Title: Improved ADM1 Model for Anaerobic Digestion Process Considering Physico-chemical Reactions

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Abstract:

The "Anaerobic Digestion Model No.1" (ADM1) was modified in the study by improving the bio-chemical framework and integrating a more detailed physico-chemical framework. Inorganic carbon and nitrogen balance terms were introduced to resolve the discrepancies in the original bio-chemical framework between the carbon and nitrogen contents in the degraders and substrates. More inorganic components and solids precipitation processes were included in the physico-chemical framework of ADM1. The modified ADM1 was validated with the experimental data and used to investigate the effects of calcium ions, magnesium ions, inorganic phosphorus and inorganic nitrogen on anaerobic digestion in batch reactor. It was found that the entire anaerobic digestion process might exist an optimal initial concentration of inorganic nitrogen for methane gas production in the presence of calcium ions, magnesium ions and inorganic phosphorus.

Keywords: anaerobic digestion; kinetic model; physico-chemical reaction

1. Introduction

The "Anaerobic Digestion Model No.1" (ADM1) developed by the International Water Association (IWA) task group is a mathematical model mainly describing the biochemical processes involved in anaerobic digestion (Batstone et al., 2002; Batstone et al., 2006). The whole process of anaerobic digestion can be divided into five steps, which are disintegration, hydrolysis, acidogenesis, acetogenesis and methanogenesis. First, composite particulate substrate is disintegrated into carbohydrates, proteins, lipids, soluble and particulate inerts in the disintegration step. Then carbohydrates, proteins, and lipids are hydrolyzed into monosaccharides (MSs), amino acids (AAs), and long chain fatty acids (LCFAs) in the hydrolysis step (Vavilin et al., 2001). Next in the acidogenesis step, MSs and AAs are degraded by acidogenic bacteria into dissolved hydrogen, carbon dioxide and volatile fatty acids (VFAs), such as propionic acid, acetic acid, butyric acid and valeric acid. Then in the acetogenesis step, these VFAs, as well as some LCFAs from the hydrolysis step, are converted into acetates, dissolved hydrogen and carbon dioxide by acetogenic bacteria. Finally in the methanogenesis step, acetates from the acetogenesis step are converted by aceticlastic methanogenic bacteria into dissolved methane, while dissolved hydrogen and carbon dioxide are converted by hydrogen-utilizing methanogenic bacteria into dissolved methane. During the whole process of anaerobic digestion, all the bacteria (or component degraders) gradually decay and become inactive. These inactive degraders maintain in the reactor as a part of substrate and involve in anaerobic digestion with the original composite particulates. ADM1 employs a set of 24 differential rate equations to describe the bio-chemical processes involved in anaerobic digestion. The

disintegration, hydrolysis and bacterial decay steps are represented by first order kinetics, while all the other steps are represented by Monod-type kinetics. Besides, ADM1 includes several inhibition factors such as LCFAs, dissolved hydrogen and ammonia (Angelidaki et al., 1993; Chen et al., 2008; Schievano et al., 2010; Zonta et al., 2013). In conjunction with the rate equations, 24 dynamic state concentration variables are set for the components involved in anaerobic digestion. These rate equations can be solved simultaneously and have complete mass balances over all components in the solid, gas and liquid phases if appropriate initial values are determined for the concentration variables.

The ADM1 modeling framework is a powerful tool that has been applied in the industrial process design and optimization for wastewater treatment (Batstone and Keller, 2003; Biernacki et al., 2013; Girault et al., 2012; Mairet et al., 2011; Parker, 2005; Shang et al., 2005). Many researches of anaerobic-digestion-involved processes are also based on the application of ADM1 modeling framework, especially the process of methane production (Antonopoulou et al., 2012; Hafez et al., 2010; Parawira et al., 2008; Takiguchi et al., 2004).

However, many deficiencies of the original ADM1 have been noted since its publication.

