dead biomass is maintained in the system as composite particulate material. Several mechanisms of inhibition are described in the model that includes pH (all groups), hydrogen (acetogenic groups) and free ammonia (aceticlastic methanogens) inhibition. pH inhibition is implemented as one of two empirical equations, while hydrogen and free ammonia inhibition are represented by non-competitive functions. The other uptake regulating functions are secondary Monod kinetics for inorganic nitrogen (ammonia and ammonium), to prevent growth when nitrogen is limited, and competitive uptake of butyrate and valerate by the single group that utilizes these two organic acids. Mechanisms included to describe physico-chemical processes are acid-base reactions (to calculate concentrations of hydrogen ions, free ammonia and carbon dioxide), and non-equilibria liquid-gas transfer. Inorganic solids formation and precipitation is not included in the model due to the complexity of the precipitation kinetics and the relatively limited effect on SCOD in acid digesters.

The objective of this work was the application and evaluation of ADM1 for the simulation of anaerobic hydrolysis and acid production processes in primary sludge acid digesters. Model calibration and verification was performed using experimental data from two bench scale acid digesters operating at different temperatures (12, 20, 27 and 34 °C) and retention times (1,2, 4 and 6 d).

## 2. Materials and methods

### 2.1. Experimental set up and analytical methods

Experiments were conducted in two bench scale 5 L primary sludge acid digestion systems. Each of the reactors operated at a different hydraulic retention time, submerged in a water bath for constant temperature maintenance. The anaerobic hydrolysis of primary sludge was studied at four different temperatures: 12, 20, 27 and 34°C, and four different HRTs 1, 2, 4 and 6 days.

The reactors were operated in a pseudo-continuous flow mechanically stirred-tank mode, without sludge recycling (HRT = SRT). The reactors were fed once a day with primary sludge from a pilot municipal wastewater treatment plant (EYDAP, Research and Development Department). The overall duration of the acid digestion experiments was 8 months. Acid digesters experimental protocol was to operate each digester at constant temperature for at least 3 HRTs to reach steady state conditions. Thereafter, digester performance was evaluated for at least 10 HRTs before proceeding to the next phase. Every day the following parameters were measured in influent and effluent sludge samples:

- total and volatile solids (TS and VS)
- total and dissolved COD (TCOD and SCOD)
- ammonia nitrogen (NH<sub>4</sub>-N)

Total Kjeldahl Nitrogen (TKN) and volatile fatty acids (VFA) concentrations were also measured in a regular basis. All analyses were conducted according to Standard Methods (1989).

### 2.2. Mathematical model

ADM1 was used for the simulation of the acid digesters operation. All ADM1 biochemical processes and inhibition forms were applied, except from free ammonia inhibition. Due to the low pH the free ammonia concentration in the fermenters was low and therefore ammonia inhibition was considered negligible. The equations describing the hydrogen and methane transfer from the liquid to the gas phase were also included:

$$p_i = k_{La,i} (S_i - 16 \cdot K_{H,i} \cdot P_{gas,i})$$

Carbon dioxide was not included in the implementation as it is not necessary for the stages of hydrolysis and acidogenesis simulation.  $P_{gas,i}$  were equal to the partial atmospheric pressure of the gases, as the pilot fermenters were open.

In a continuous-flow stirred-tank reactor with constant volume  $V$ , constant inflow and outflow  $q$ , inflow dissolved and particulate constituents concentrations  $S_{i,in}$  and  $X_{i,in}$ , and effluent concentrations  $S_i$  and  $X_i$ , the mass balance for the dissolved constituents is:

$$\frac{dV S_i}{dt} = q S_{i,in} - q S_i + V r_i \Rightarrow \frac{dS_i}{dt} = \frac{1}{HRT} (S_{i,in} - S_i) + r_i$$

where  $r_i$  is the rate of constituent  $i$  production due to biochemical and liquid-gas transfer processes. The same equation applies for particulate constituents (SRT = HRT).

The key criticism of structured models to describe biological processes is the large number of parameters employed. In order to evaluate the effect of the various parameters employed on the output of the model, sensitivity analysis was performed for the different model parameters and particularly for:

- Different microorganism groups maximum specific uptake rates
- pH
- disintegration and hydrolysis first order parameters

- the carbohydrates, proteins and lipids concentration in the feed
- the anaerobic biomass concentration in the feed
- the acid/acetogens and methanogens percentage in this biomass.

