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Modeling and simulation of lab-scale anaerobic co-digestion of MEA waste

S. Wang [1] J. Hovland [2] R. Bakke [1]

[1] *Department of Process, Energy, and Environmental Technology, Telemark University College, Kjølnes Ring 56, Postboks 203, 3910 Porsgrunn, Norway. E-mail:* wang.shuai@hit.no; Rune.Bakke@hit.no

Kjølnes Ring 30, 3918 Porsgrunn, Norway.E-mail: Jon.Hovland@tel-tek.no

Abstract

Anaerobic digestion model No.1 (ADM1) was applied and expanded in this study to model and simulate anaerobic digestion (AD) of an industrial carbon capture reclaimer MEA (monoethanolamine) waste (MEAw) together with easily degradable organics. The general structure of ADM1 was not changed except for introducing state variables of MEA and complex organics (CO) in the waste and biochemical reactions of MEA uptake and CO hydrolysis in the model ADM1_MEAw. Experimental batch test results were used for calibrating kinetics variables. The obtained kinetics were employed in the ADM1_MEAw to simulate semi-continuously fed experimental test for 486 days at room temperature ($22 \pm 2\ ^oC$). The validation results show that the ADM1_MEAw was able to predict the process performance with reasonable accuracy, including process pH, biogas generation and inorganic nitrogen concentrations, for a wide range of feed scenarios. Free ammonia inhibition, was observed to be the main inhibitory effects on acetoclastic methanogenesis, leading to volatile fatty acids (VFA) accumulation at high loads. Inhibition assumed to be caused by potentially toxic constituents of MEAw appears to be much less important than ammonia, suggesting that such constituents were broken down by AD.

Keywords: ADM1, CO_2 capture, monoethanolamine waste, anaerobic digestion

1 Introduction

The anaerobic digestion model No.1 (ADM1) is a sophisticated model generated by the IWA Task Group for Mathematical Modeling of Anaerobic Digestion Processes (Batstone et al., 2002). The model includes 26 dynamic state variables, 19 biochemical and 3 gas-liquid transfer kinetic processes. It describes the AD processes of complex particulates through disintegration, hydrolysis, acidogenesis, acetogenesis to methanogenesis (Batstone et al., 2002). Disintegration is a physical process and the rest four biochemical processes are catalyzed by intra- or extracellular enzymes. The ADM1 model has been implemented to simulate AD of different industrial wastes and proved to be successful (Derbal et al., 2009; Ozkan-Yucel and Gokcay, 2010). Some extensions of the ADM1 were also established to account for the effects of micro-oxygen (Botheju et al., 2010), the degradation of phenolic compounds (Fezzani and Cheikh, 2009), and the formation and emission of odorants (Parker and Wu, 2006). Modifications that focus on specific process functions such as hydrolysis regarding the characteristics difference of feed organics (Yasui et al., 2008; Ramirez et al., 2009) were also implemented in ADM1. The ADM1 model is widely acknowledged as a powerful tool for investigating AD processes at various operating conditions and helpful in predicting the behavior of anaerobic digesters (Batstone et al., 2006).

Challenges in application of the ADM1 model also emerge. The structured model demands detailed characterizations of the organic compounds feeding in to

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the anaerobic digesters, including organics compositions of carbohydrates, protein, lipids and the inerts fractions to get reasonable model predictions (Kleerebezem and Loosdrecht, 2006). However, characterizations of the individual variables are generally not practical, at least not on a regular basis. Reasonably approximations are commonly made depending on the available characterization of the raw material and the waste measurements (such as Chemical Oxygen Demand (COD), Total Kjeldahl Nitrogen (TKN)) (Ramirez et al., 2009). The kinetic values of disintegration, hydrolysis and other biochemical processes can also vary in a large range, which require specifications for different investigated cases (Batstone et al., 2002).

In this study a new model ADM1_MEAw based on ADM1 was generated to investigate the AD of industrial reclaimer MEAw with easily bio-degradable organics. MEAw degradation processes and the observed inhibitory effects associated with MEAw degradation (Wang et al., 2013b) were included in ADM1_MEAw. Newly applied kinetic parameters were calibrated based on batch experimental study. The recommended kinetic parameters in standard ADM1 were mostly maintained with adjustments of the maximum uptake rates based on temperature effect. The aim was to assess to what extend the expanded model can simulate and predict the degradation process without applying fundamental changes in the ADM1 parameters. 486 days of lab-scale semi-continuously fed digester experimental data was applied for verifying the model parameters by comparing with simulation results. Biogas generation, pH, VFA accumulation etc. were simulated to assess the performance of model ADM1_MEAw.

2 Co-feed organics specification

Easily degradable organics: starch, glucose, peptone and yeast extract (Wang et al., 2013b) were used to co-digest with MEAw in AD. The co-feed substrates were used to provid necessary nutrients, minerals and easily degradable organics for cultivating healthy biomass that can tolerate exposure to toxic and inhibitory chemicals from the MEAw. Components of the easily degradable organics were specified according to the provided products' analysis information which contained mainly carbohydrate and amino acids (Table. 1) and their feed concentrations expressed in units consistent with ADM1 simulations are given in Table. 2.