First, the ADM1 does not accommodate complete component mass balances over the nitrogen and carbon components, which can result in the discrepancies between the carbon and nitrogen contents in the biomass and those in the composite particulate material (Blumensaat and Keller, 2005). Second, the ADM1 does not consider too much physico-chemical processes which are not directly mediated by microbes but can affect the biochemical processes of anaerobic digestion (Horiuchi et al., 2001; Loewenthal et al., 1989; Loewenthal et al., 1991; Mikkelsen and Keiding, 2002). The most critical physico-chemical

processes omitted in the ADM1 are the solids precipitation processes caused by metal ions. The main reason of excluding the solids precipitation processes from the ADM is that the range of precipitating ions is wide, which leads to a large number of precipitate types (Ekama et al., 2006). Also, the presence of some types of metal ions may have inhibition effects on the precipitation processes involving other metal ion types. In addition, precipitates formed by same ions may exist two different forms: amorphous precipitates and crystalline precipitates, which have different formation mechanisms, precipitation kinetics and the rate-limited factors (Koutsoukos et al., 1980). Third, the ADM1 does not consider phosphoric acid and phosphate as components involved in the physico-chemical processes of anaerobic digestion. It has been shown in many studies that metal ions and phosphate may cause solids precipitation, such as struvite (MgNH_4PO_4), affect the pH of the anaerobic digestion circumstances and have strong effects on bio-chemical processes as well as physico-chemical processes (Britton et al., 2005).

The deficiencies of the original ADM1 will unavoidably limit the ability of the model to precisely represent the changing rates of some of the components and to correctly predict the final concentrations of these components. Recently, many studies have focused on developing a more complicated anaerobic digestion model (Fedorovich et al., 2003; Musvoto et al., 2000a; Musvoto et al., 2000b; Sotemann et al., 2005a; Sotemann et al., 2005b). However, most of them do not consider critical inorganic components and physico-chemical processes in all three phases. In this study, the original ADM1 is extended to incorporate more inorganic components, such as metal ions and phosphates, and more physico-chemical processes, such as the association/dissociation processes of carbonate and phosphate ions and the solids precipitation processes of metal ions. Integrating a more

detailed physico-chemical framework into ADM1 can enhance its abilities of keeping track of the change of circumstances pH value and each component involved in anaerobic digestion. The modifications to the original ADM1 may contribute useful information for its further development. After the model validation, the improved ADM1 is used to investigate the effects of some dissolved metal ions and inorganic components on the whole process of anaerobic digestion. Findings of the investigation may be useful for the design and scale-up of anaerobic digestion units for waste water treatment and biogas production processes.

2. Materials and Methods

The structures of the modified AMD1 are shown in Tables 1-5. The entire model can be categorized into two bio-chemical framework and physico-chemical framework and contains totally 47 dynamic state variables representing the concentrations of 47 components in three phases during anaerobic digestion. In addition, the model describes 38 possible bio-chemical and physico-chemical processes involved in anaerobic digestion. The kinetic rate of each process is represented by ρ_j and the detailed expressions are given in the *supplementary material* and the parameter values can be found in the work of Batstone et al. (2002).

2.1. Bio-chemical framework

Anaerobic digestion mainly includes two extracellular steps (i.e. disintegration and hydrolysis) and three intracellular steps (i.e. acidogenesis, acetogenesis and methanogenesis). In the intracellular steps, inorganic carbon is the carbon source for, or a product of, the uptake of sugars, amino acids, propionate, acetate and hydrogen, while inorganic nitrogen is the nitrogen source for the uptake of sugars, amino acids, LCFA,

valerate, butyrate, propionate, acetate and hydrogen. However, the original ADM1 did not consider the inorganic carbon and nitrogen changes for some possible processes, especially the decay processes of component degraders. Since the decaying component degraders remain in the reactor and involve in the anaerobic digestion processes together with the original composite particulates, the carbon balance and nitrogen balance must be closed by adding balance terms of inorganic carbon and nitrogen for the bacteria decay processes. In the work of Blumensaat and Keller (2005), two balance terms were introduced to resolve the discrepancies between the carbon and nitrogen contents in the degraders and substrates, which were Eq. (1) (used to close the carbon cycle) and Eq. (2) (used to close the nitrogen cycle). These two terms describe inorganic carbon and nitrogen releases caused by the decay of degraders and the effects on the total dissolved inorganic carbon and nitrogen contents.