### 3. Results and discussion

#### 3.1. Sensitivity analysis

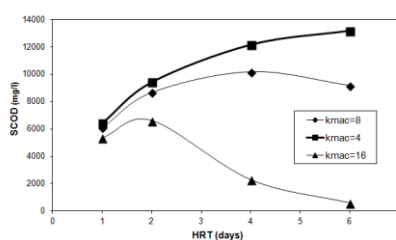
Sensitivity analysis was performed in order to evaluate the effects of the various model parameters on the output of ADM1 model.

**Table 1.** Primary sludge feed characteristics

Parameter	Value
TCOD (mg/l)	50.000
SCOD (mg/l)	1040
Inert SCOD $S_i$ (mg/l)	104 (10% SCOD)
Inert PCOD $X_i$ (mg/l)	2938 (6% PCOD)
TKN (mgN/l)	780
NH <sub>3</sub> -N (mgN/l)	110
Biomass (mgCOD/l)	6.500 (13% TCOD)
Acid/acetogen biomass (mgCOD/l)	5.850 (90% biomass)
Sugar ( $X_{su}$ ), amino acid ( $X_{aa}$ ), LCFA ( $X_{fa}$ ), valerate and butyrate ( $X_{c4}$ ), propionate degraders ( $X_{pro}$ ) (mgCOD/l)	1170 (each 18% of acid/acetogen biomass)
Methanogen biomass (mgCOD/l)	650 (10% biomass)
Aceticlastic ( $X_{ac}$ ) and hydrogen ( $X_{h2}$ )methanogens (mgCOD/l)	325 (5% biomass)
Butyric acid (mgCOD/l)	180
Propionic acid (mgCOD/l)	140
Acetic acid (mgCOD/l)	90
Sugars ( $S_{su}$ ), aminoacids ( $S_{aa}$ ), LCFA ( $S_{fa}$ ) and valeric acid ( $S_{va}$ ) (mgCOD/l)	Each component equal to $(SCOD-VFA-S_i)/4 = 131,5$
Carbohydrates ( $X_{ch}$ ), proteins ( $X_{pr}$ ), lipids ( $X_{li}$ ) (mgCOD/l)	0
Composite particulates $X_c$ (mgCOD/l)	PCOD - $X_i$ - biomass = 39.522

#### 3.1.1. Substrate maximum specific uptake rates

The model was solved for three different values of each microorganisms group maximum specific uptake rate: the ADM1 suggested value, 50% and 200% of this value (variability 100%). Especially for the fatty acids uptake rate 25% and 400% of the suggested value were also included (variability 400%). As it was expected, the value of each specific substrate uptake rate had a significant impact in the relative food concentration (sugars, aminoacids, fatty acids, butyrate, propionate, acetate, hydrogen). These substrate specific uptake rates however (except for acetate uptake rate) proved to have an insignificant effect on the final VFA concentration. On the other hand, as shown in Figure 1, acetate uptake rate exerted a significant impact in SCOD and VFA concentration.

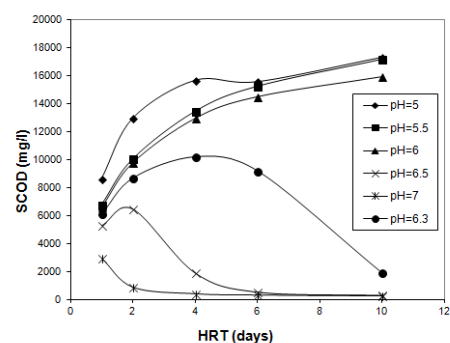


**Figure 1.** Acetate specific uptake rate effect in SCOD production

The impact of the model parameters on SCOD and especially on VFA production, was examined. The primary sludge feed characteristics used in the model sensitivity analysis are shown in Table 1. Anaerobic biomass in the feed was taken 13% of the TCOD as estimated by *Munch et al.* (1999). The same authors estimated that the portion of acid/acetogens and methanogens in the anaerobic biomass was equal to 90% and 10%, respectively. The operating digester temperature was 35°C, because ADM1 model parameters suggested values are set at 35°C, and pH = 6.3.