3 MEA waste specification

The MEAw used in the experimental AD test was obtained from an industrial reclaimer unit for solvent recovery at a coal fired power plant where MEA was used as the CO_2 capture solvent. The MEA waste was generated due to MEA degradation, reactions with flue gas impurities etc. in the carbon capture process and accumulated together with added chemicals (e.g. corrosion inhibitors) at the bottom of the reclaimer unit after the solvent regeneration (da Silva et al., 2012; ElMoudir et al., 2012). The waste contained complex and not well identified chemicals, including MEA, organic chemicals from MEA degradation, corrosion inhibitors, heat stable salts and other inorganic components (Strazisar et al., 2003; Thitakamol et al., 2007). The detected chemicals were not well quantified, while MEA (C_2H_7NO), N-acetylethanolamine ($C_4H_9NO_2$, Eq. 1) and carboxylic acids (acetic, propionic and n-butyric acid) were supposed to be the main components in the MEAw used for the AD test (Strazisar et al., 2003, 2001).

$$C_2H_4O_2 + C_2H_7NO <=> C_4H_9NO_2 + H_2O \quad (1)$$

Implementation of all detected MEAw compounds to ADM1_MEAw is practically impossible and can easily cause errors due to the limited quantification data. Thus, MEAw composition was simplified to MEA and complex organics (CO) which contained inerts, degradable organics (e.g. N-acetylethanolamine) etc. Measurements showed that MEAw COD varied in a range from 450 to 900 mg-COD/g-waste, where MEA COD was assumed to be constant at 44% of the MEAw COD and the rest (56%) was CO COD. According to measurements and calculations, the MEA and nitrogen fractions were around 18 to 30 wt% and 7 - 14 wt%, respectively (Wang et al., 2013b). Alkalinity of the applied MEAw was measured to be 0.31 g/g MEAw ($CaCO_3$ equivalent) and was used to calculate the feed inorganic carbon concentrations in the model (Table. 2).

CO (Strazisar et al., 2003) was assumed to consist of mainly N-acetylethanolamine (0.46), inerts (0.54) and inorganic nitrogen (Table. 1). A portion of 30 % of the feed MEAw COD was termed as inerts (Table. 1 and 2) based on the conclusion that over 70 % MEAw was degraded in AD (Wang et al., 2013b). These inerts was determined to be not biodegraded and reluctant to biodegradation in the 486 days simulation of semi-continuously fed experimental test.

4 Suggested modification to ADM1

4.1 Modification of the basic ADM1 structure

Anaerobic degradation of MEAw involves mainly the degradation of MEA and MEA degradation products

Table 1: Characterizations of the feed organics

Stoichiometric parameters COD basis	Names	Values
f_{ch_Sta}	Particulate carbohydrate fraction in starch	1
f_{su_Glu}	Monosaccharides fraction in glucose	1
f_{aa_Ye}	Amino acid fraction in yeast extract	1
f_{aa_Pep}	Amino acid fraction in peptone	0.83
f_{su_Pep}	Monosaccharides fraction in peptone	0.17
f_{ac_CO}	Acetate fraction in CO	0.20^a
f_{MEA_CO}	MEA fraction in CO	0.26^a
f_{SI_CO}	Soluble inerts fraction in CO	0.54^b
f_{IN_CO}	Inorganic nitrogen released from CO	$0.0029 - 0.0039^c$

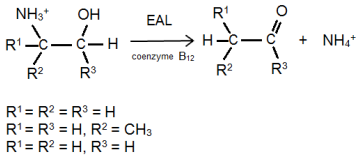
a, According to Eq. 1. b, Specified according to batch test with an assumption of 30 % inerts in the feed MEAw COD. c, calculated based on IN content in the MEAw.

Table 2: Characterizations of the feed organics

Compostion	Units	Feed concentration
Total carbohydrates	g-COD/L	2.6
Particulate carbohydrates	g-COD/L	$1.8(0)^a$
Soluble carbohydrates	g-COD/L	$0.8(2.6)^a$
Amino acid	g-COD/L	7.0
MEA	g-COD/L	0.8-6.9
Complex organics (CO)	g-COD/L	1.0-8.8
Inorganic carbon (IC)	$kmol/m^3$	$8 * 10^{-3}$-$4 * 10^{-2}$

a, when glucose was used instead of starch after 250 days in the semi-continuously fed test (Wang et al., 2013 b)

(e.g.N-acetylethanolamine) formed in the carbon capture process. Two hydrolysis processes were proposed for MEA degradation (Ndegwa et al., 2004). They are the hydrolysis of MEA to ammonium and acetaldehyde and the hydrolysis of acetaldehyde to ethanol and acetate. Two mechanisms are used to explain the synthesis of acetaldehyde from the degradation of MEA. One is the deamination by coenzyme B_{12}-dependent ethanolamine ammonia-lyase (Eq. 2) (Abend et al., 1999) and the other mechanism is the rearrangement of the NH_2 group by the process of bacterium LuTria3 (Speranza et al., 2006). Acetaldehyde can be directly degraded to acetate by consuming CO_2 in the anaerobic condition (Speranza et al., 2006).