$$v_{10,j} = -\sum_{i=13,17\sim 23} C_i v_{i,j} \quad (1)$$

$$v_{33,j} = -\sum_{i=13,17\sim 23} N_i v_{i,j} \quad (2)$$

2.2. Physico-chemical framework

2.2.1. Liquid-gas processes

Liquid-gas transfer processes were originally incorporated in ADM1 as major physico-chemical processes. Hydrogen (H₂), methane (CH₄) and carbon dioxide (CO₂) were considered in the reactor not only in liquid phase, but also in gas phase and represented as dynamic state concentration variables in the ADM1. At steady-state the relationship between the partial pressure of each biogas component in gas phase and its concentration in liquid phase was described by the Henry's law as Eq. (3). However during the dynamic

anaerobic digestion process each biogas component in the reactor would become supersaturated in liquid phase and transfer into gas phase, which was described by the gas transfer rate equation shown as Eq. (4).

$$0 = S_{liq,i,ss} - K_{H,i}P_{gas,i,ss} \quad (3)$$

$$\rho_{T,i} = k_L a_i (S_{liq,i} - K_{H,i}P_{gas,i}) \quad (4)$$

The concentrations of biogas components were obtained by solving the gas transfer rate equations together with the differential rate equations in liquid phase describing the biochemical processes. Due to the fact that liquid-gas transfer of ammonia (NH₃) may occur in high pH solution, NH₃ is introduced in the ADM1 as a new component of biogas in this study as shown in Table 3.

2.2.2. Liquid-liquid processes

The original ADM1 incorporated 6 acid-base reactions which described the acid/base equilibria of acetic acid/acetate, propionic acid/propionate, butyric acid/butyrate, valeric acid/valerate, dissolved carbon dioxide/bicarbonate and ammonium/ammonia. When considering the acid-base reactions in ADM1, 6 original dynamic state concentration variables (i.e. valerate, butyrate, propionate, acetate, inorganic carbon and inorganic nitrogen) were separated into 6 pairs of acid/base variables, generating 6 additional variables in the model. The acid-base reaction rates were applied to the differential equations of the 6 pairs of acid/base variables as shown in Eq. (5).

$$\rho_{A,i} = k_{A|B,i} (S_{liq,H} S_{liq,i} - K_{a,i} S_{liq,Hi}) \quad (5)$$

To better describe the acid-base reactions and their effects on other processes, more inorganic components and acid/base equilibria are incorporated into the original ADM1

model as shown in Table 5. First, the inorganic carbon components in liquid phase include dissolved carbon dioxide (CO_2), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) for considering the carbonate precipitation process together with the equilibrium among the three inorganic carbon components ($\text{CO}_2/\text{HCO}_3^-/\text{CO}_3^{2-}$). Second, phosphate (PO_4^{3-}), hydrogen phosphate (HPO_4^{2-}), dihydrogen phosphate (H_2PO_4^-) and phosphoric acid (H_3PO_4) are introduced in the model as inorganic phosphorus components for considering the phosphate precipitation together with the equilibrium among the four inorganic phosphorus components ($\text{PO}_4^{3-}/\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^-/\text{H}_3\text{PO}_4$). Furthermore, the charge balance equation is used to calculate the concentration of H^+ (S_H) so as to keep track of the pH value. As shown in Eq. (6), the total concentration of cationic ions is always equal to the total concentration of anionic ions. S_{CAT} and S_{AN} represent the inert cationic and anionic ions respectively with no changing rate terms in the model. The concentration of OH^- (S_{OH}) is always equal to 10^{-14} divided by S_H based on the acid/base equilibrium of water.

$$S_{CAT} + S_{NH_4} + 2S_{Mg} + 2S_{Ca} + S_H - S_{AN} - S_{va}/208 - S_{bu}/160 - S_{pro}/112 - S_{ac}/64 - S_{HCO_3} - 2S_{CO_3} - 3S_{PO_4} - 2S_{HPO_4} - S_{H_2PO_4} - S_{OH} = 0 \quad (6)$$

2.2.3. Liquid-solid processes

Solids precipitation processes are major liquid-solid processes that were not included in the original ADM1. The presence of the precipitates could affect other physico-chemical processes and even the bio-chemical processes. To improve the model's ability to describe the non-biologically mediated processes during anaerobic digestion, Eq. (7) is introduced in the original ADM1 to describe the formation rate of precipitates.

$$\frac{d}{dt} M_{v+A_{v-}} = k'_{r,M_{v+A_{v-}}} \left[([M^{m+}]^{v+} [A^{a-}]^{v-})^{1/v} - K'_{sp,M_{v+A_{v-}}} \right]^{1/v} \quad (7)$$