#### 3.1.2. pH

pH values effect considerably the anaerobic sludge hydrolysis yield. At pH values of less than 6, increasing residence time up to 20 days, results in a significant increase in effluent SCOD concentration due to a complete inhibition of methanogenesis. At pH values greater than 6, effluent SCOD concentration appears to have a maximum point, at a residence time between 2–4 days. Following that, SCOD concentration decreases with increasing residence time due to methane production (Figure 2).



**Figure 2.** pH effect in SCOD production

### 3.1.3. Disintegration and hydrolysis kinetic parameters

The disintegration first order parameter affects the effluent soluble COD concentration more than the respective hydrolysis constant, as according to the model, disintegration is considered the rate limiting step for particulate COD consumption and SCOD production. Therefore although the concentration of the particulate COD fractions (complex particulate, carbohydrate, protein and lipids) varies according to the value of the hydrolysis rate the concentrations of dissolved constituents, that are the final products of particulate substrates, are affected only by the disintegration rate variation.

### 3.1.4. Particulate material composition

Evaluation of the influence of particulate COD fractions (i.e. carbohydrates, proteins, lipids and inert COD) on the effluent SCOD and VFA production is very interesting as their actual measurement is difficult and time consuming. ADM1 task group assumes that primary sludge disintegrates to carbohydrates, lipids, proteins and inert material. The suggested fractions, reported as percent of the total influent COD are 20% for proteins and carbohydrates, 25% for lipids 25% for inert particulate COD and 10% for dissolved COD. Model sensitivity analysis showed that an increase in lipids from 20 to 45% of the total COD exerted a minor effect on SCOD and VFA yield. The same increase in proteins and carbohydrates fractions resulted in a small increase and decrease respectively in SCOD production, due to the decrease and increase respectively observed in the amount of methane produced from hydrogen consumption.

### 3.1.5. Biomass concentration in primary sludge

The concentration of each microorganism group in primary sludge is required as an input to the model. Estimation of anaerobic biomass concentration in primary sludge is difficult, and estimation of each microorganisms group concentration is almost impossible. Model sensitivity analysis was conducted for a total anaerobic biomass of 6%, 13% and 26% of TCOD in the feed and a methanogenic biomass of 10% and 30% of total anaerobic biomass. As shown in Table 1, acid/acetogen and methanogen biomass was divided equally among the various microorganism groups. According to sensitivity analysis the influence of biomass composition on SCOD production is very significant, due to the respective variation of available food and methane production. Methanogen biomass increase results in an increased methane production and a subsequent significant decrease in SCOD and VFA production.

### 3.2. Model calibration with experimental data

Preliminary model simulations according to the default values proposed by ADM1, resulted in effluent SCOD concentrations significantly higher than the measured ones. Therefore calibration of the model parameters was attempted in order to obtain a closer agreement to operational results of the two bench scale acid digesters. As described previously anaerobic sludge hydrolysis was studied at four different temperatures: 12, 20, 27 and 34°C, and four different HRTs 1, 2, 4 and 6 days.

The parameters describing methanogenesis (i.e. specific methanogenesis rate, methanogen biomass concentration in feed and pH inhibition coefficients) were estimated according to TCOD in the influent and effluent sludge samples. The difference between influent and effluent TCOD concentration was considered equal to methane production as hydrogen production was considered negligible. By SCOD and NH<sub>4</sub>-N fitting, disintegration and hydrolysis parameters were estimated, as NH<sub>4</sub>-N production is affected significantly only from these processes, and SCOD production is influenced by disintegration, hydrolysis and methane production.

During the experiments TCOD, SCOD and VFA (acetic, propionic and butyric acid) concentrations were measured in influent and effluent sludge samples obtained from the two lab scale acid digesters. The various fractions of SCOD were determined as follows: 10% of SCOD was considered to be inert COD, VFA concentration was set equal to the measured values and the non-VFA SCOD was divided equally to the remaining dissolved constituents of the model: sugars, aminoacids, LCFA and valeric acid. The various fractions of particulate COD (PCOD) were determined as follows: 6% PCOD was considered to be inert, and the rest PCOD was considered to be composite particulate material and biomass, while pure particulate constituents (carbohydrates, proteins and lipids) were supposed to be negligible. Anaerobic biomass in the feed sludge was 6% of the TCOD, and 10% of total anaerobic biomass was supposed to be methanogen. Disintegration of this composite particulate material yields 25% carbohydrates, proteins, lipids and inert particulate COD. Yield to inert soluble COD was supposed to be zero, as VFA concentration in pilot plant effluent was almost equal with SCOD.