(2)

To generally represent the degradation processes involved in AD of MEAw and comply with the composition simplifications, biodegradation of MEA to ammonium and acetate was included in ADM1_MEAw without considering the intermediate product acetaldehyde (Eq. 3). The biomass yield, Y_{MEA} was assumed to be 0.08 kg-COD biomass/kg-COD MEA (assumed to be the same as the standard organisms growing on amino acid) (Botheju et al., 2010). Empirical formula $CH_{1.4}O_{0.4}N_{0.2}$ ($C_5H_7O_2N$) (Eq. 3) was used to represent biomass (Eastman and Ferguson, 1981). Ethanol, which was not included in the standard ADM1 for its low concentration in AD digesters (Batstone et al., 2002) was also not considered here.

$$-\mathrm{NH_2CH_2CH_2OH}\text{-}0.488HCO_3^- + 0.696H^+ + 0.096H_2O + 0.96\mathrm{NH_4^+} + 1.144CH_3COOH + 0.2CH_{1.4}O_{0.4}N_{0.2} = 0 \quad (3)$$

The degradation of other MEAw organics was simplified to hydrolysis of CO. CO was assumed to consist of mainly N-acetylethanolamine, inerts and inorganic nitrogen (Table. 1). N-acetylethanolamine can be hydrolyzed to MEA and acetate (Eq. 1). In order to reduce the involved state variables, N-acetylethanolamine state variable was not created but its degradation products MEA and acetate were assumed to be released directly from CO hydrolysis. Inerts and inorganic nitrogen (IN) were also assumed to be released due to hydrolysis of CO in digester (Table. 1) to allow for a COD balance and an exact stoichiometric analysis. Inerts were defined as the organics that are not degraded in AD, for simplicity and avoiding an extra state, even if they may be degrad-

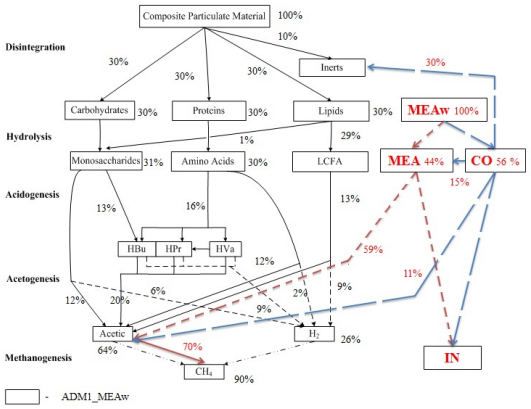


Figure 1: COD flux for the original ADM1 (black line) and the expanded ADM1_MEAw (color dashed lines). HBu - Butyric acid, HPr Propionic acid, HVa Valeric acid, LCPA - long chain fatty acid, MEA monoethanolamine, MEAw monoethanolamine waste, CO complex organics, IN inorganic nitrogen

able by giving favorable conditions. The schematic of the ADM1_MEAw is shown in Fig. 1.

First order kinetics was used for simulating CO hydrolysis. Monod kinetics was applied for the biodegradation of MEA (Botheju et al., 2010). Due to the organic structure similarity of MEA and amino acid, the MEA consuming biomass was assumed to be the standard amino acid degradation biomass, avoiding an extra state variable (Botheju et al., 2010). The added kinetics was shown in Table. 3. Initial standard ADM1 biochemical processes were unchanged in the extended model.

4.2 Inhibition simulation

The feed MEAw contains recalcitrant chemicals, for example corrosion inhibitors that are slowly or non-biodegradable and that may also inhibit microbial growth (Eide-Haugmo et al., 2009). A commonly used non-competitive inhibition function was applied in the extended ADM1 to account for the possible toxic effects on acetoclastic methanogenesis due to inhibition from the input MEAw and/or its degradation products (I_{MEAw}, Table. 3) (Wang et al., 2013b, 2014). Inhibition effect from free ammonia, included in the original ADM1 was the other inhibition factor anticipated in the AD of the MEAw due to the release of inorganic nitrogen. Together with the standard inhibition factors (pH, free ammonia and inorganic nitrogen limitation) (Batstone et al., 2002), the new acetate uptake inhibition is given in Eq. 4. Other inhibition factors in the original ADM1 processes were maintained.