In Eq. (7) $[M^{m+}]$ and $[A^{a-}]$ are the concentrations of M^{m+} and A^{a-} ions respectively; $k'_{r,M_{v^+}A_{v^-}}$ and $K'_{sp,M_{v^+}A_{v^-}}$ are the precipitation rate constant and solubility product respectively. v^+ and v^- are the total number of cationic and anionic species respectively with $mv^+ = av^-$ and $v = v^+ + v^-$. The precipitation processes are irreversible in the model so Eq. (7) will have valid value only if the value of $[M^{m+}]^{v^+}[A^{a-}]^{v^-}$ is larger than $K'_{sp,M_{v^+}A_{v^-}}$. In this study, calcium ions (Ca^{2+}) and magnesium ions (Mg^{2+}) are considered as two types of M^{m+} ions that will cause 5 major types of precipitates based on the reactions shown in Table 6. Not like the common methods of modeling precipitation which usually use simple rate equations based on the pseudo-equilibrium with first order rate coefficients, the form of Eq. (7) is based on the fundamental relationship used for crystallization process (Koutsoukos et al., 1980), which can better describe the mechanisms of solids precipitation

3. Results and Discussion

3.1 Model validation

In order to testify the accuracy and the predictive ability of the physico-chemical framework of the modified model, the model outputs were compared with experimental data measured at 25°C in the work of Musvoto et al. (2000a). As can be seen in Figure 1 and Figure 2, the model results accurately predict the changing trends of inorganic components and pH value in the batch reactor, and exhibit good agreement with the experimental results. The comparison demonstrates that the model is able to accurately predict the changes of physico-chemical processes involved inorganic components. Such ability enables the further application of the model for investigating the effects of the inorganic components on the entire anaerobic digestion process.

3.2 Effects of Inorganic Components on Anaerobic Digestion

In this section, the validated model was used to investigate the effects of dissolved Ca^{2+} , Mg^{2+} , inorganic phosphorus (P_i) and inorganic nitrogen (N_i) on anaerobic digestion in batch reactor. Compared with the original ADM1, dissolved Ca^{2+} , Mg^{2+} and P_i were new components and N_i had different rate equations. The temperature was still set at 25°C so that it would not influence the precipitation rates of metal ions.

First the impacts of dissolved Ca^{2+} and Mg^{2+} on anaerobic digestion were examined by removing one or both of their initial concentrations. As shown in Figure 3a-b, the presence of Ca^{2+} and Mg^{2+} in liquid phase not only affects the formation rate of precipitates, but also the release rate of biogases, especially ammonia (NH_3) gas, indicating that the liquid-gas processes could be affected by the liquid-solid processes during anaerobic digestion. To better understand how Ca^{2+} and Mg^{2+} impact biogas release and precipitates generation during anaerobic digestion, different initial ratios of Ca^{2+} to Mg^{2+} were tested with a fixed total concentration in the model. As can be seen in Figure 3c, higher initial ratio of Ca^{2+} to Mg^{2+} result in slower production rate of ammonia gas. In addition, the generation process of each type of precipitate also changes significantly as the initial ratio of Ca^{2+} to Mg^{2+} decreases. As shown in Figure 3d, at the 2:1 initial ratio of Ca^{2+} to Mg^{2+} , only two types of precipitate, struvite (MgNH_4PO_4) and $\text{Ca}_3(\text{PO}_4)_2$, are generated, but when the initial ratio decreases to 1:2, CaCO_3 will be generated as another type of Ca^{2+} precipitate with $\text{Ca}_3(\text{PO}_4)_2$ and MgNH_4PO_4 together. The simulation results in Figure 3d reveals that substituting Mg^{2+} for Ca^{2+} may increase the formation rate of CaCO_3 in the presence of PO_4^{3-} although the precipitation rate of $\text{Ca}_3(\text{PO}_4)_2$ is much faster than CaCO_3 .

Then the effect of dissolved P_i was examined by changing its initial concentration.