ADM1 default values of various parameters are at 35°C. The influence of the temperature on the kinetic expressions (uptake rate, Monod and inhibition constants) is assumed to be exponential:  $F(T) = \exp[\theta(T-35)]$ , where  $\theta$  is the temperature coefficient. Parameters values in other temperatures were estimated using the temperature coefficients proposed by Siegrist *et al.* (2002).

Based on the experimental results obtained at 27°C, an overall TCOD reduction of approximately 20% was observed in the acid digesters. These results indicate that significant methane production was occurring at pH values between 5.5–6. However according to the initial values of pH inhibition coefficients, proposed by ADM1, negligible methane production should be expected at this low pH range. To simulate more accurately the experimental data pH inhibition coefficients were decreased to  $pH_{UL} = 6.5$  and  $pH_{LL} = 5$  from 7 and 6 respectively. Similarly according to the default model parameters there was a significant difference between SCOD concentration measured in effluent sludge samples and model output that tend to increase with increasing residence time. To obtain a closer agreement disintegration and hydrolysis rate were decreased and specific uptake rate from aceticlastic biomass was increased.

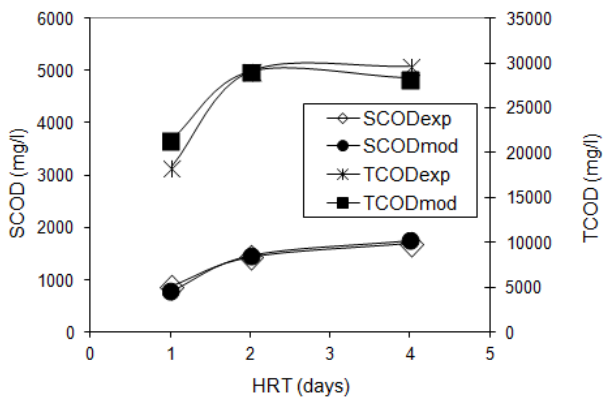


Figure 3. Experimental versus model results at 12 °C

Figures 3–6 illustrate the final results of the model simulation in comparison to the experimental results obtained at different temperatures and residence time. Model simulation is in good agreement with lab scale results especially at operating temperatures of 12°C and 20°C. Model results obtained at 27°C and 34°C and 4-6 days residence time appear to predict a higher hydrolysis increase compared to experimental data. This difference may be attributed to a higher inert particulate COD content in sludge feed than the one assumed by the model.

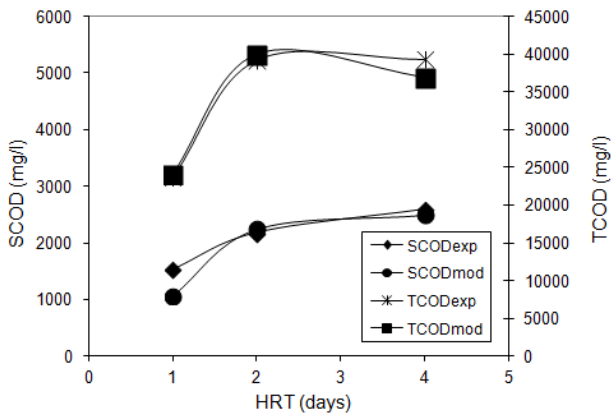


Figure 4. Experimental versus model results at 20 °C

The final values for disintegration and hydrolysis first order parameters and acetoclastic methanogenesis specific uptake rate estimated at various temperatures are shown

Table 2. Disintegration and hydrolysis first order parameters and acetoclastic methanogenesis specific uptake rate at various temperatures

Kinetic parameters	12°C	20°C	27°C	34°C
Disintegration first order kinetic parameter, $k_{dis}$ ( $d^{-1}$ )	0,095	0,14	0,22	0,30
Hydrolysis first order kinetic parameter, $k_{hyd}$ ( $d^{-1}$ )	1,90	2,80	4,40	6,00
Acetoclastic methanogenesis, $k_{m_{ac}}$ ( $d^{-1}$ )	3,30	4,40	10,50	14,00

in Table 2. From these values the following temperature dependence equations were derived:

- $k_{dis}(T) = 0.32 \exp[0.053(T-35)]$
- $k_{hyd}(T) = 6.4 \exp[0.053(T-35)]$
- $k_{m_{ac}}(T) = 15.7 \exp[0.071(T-35)]$

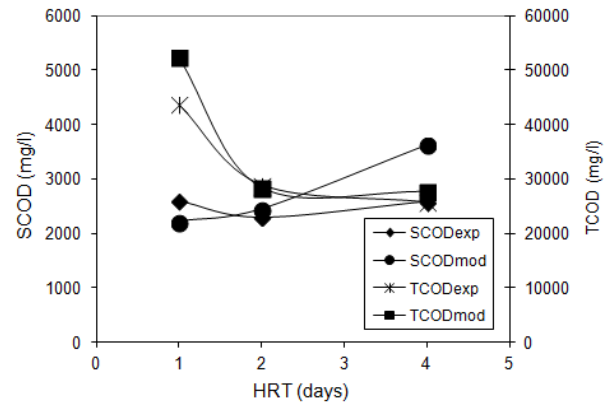


Figure 5. Experimental versus model results at 27 °C

The temperature dependence coefficient for disintegration and hydrolysis was 0.053, a value significantly higher than 0.024 reported by Siegrist *et al.* (2002), but comparable to 0,054 proposed by Ferreiro *et al.* (2003) for primary sludge hydrolysis. The temperature dependence coefficient for methanogenesis according to model calibration was equal to 0.071 in good agreement with the values reported by Siegrist *et al.* (0,069).

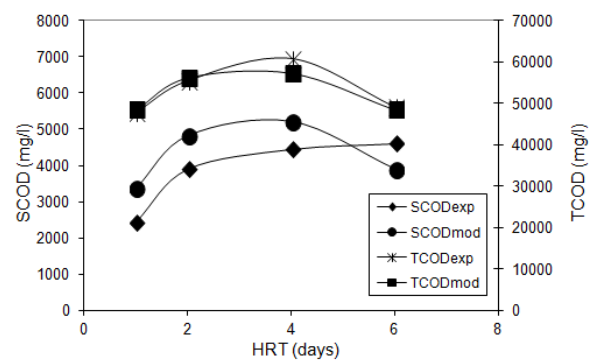


Figure 6. Experimental versus model results at 34 °C

The values of the disintegration and hydrolysis coefficients at 35°C, obtained according to the model and the experimental results presented in this study ( $k_{dis} = 0.32$ ,  $k_{hyd} = 6.4$ ) were lower than the ones proposed by ADM1 ( $k_{dis} = 0.5$ ,  $k_{hyd} = 10$ ). This was attributed to the long sludge retention time in the primary settling tank and the consequently high VFA concentration in the influent sludge indicating that fermentation of sludge commenced in the settling tanks. For the same reason the estimated value of acetoclastic methanogenesis parameter ( $k_{m\_ac} = 15.7$ ) appeared significantly higher than the default value ( $k_{m\_ac} = 8$ ) proposed by ADM1. The estimated values however are in agreement with the ones reported by Siegrist *et al.* (2002)  $k_{hyd} = 0.25$  (one step hydrolysis) and  $k_{m\_ac} = 14.8$ .

#### 4. Conclusions

ADM1 appears to simulate quite accurately the operation of acid digesters. However a complex problem is the estimation of the values of various substrate components concentrations, kinetic parameters and stoichiometric coefficients.

Model sensitivity analysis showed a significant dependence of the soluble COD and VFA yield from the pH value, disintegration kinetic parameter and acetoclastic methanogenesis specific rate, as well as biomass and inert soluble COD concentration in primary sludge.

Following calibration, model simulation was in good agreement with lab scale results at operating temperatures in the range from 12°C-34°C and residence time from 1-6 days. The values of rate parameters (disintegration and hydrolysis kinetic parameters) as well as their temperature dependence, estimated according to the model were comparable to values reported in the literature. Acetoclastic methanogenesis kinetic parameter according to model calibration was higher than the values reported in the literature. The higher acetoclastic methanogenesis kinetic parameter obtained according to the model was attributed to the long sludge retention time in the primary settling tank.

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