$$I_{ac} = I_{pH,ac} I_{IN,lim} I_{NH_3} I_{MEAw} \tag{4}$$

The MEAw inhibition, $I_{MEAw} was formed as in Eq. 5$:

$$I_{MEAw} = \frac{1}{1 + S_{MEAw}/K_{IMEAw}} \tag{5}$$

4.3 Temperature effect

The lab-scale semi-continuously fed experiment was performed at room temperature ($22 \pm 2\ ^oC$), while batch experimental test and the original ADM1 were implemented in AQUASIM at standard 35 ^oC. Temperature is an important factor in determining the digestion rate, particular the rate of hydrolysis and methane formation (Tchobanoglous et al., 2003). Therefore, the temperature effects on the maximum uptake rates were accounted for in the extended model and modified by applying van′t Hoff-Arrhenius relationship as shown in Eq. 6, with a simplification in Eq. 7 (Tchobanoglous et al., 2003):

$$\frac{d(lnk)}{dT} = \frac{E}{RT^2} \tag{6}$$

Where, k = reaction rate constant, T = temperature, K= 273.15 $+^o C$, E = a constant characteristic of the reaction, J/mol, R = ideal gas constant, 8.314 J/mol·K.

Temperature coefficient θ was generated according to Arrhenius' equation:

$$\frac{k_2}{k_1} = \theta^{T_2 - T_1} \tag{7}$$

Where, T1 and T2 are the two temperatures and k_1 and k_2 are rate constants before and after adjustments, respectively. Typical values for θ vary from 1.02 to 1.10 for some biological treatment system (Tchobanoglous et al., 2003). A value of 1.05 was used to adjust all maximum uptake rates in the model from standard values given at 35 ^oC (Batstone et al., 2002).

4.4 Simple kinetic model development

A lab-scale hybrid digester was used in semi-continuously fed AD of MEAw (Wang et al., 2013a,b). The digester has two suspended phases and a biofilm phase in between and stacked in a plastic cylinder to retain long sludge retention times (Wang et al., 2013a,b). To comply with this concept, biomass retention factor $tres,_X$ (solids retention time in addition to hydraulic retention time) was employed in the expanded ADM1 and assigned a specific value. The mass balances for all

Table 3: State variables and parameters added in the extended ADM1

Parameter	Description	Units
S_{CO}	Complex organics (CO) concentration	$kg-COD/m^3$
S_{MEA}	MEA concentration	$kg-COD/m^3$
k_{hyd_CO}	First order CO hydrolysis rate	d^{-1}
K_{s_MEA}	Half saturation constant of MEA	$kg-COD/m^3$
K_{m_MEA}	Monod maximum specific uptake rate of MEA	d^{-1}
Y_{MEA}	Yield of biomass on MEA	kg-COD B/kg-COD S
I_{MEAw}	Inhibition function of MEAw	-
K_{I_MEAw}	50 % inhibitory MEAw concentration	$kg-COD/m^3$

the soluble and particulate state variables were modeled as given by Eq. 8, 9 and 10 (Batstone et al., 2002):

$$V\frac{dS}{dt} = Q(S_{in} - S) - r_s V \tag{8}$$

$$V\frac{dX}{dt} = Q(X_{in} - S) - \frac{X}{t_{res,X}/V + 1/Q} + \mu \mathrm{XV} \tag{9}$$

$$r_s = \mu_m S/(\mathrm{K}_s + S)\,\frac{X}{Y} \;=\; \mu \mathrm{X/Y} \tag{10}$$

Where S_{in} and S $(kg-COD/m^3)$ represent the COD feed in and flow out of the digester, respectively; V is the reactor working volume (m^3); Q is the flow rate (m^3/d); r_s is the COD consumption rate $(kg{-}COD/m^3{\cdot}d)$. X_{in} and X are biomass flows of the system, μ is the specific biomass growth rate (d^{-1}). Y $(kg-COD\ biomass/kg-COD)$ is the biomass yield. K_s is the half saturation constant $(kg{-}COD/m^3)$ and μ_m is the maximum biomass growth rate (d^{-1}).

4.5 Ion balance

The charge balance equation in ADM1 was modified to account for the MEA acidification (Eq. 11). MEA has a pK_a of 9.5 with buffer capacity and can influence the pH values in the AD reactor.

$$\begin{aligned} S_{H^+} - S_{OH^-} = S_{HCO_3^-} + \frac{S_{ac^-}}{64} + \frac{S_{pro^-}}{112} + \frac{S_{bu^-}}{160} \\ + \frac{S_{va^-}}{208} + S_{An^-} - \frac{S_{MEA^+}}{80} - S_{Cat^+} - S_{NH_4^+} \end{aligned} \tag{11}$$

Where $S_{MEA^+}$is the MEA ion concentration implemented in the ADM1, the concentration was calculated as follows:

$$S_{MEA,total} = S_{MEA^+} + S_{MEA} \tag{12}$$

The algebraic equation was formulated as:

$$S_{MEA^+} - \frac{S_{MEA,total} * S_{H^+}}{K_{a,MEA^+} + S_{H^+}} = 0 \tag{13}$$

5 Results and discussion

Model ADM1_MEAw based on ADM1 was calibrated first by implementing batch experimental data from the AD of MEAw with easily degradable organics at 35 ^oC. The calibrated kinetics and inhibitory factors (Table. 4) were then employed in ADM1_MEAw for the simulation of the semi-continuously fed digester performance at room temperature. 486 days of experimental data (Wang et al., 2013b) was used to compare with the model simulations.