Dissolved P_i was composed of 4 components in the new model, which were phosphate (PO_4^{3-}), hydrogen phosphate (HPO_4^{2-}), dihydrogen phosphate ($H_2PO_4^-$) and phosphoric acid (H_3PO_4). Among these 4 components, PO_4^{3-} and HPO_4^{2-} were involved in both liquid-liquid and liquid-solid processes of anaerobic digestion while others were only involved in the Liquid-liquid processes. However, as shown in Figure 3a-c, the final yields of methane (CH_4), carbon dioxide (CO_2) and ammonia (NH_3) in gas phase can also be influenced by the initial concentration of dissolved P_i , indicating that the presence of P_i in liquid phase has a noticeable effect on liquid-gas processes of anaerobic digestion. Furthermore, as shown in Figure 4d, the total concentration of acetate and acetic acid ($S_{ac}+S_{Hac}$) will have different changing trends as the initial concentration of P_i changes in liquid phase, indicating that the presence of P_i in liquid phase may affect bio-chemical processes of anaerobic digestion such as the uptake of acetate, the decay of acetate degraders (X_{ac}) and the generation of CH_4 in liquid phase. In addition, as demonstrated in Figure 3a, increasing the initial concentration of P_i will decrease the final yield of CH_4 gas. As the initial concentration of P_i becomes higher, less $CaCO_3$ and $MgCO_3$ will form in solid phase, as shown in Figure 4f, and more CO_3^{2-} will remain in solution, which will increase the concentration of CO_2 in liquid phase as well as gas phase and thus affect the concentration of CH_4 in gas phase.

Next the effect of dissolved N_i was examined also by changing its initial concentration.

Dissolved N_i was originally considered in the ADM1 model as NH_4^+ and NH_3 which were only involved in bio-chemical and liquid-liquid processes. In this study, NH_4^+ was considered to be able to form precipitate with Mg^{2+} (Britton et al., 2005) and NH_3 was

considered as a components in both liquid and gas phase. Since dissolved N_i is involved in all kinds of anaerobic digestion processes in the model, changing the initial concentration of dissolved N_i will inevitably affect the yields of many components in liquid, gas or solid phase. As shown in Figure 5a, neither increasing nor decreasing the initial concentration of N_i in liquid phase can increase the yield of CH_4 in gas phase, indicating that for CH_4 gas production during anaerobic digestion there may be an optimal initial concentration of dissolved N_i in the presence of Mg^{2+} , Ca^{2+} and dissolved P_i . If the initial concentration of N_i is too high, large amount of NH_3 may remain in solution after Mg^{2+} being precipitated and result in strong inhibition effect on the production of CH_4 in liquid phase. Besides, high concentration of NH_3 in liquid phase may also cause high percentage of NH_3 in gas phase and thus affect the content of CH_4 gas. However, as shown in Figure 5f, if the initial concentration of N_i is too low, no $CaCO_3$ will form in solution. The reason may be that low initial concentration of N_i leads to low initial pH in solution, which will inhibit the formation of $CaCO_3$ in solution. So large amount of CO_3^{2-} will remain in solution after Ca^{2+} being precipitated, which will increase the concentration of CO_2 in liquid phase as well as gas phase and affect the content of CH_4 gas.

To understand how dissolved N_i and P_i together can impact the yield of CH_4 gas during anaerobic digestion, different initial dissolved N_i to P_i ratios ($N_i:P_i$) were tested with different fixed initial concentrations of dissolved N_i and P_i (N_i+P_i) in the model. Several specific measurement results about the initial $N_i:P_i$ ratio were found in the literature. For example, in the work of Musvoto et al. (2000b) the initial $N_i:P_i$ ratios in real situations were from 2.21 to 9.21. So it is believe that the initial $N_i:P_i$ ratio differs case by case and varies in a very large range in real situations. As shown in Figure 6a, increasing the initial $N_i:P_i$

ratio will have a positive effect on the final yield of CH₄ gas. Then the initial concentration of "N_i+P_i" was set as 10% of the original value. As shown in Figure 6b, higher initial N_i:P_i ratio will also result in higher yield of CH₄ gas in the 1st day and after the 3rd day.

However during the 1st and 3rd day, the CH₄ gas production rate with lower initial N_i:P_i ratio becomes a little faster, which results in more CH₄ gas during this time period. After that the initial concentration of "N_i+P_i" was set as 1000% of the original value. As shown in Figure 6c, the effect of initial N_i:P_i ratio will become significantly different compared to those with lower initial "N_i+P_i" concentrations. As the initial N_i:P_i ratio increases, the yield of CH₄ gas will drop a lot, meaning that in the case of high initial "N_i+P_i" concentration, high initial N_i:P_i ratio may have negative effect on the yield of CH₄ gas. These simulations reflect the complex combination effects of dissolved P_i and N_i on the yield of CH₄ gas in the presence of Mg²⁺ and Ca²⁺.