5.1 Batch model simulation

The calibrated kinetic values for the batch model are given in Table. 4. An inhibition factor including both free ammonia and MEAw was introduced in the model (Eq. 4 and 5), where the input MEAw concentration was considered to be inhibitive to aceoclastic methanogenesis (Wang et al., 2013b) and the inhibition effects reduced along with the waste degradation. It is shown that simulated biogas accumulation complied with the experimental data reasonably well (Fig. 2, A). The simulated methane partial pressure accounted for 80 % in the biogas (Fig. 2, B), which was in similar level as that obtained in the semi-continuously fed experimental test (Wang et al., 2013b).

Simulated pH varied and stabilized around 8.0 (Fig. 3, A) when the biogas generation almost ceased after 7 days of retention (Fig. 2, A). The simulated finial pH was close to the measurement of pH 8.2. Simulation showed that acetate uptake was inhibited mainly by free ammonia (Fig. 3, B). The inhibition from MEAw and hydrogen (Batstone et al., 2002) were strong at the beginning of the test and gradually reduced with time, attributing to the degradation of the inhibitory chemicals (Fig. 3, B). VFA accumulation was not observed at the end of both the test and simulation.

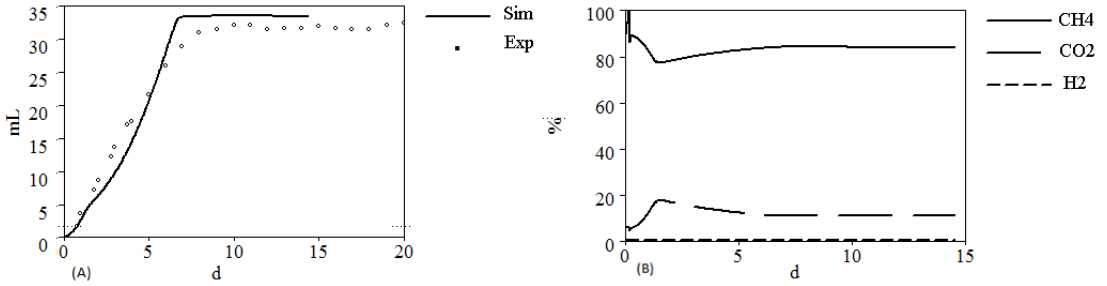


Figure 2: Biogas accumulation (A) and partial gas pressure (B) simulated by the extended model

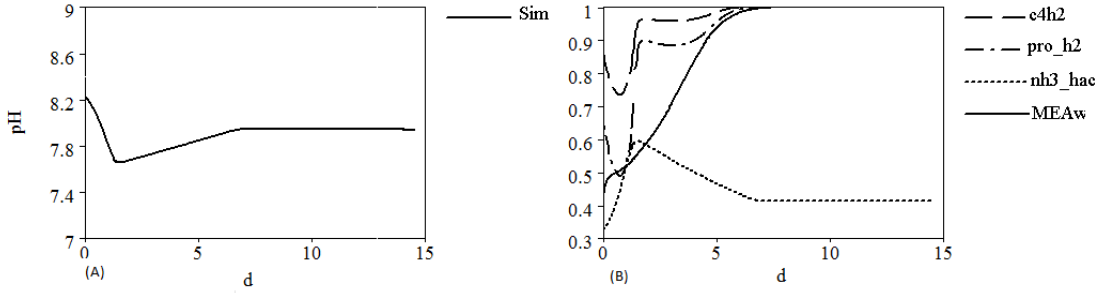


Figure 3: Simulated pH (A) and inhibition effects (B), c4h2, pro_h2, nh3_hac and MEAw are inhibitions of hydrogen on butyrate, propionate degradation, free ammonia and MEAw on acetate degradation, respectively

Table 4: Parameters value specification

Parameter	Description	Units	Batch model	Semi-continuous feed model
K_{hyd_ch}	First order hydrolysis rate of particulate carbohydrate	d^{-1}	10^a	6^c
k_{hyd_CO}	First order hydrolysis rate of CO	d^{-1}	10^b	10
K_{m_MEA}	Monod maximum specific uptake rate of MEA	d^{-1}	5^b	3^c
K_{s_MEA}	Half saturation constant of MEA	$kg-COD/m^3$	0.48^b	0.48
K_{I_MEAw}	50 % inhibitory MEAw concentration	$kg-COD/m^3$	1^b	1
Y_{MEA}	Yield of biomass on MEA	kg-COD B/kg-COD S	0.08^a	0.08
$K_{I\_nh3\_ac}$	50% inhibitory concentration of NH_3	$kmol/m^3$	0.0018^a	0.0018

a, Standard ADM1 value; b, Estimated for batch test; c, Adjusted based on temperature effect (Eq. 6 and 7)