4. Conclusions

The original ADM1 has been modified by improving its bio-chemical framework and integrating a more detailed physico-chemical framework. The modified ADM1 was validated by a set of experimental data and used to investigate the effects of dissolved calcium and magnesium ions, inorganic phosphorus and nitrogen on anaerobic digestion in batch reactor. The modifications improved the ADM1's ability to keep track of the biogas production in gas phase, the pH value in liquid phase and the precipitates in solid phase, and provided a way of developing a complete anaerobic digestion mathematical model in future.

Nomenclature

A_i: acid-base reaction index involving *i* component

C_i : carbon content of component i (kmole/kgCOD)
 $f_{\text{product,substrate}}$: yield of product on substrate
 i : component index
 j : process index
 N_i : nitrogen content of component i (kmole/kgCOD)
 P_i : precipitation process index involving i component
 S_{su} : sugar (monosaccharides) (kgCOD/m³)
 S_{aa} : amini acids (kgCOD/m³)
 S_{fa} : fatty acids (long chain) (kgCOD/m³)
 S_{va} : valerate (kgCOD/m³)
 S_{bu} : butyrate (kgCOD/m³)
 S_{pro} : propionate (kgCOD/m³)
 S_{ac} : acetate (kgCOD/m³)
 S_{H2} : hydrogen gas (dissolved) (kgCOD/m³)
 S_{CH4} : methane gas (dissolved) (kgCOD/m³)
 S_{HCO3} : bicarbonate (M)
 S_{NH3} : ammonia gas (dissolved) (M)
 S_{I} : inerts (dissolved) (kgCOD/m³)
 S_{Hva} : valeric acid (kgCOD/m³)
 S_{Hbu} : butyric acid (kgCOD/m³)
 S_{Hpro} : propionic acid (kgCOD/m³)
 S_{Hac} : acetic acid (kgCOD/m³)
 S_{CO2} : carbon dioxide gas (dissolved) (M)

S_{NH4} : ammonium (M)

S_{Ca} : calcium ions (M)

S_{Mg} : magnesium ions (M)

S_{H3PO4} : phosphoric acid (M)

S_{H2PO4} : dihydrogen phosphate (M)

S_{HPO4} : hydrogen phosphate (M)

S_{PO4} : phosphate (M)

S_{CO3} : carbonate (M)

T_i : liquid-gas transfer process index involving i component

v_{ij} : rate coefficients for component i on process j

X_c : composites (kgCOD/m³)

X_{ch} : carbohydrates (kgCOD/m³)

X_{pr} : proteins (kgCOD/m³)

X_{li} : lipids (kgCOD/m³)

X_{su} : sugar degraders (monosaccharides) (kgCOD/m³)

X_{aa} : amino acids degraders (kgCOD/m³)

X_{fa} : LCFA degraders (kgCOD/m³)

X_{c4} : valerate and butyrate degraders (kgCOD/m³)

X_{pro} : propionate degraders (kgCOD/m³)

X_{ac} : acetate degraders (kgCOD/m³)

X_{H2} : hydrogen degraders (kgCOD/m³)

X_I : inerts (particulate) (kgCOD/m³)

$Y_{substrate}$: yield of biomass on substrate

ρ_j : kinetic rate of process j

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Figure Captions

Figure 1. Comparison between the predicted (pred.) and measured (meas.) data for calcium and magnesium ions, total carbonate, phosphate, ammonia/ammonium, pH in liquid phase and model prediction of precipitate generation rates in solid phase.

Figure 2. Comparison between the simulation results and experimental data of final concentrations of precipitates.

Figure 3. Effects of metal ions on biogas production and precipitates generation.

Figure 4. Effects of inorganic phosphorus on biogas in gas phase, substrate in liquid phase and precipitates in solid phase.

Figure 5. Effects of inorganic nitrogen on biogas in gas phase, substrate in liquid phase and precipitates in solid phase.