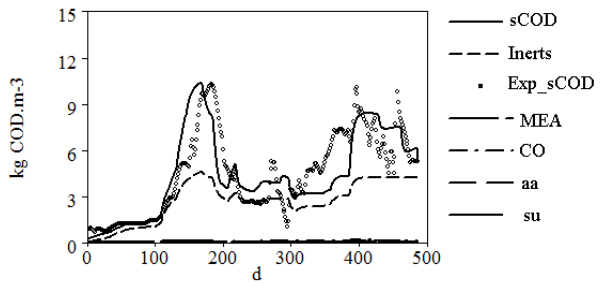


Figure 4: Simulated and experimental effluent components concentrations (COD based). aa, amino acid; su, monosaccharides

5.2 Semi-continuously fed digester simulations

The standard and calibrated kinetic parameters from the batch model (Table. 4) were employed in ADM1_MEAw for simulating AD of MEAw in the semi-continuously fed digester at $22 \pm 2\ ^oC$ (Wang et al., 2013a,b). The kinetic values were adjusted based on temperature effects according to Eq. 6 and 7. 486 days of experimental data was used to verify the parameters and test the model flexibility in predicting MEAw degradation at different feed scenarios (Wang et al., 2013b).

The simulated effluent soluble COD (sCOD) concentrations were generally close to the experimental measurements with some deviations observed at high load scenarios (Fig. 4). During 100 - 200 days, simulated effluent sCOD accumulated earlier than the experimental observations. The simulated effluent sCOD was overall higher than the measured data between 200 and 300 days (Fig. 4), suggesting an underestimated feed degradation in the simulation. Simulation showed that inerts COD constituted the main part of the effluent sCOD and was almost equal to the measured effluent sCOD during this period (Fig. 4). It indicates that the assumed 30 % inerts COD in the feed MEAw was higher than the actual portion. When in the experiment about 80 % of feed COD was degraded during this period (Wang et al., 2013b). Biomass acclimation was believed to lead to the increased feed MEAw degradation ratios (Wang et al., 2013b), while the effects were not accounted for in the model. From 300 to 400 days, an underestimation of sCOD accumulation was shown in the simulation, which was attributed to the predicted low inhibition levels (Fig. 5). Other feed organics (e.g. MEA) were observed to be mostly degraded which was in accordance with the experimental observations (Wang et al., 2013b).

5.3 Inhibition

The accumulation of sCOD in AD effluent was attributed to feed MEAw inerts and the organics (e.g. acetate) accumulation due to the inhibition effects on organisms from MEAw and/or its degradation products and ammonia (Wang et al., 2013b). Experimental observation showed that feed MEAw had strong negative effects on biogas yield (Wang et al., 2013b). Complex MEAw chemicals may impose inhibition on ancetoclastic methanogenesis, while no specific inhibition factor has yet been identified. MEAw effects were accounted for in the model by adopting feed MEAw concentration (Eq. 4 and 5), causing acetate accumulation. The free ammonia inhibition coefficient (0.0018 M) was maintained as in the standard ADM1 since it is considered to be a low variability parameter between systems in continuous reactors (Siegrist and Batstone, 2001).

Simulation showed that acetate uptake was mainly affected by free ammonia in AD (Fig. 5, A). Inhibitory effects of MEAw were observed to be in comparably low levels (Fig. 5, A). PCA (principle component analysis) (Wang et al., 2013b) showed that VFA concentration was closely related to free ammonia and feed MEAw concentration (Wang et al., 2013b). The simulated stronger free ammonia inhibition effects indicate that the inhibitory chemicals in MEAw were broken down by AD and caused less acetoclastic methanogensis inhibition. Other inhibitions (e.g. hydrogen inhibition) (Fig. 5, A) were also observed in the simulation which affected the degradation of propionic acid for example.

Accumulated VFA was mainly acetate with other acids observed in much lower levels (Fig. 5, B) which complied with the experimental observations (Wang et al., 2013a,b). However, the acetate accumulation was simulated to be much higher and started at an early phase (108 days) than experimental data (124 days) (Fig. 5, B). The simulation predicted a relatively high pH value at 108 days (Fig. 6, A), which led to a free ammonia overestimation (Fig. 6, B). VFA accumulation soared immediately after the overestimation of free ammonia (Fig. 6, B). The combined effects from inhibition of free ammonia and MEAw in the model (Fig. 6, A) amplified the inhibition effects and led to a higher VFA accumulation during 100 - 220 days. Simulated acetate accumulation at the end of the test was very close to that observed in the experiment (Fig. 6, B), which indicates that the combined inhibition effects were in reasonable levels at these stages of simulation.