Figure 6. Effects of different initial inorganic phosphorus to nitrogen ratios on the production of CH₄ in gas phase

Figures and Tables (black-and-white)

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Table 1. Matrix representation of the rate coefficients and equations for ADM1 bio-chemical framework part 1: soluble components

j	Process	Component i												Rate
		1 S_{su}	2 S_{aa}	3 S_{fa}	4 S_{va}	5 S_{bu}	6 S_{pro}	7 S_{ac}	8 S_{H2}	9 S_{CH4}	10 S_{HCO3}	12 S_I	33 S_{NH4}	
1	Disintegration												$f_{sl,xc}$	ρ_1
2	Hydrolysis Carbohydrates	1												ρ_2
3	Hydrolysis of Proteins		1											ρ_3
4	Hydrolysis of Lipids	$1-f_{fa,li}$		$f_{fa,li}$										ρ_4
5	Uptake of Sugars	-1				$(1-Y_{su})f_{bu,su}$	$(1-Y_{su})f_{pro,su}$	$(1-Y_{su})f_{ac,su}$	$(1-Y_{su})f_{H2,su}$		$v_{10,5}$		$(-Y_{su})N_{bac}$	ρ_5
6	Uptake of Amino Acids		-1		$(1-Y_{aa})f_{va,aa}$	$(1-Y_{aa})f_{bu,aa}$	$(1-Y_{aa})f_{pro,aa}$	$(1-Y_{aa})f_{ac,aa}$	$(1-Y_{aa})f_{H2,aa}$		$v_{10,6}$		$N_{aa}-Y_{aa}N_{bac}$	ρ_6
7	Uptake of LCFA			-1				$(1-Y_{fa})0.7$	$(1-Y_{fa})0.3$				$(-Y_{fa})N_{bac}$	ρ_7
8	Uptake of Valerate				-1		$(1-Y_{c4})0.54$	$(1-Y_{c4})0.31$	$(1-Y_{c4})0.15$				$(-Y_{c4})N_{bac}$	ρ_8
9	Uptake of Butyrate					-1		$(1-Y_{c4})0.8$	$(1-Y_{c4})0.2$				$(-Y_{c4})N_{bac}$	ρ_9
10	Uptake of Propionate						-1	$(1-Y_{pro})0.57$	$(1-Y_{pro})0.43$		$v_{10,10}$		$(-Y_{pro})N_{bac}$	ρ_{10}
11	Uptake of Acetate							-1		$(1-Y_{ac})$	$v_{10,11}$		$(-Y_{ac})N_{bac}$	ρ_{11}
12	Uptake of Hydrogen								-1	$(1-Y_{H2})$	$v_{10,12}$		$(-Y_{H2})N_{bac}$	ρ_{12}
13	Decay of X_{su}										$v_{10,13}$		$v_{33,13}$	ρ_{13}
14	Decay of X_{aa}										$v_{10,14}$		$v_{33,14}$	ρ_{14}
15	Decay of X_{fa}										$v_{10,15}$		$v_{33,15}$	ρ_{15}
16	Decay of X_{c4}										$v_{10,16}$		$v_{33,16}$	ρ_{16}
17	Decay of X_{pro}										$v_{10,17}$		$v_{33,17}$	ρ_{17}
18	Decay of X_{ac}										$v_{10,18}$		$v_{33,18}$	ρ_{18}
19	Decay of X_{H2}										$v_{10,19}$		$v_{33,19}$	ρ_{19}

Table 2. Matrix representation of the rate coefficients and equations for ADM1 bio-chemical framework part 2: particulate components

j	Process	Component i												Rate
		13	14	15	16	17	18	19	20	21	22	23	24	
		X_c	X_{ch}	X_{pr}	X_{li}	X_{su}	X_{aa}	X_{fa}	X_{c4}	X_{pro}	X_{ac}	X_{H2}	X_I	ρ_i
1	Disintegration	-1	$f_{oh,xc}$	$f_{pr,xc}$	$f_{li,xc}$								$f_{xl,xc}$	ρ_1
2	Hydrolysis Carbohydrates		-1											ρ_2
3	Hydrolysis of Proteins			-1										ρ_3
4	Hydrolysis of Lipids				-1									ρ_4
5	Uptake of Sugars					Y_{su}								ρ_5
6	Uptake of Amino Acids						Y_{aa}							ρ_6
7	Uptake of LCFA							Y_{fa}						ρ_7
8	Uptake of Valerate								Y_{c4}					ρ_8
9	Uptake of Butyrate								Y_{c4}					ρ_9
10	Uptake of Propionate									Y_{pro}				ρ_{10}
11	Uptake of Acetate										Y_{ac}			ρ_{11}
12	Uptake of Hydrogen											Y_{H2}		ρ_{12}
13	Decay of X_{su}	1				-1								ρ_{13}
14	Decay of X_{aa}	1					-1							ρ_{14}
15	Decay of X_{fa}	1						-1						ρ_{15}
16	Decay of X_{c4}	1							-1					ρ_{16}
17	Decay of X_{pro}	1								-1				ρ_{17}
18	Decay of X_{ac}	1									-1			ρ_{18}
19	Decay of X_{H2}	1										-1		ρ_{19}