5.4 pH and ammonia

Ammonia (ammonium + free ammonia) nitrogen in the AD digester was originated from nitrogenous con-

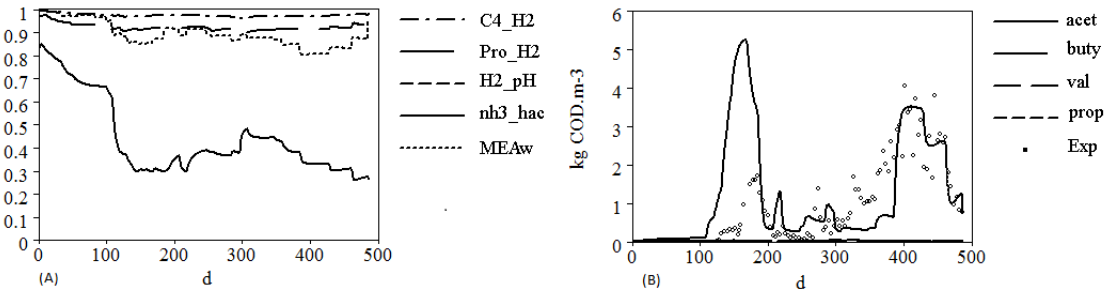


Figure 5: Simulated inhibition effects (A) from H2 on butyrate and propionate degradation (C4_H2 and Pro_H2), pH effects on hydrogen degradation (H2_pH) and NH_3 and MEAw effects on acetate degradation (nh3_hac and MEAw) in AD of MEAw. VFA accumulation (B), acet, acetate; buty, butyrate; val, valerate; prop, propionate

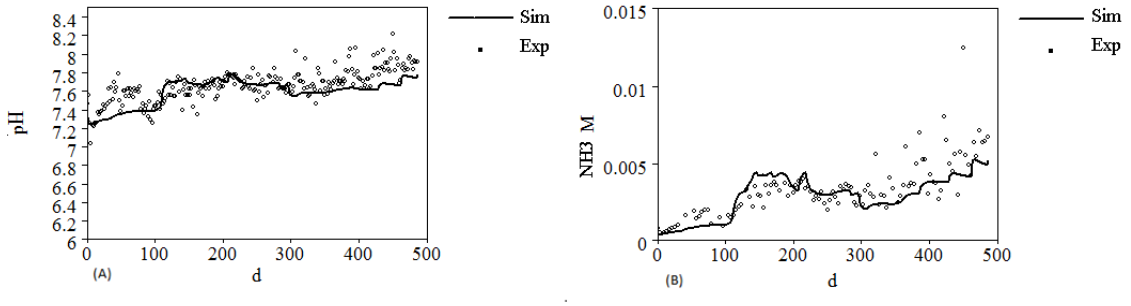


Figure 6: Simulated and experimental pH (A) and free ammonia concentration (B)

Table 5: Calculated RMSD for the simulation and experimental results for the entire 486 d experiment and for phase 1-3 with distinctly different operational conditions.

Variables	Units	0-486 d	Phase 1 (0-184 d)	Phase 2 (185-296 d)	Phase 3 (297-486 d)
Biogas flow	m^3/d	2.35E-04	1.25E-04	1.85E-04	3.28E-04
CH_4 partial pressure	%	4.63	5.28	2.12	5.02
CO_2 partial pressure	%	3.56	4.53	3.01	2.63
IN	M	0.02	0.02	0.01	0.03
Free ammonia	M	1.35E-03	8.50E-04	5.28E-04	1.91E-03
Acetate	$kg-COD/m^3$	1.17	1.48	0.49	0.80
pH	-	0.16	0.17	0.08	0.19
sCOD	$kg-COD/m^3$	1.61	1.43	1.74	1.68

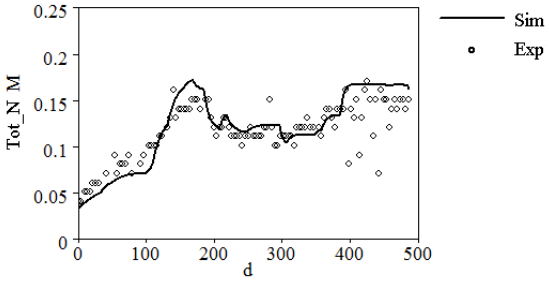


Figure 7: Simulated and experimental total ammonia concentration

tent organics in both MEAw and co-feed substrates. The simulated ammonia concentration was generally close to the experimental observations with some under/overestimation in before 200 days (Fig. 6, B and Fig. 7). Free ammonia concentrations were calculated based on equilibrium of pH, ammonia and temperature (Angelidaki and Ahring, 1993), of which temperature was constant in the simulation. Simulated free ammonia variations were mainly determined by the pH (Fig. 6, A) and total ammonia concentrations (Fig. 7) from model prediction, the relatively low accuracy of those two state variables can lead to the variations of inhibitory effects in Fig. 5.

pH was simulated in ADM1 by accounting for different chemicals' ions concentrations in charge balance

5.5 Biogas generation

Simulated biogas flow rates show a comparable good correlation with the experimental results (Fig. 8, A). Biogas overestimation was observed at around 200 days, when in the experiment, VFA peak showed (Fig. 5, B). The overestimation was attributed to the simulated relatively early VFA accumulation at around 160 days due to inhibition effects (Fig. 5). From 300 days to the end, simulated biogas flow rates are in the high range of the measured biogas flows that fluctuate very much in the experiment (Fig. 8, A). The simulated CO_2 partial pressure was relatively high before 110 days (Fig. 8, B) attributing to the inaccurate IC input in the model. The partial pressure of both methane and CO_2 were in good correlation with the experimental data after 110 days (Fig. 8, B).