Table 3. Matrix representation of the rate coefficients and equations for ADM1 physico-chemical framework part 1: liquid-gas processes

j	Process	Component i				Rate
		8	9	11	32	
		S_{H_2}	S_{CH_4}	S_{NH_3}	S_{CO_2}	ρ_j
T8	H ₂ Transfer	-1				ρ_{T8}
T9	CH ₄ Transfer		-1			ρ_{T9}
T11	NH ₃ Transfer			-1		ρ_{T11}
T32	CO ₂ Transfer				-1	ρ_{T32}

Table 4. Matrix representation of the rate coefficients and equations for ADM1 physico-chemical framework part 2: liquid-liquid processes

j	Process	Component i																	Rate ρ_i
		4 S_{va}	5 S_{bu}	6 S_{pro}	7 S_{ac}	10 S_{HCO_3}	11 S_{NH_3}	28 S_{Hva}	29 S_{Hbu}	30 S_{Hpro}	31 S_{Hac}	32 S_{CO_2}	33 S_{NH_4}	37 $S_{H_3PO_4}$	38 $S_{H_2PO_4}$	39 S_{HPO_4}	40 S_{PO_4}	41 S_{CO_3}	
A4	Valerate Acid-Base	-1						1											ρ_{A4}
A5	Butyrate Acid-Base		-1						1										ρ_{A5}
A6	Propionate Acid-Base			-1						1									ρ_{A6}
A7	Acetate Acid-Base				-1						1								ρ_{A7}
A10	HCO_3^- Acid-Base					-1						1							ρ_{A10}
A11	NH_4^+ Acid-Base						-1						1						ρ_{A11}
A38	$H_2PO_4^-$ Acid-Base													1	-1				ρ_{A38}
A39	HPO_4^{2-} Acid-Base														1	-1			ρ_{A39}
A40	PO_4^{3-} Acid-Base															1	-1		ρ_{A40}
A41	CO_3^{2-} Acid-Base					1												-1	ρ_{A41}

Table 5. Matrix representation of the rate coefficients and equations for ADM1 physico-chemical framework part 3: liquid-solid processes

j	Process	Component i						Rate
		33 S_{NH4}	35 S_{Ca}	36 S_{Mg}	39 S_{HPO4}	40 S_{PO4}	41 S_{CO3}	
P42	$CaCO_3$ Precipitation		-1				-1	ρ_{P42}
P43	$MgCO_3$ Precipitation			-1			-1	ρ_{P43}
P44	$MgNH_4PO_3$ Precipitation	-1		-1		-1		ρ_{P44}
P45	$MgHPO_4$ Precipitation			-1	-1			ρ_{P45}
P46	$Ca_3(PO_4)_2$ Precipitation		-1			- 2/3		ρ_{P46}

Table 6. Acid-base and precipitation reactions considered in anaerobic digestion

Acid-base reactions	Precipitation reactions
$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$	$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3 (s)$
$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$	$Mg^{2+} + CO_3^{2-} \rightleftharpoons MgCO_3 (s)$
$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$	$Mg^{2+} + NH_4^+ + PO_4^{3-} \rightleftharpoons MgNH_4PO_4 (s)$
$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	$Mg^{2+} + HPO_4^{2-} \rightleftharpoons MgHPO_4 (s)$
$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	$3Ca^{2+} + 2PO_4^{3-} \rightleftharpoons Ca_3(PO_4)_2 (s)$
$NH_4^+ \rightleftharpoons H^+ + NH_3$	
$Hva \rightleftharpoons H^+ + va^-$	
$Hbu \rightleftharpoons H^+ + bu^-$	
$Hpro \rightleftharpoons H^+ + pro^-$	
$Hac \rightleftharpoons H^+ + ac^-$	