Anaerobic digestion of MEA is coupled with consuming CO_2 as a reactant (Eq. 3 and (Speranza et al., 2006)). Accurate prediction of MEA and other ethanol amine concentrations in the MEAw are thus important for biogas simulations, especially for the biogas partial pressure predictions. It showed in the experiment that the biogas generation was gradually increasing in inhibitory conditions due to acclimation effects (Wang et al., 2013b), while these effects were not included in the model. The $tres,_X$ (extended retention of solid) applied in the model was observed to play an similar role as acclimation effects that with increased biomass retention, increased feed degradation rate and reduced inhibition effects were obtained. Other biochemical processes (e.g. syntrophic acetate oxidation (Schnurer et al., 1994) may have also occurred in the digester which was not specified experimentally or implemented in the model.

5.6 Simulation validaiton

Root mean square deviations (RMSD) were calculated for the ADM1_MEAw simulations with respect to the data for eight key process variables for each of three experimental phases conducted in the experimental test. The distinctions of the three phases are described in greater detail in Wang et al. (2013b). These three separate RMSD values are shown in Table. 5 together with an overall RMSD value for the complete 486 days experiment. The RMSD values of the three phases are generally in the same order of magnitudes as the RMSD values for the entire experiment. Relatively lower RMSD values of simulated CH_4 partial pressure, IN, acetate concentrations and pH in experimental phase 2 may be a result of a less load variations than during the other two phases. The absence of other patterns in the calculated deviations (Table. 5) shows that the model predicts the process behavior with similar precision for the entire 486 d experiment. Generally the simulations comply well with the experimental data.

6 Conclusion

The model ADM1_MEAw was generated based on ADM1 for the simulation of anaerobic degradation of MEA waste with easily degradable organics at room temperature. The model was based on the assumptions of 1) MEAw COD consisted of 44 % MEA and 56 % complex organics (CO), in which degradable organics and inerts accounted 26 % and 30 %, respectively; 2) MEA and acetate were hydrolysis products of the degradable organics. 3) MEA was degraded to ammonium and acetate (Eq. 3); 4) Monod kinetics and standard organisms for amino acids degradation were applied for MEA uptake (Botheju et al., 2010); 5) Observed MEAw and ammonia inhibition on acetoclastic methanogenesis were included in the inhibition factor; 6) The long AD sludge retention time was accounted for in the model by a parameter $tres,_X$ that allows particles (X) to be retained in the reactor longer than the

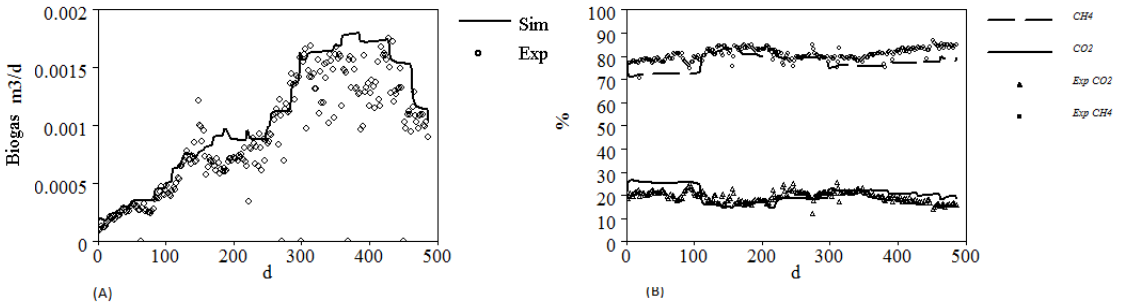


Figure 8: Simulated and experimental biogas generation (A) and CH_4 and CO_2 partial pressures (B)

liquid.

The expanded model ADM1_MEAw based on ADM1 and assumptions according to experimental investigation of AD of MEAw was constructed in the project. ADM1_MEAw applied standard ADM1 variables and kinetics of the newly added biochemical processes calibrated based on batch test were able to successfully predict the reactor performance under varying experimental scenarios. Simulated COD removal, pH and inorganic nitrogen concentrations etc. through large feed input variations complied well with the 486 days of semi-continuously fed experimental data. Predicted acetate accumulation generally complied with the experimental observations, with deviations attributed to less accurate predicted inhibitory effects. Most feed MEAw was degraded in the simulation and its inhibitory effects on acetate uptake were comparably lower than free ammonia which was the dominant inhibitor in acetate degradation.

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