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High-solids anaerobic digestion model for homogenized reactors

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ABSTRACT

During high-solids anaerobic digestion (HS-AD) of the organic fraction of municipal solid waste (OFMSW), an important total solid (TS) removal occurs, leading to the modification of the reactor content mass/volume, in contrast to 'wet' anaerobic digestion (AD). Therefore, HS-AD mathematical simulations need to be approached differently than 'wet' AD simulations. This study aimed to develop a modelling tool based on the anaerobic digestion model 1 (ADM1) capable of simulating the TS and the reactor mass/volume dynamics in HS-AD of OFMSW. Four hypotheses were used, including the effects of apparent concentrations at high TS. The model simulated adequately HS-AD of OFMSW in batch and continuous mode, particularly the evolution of TS, reactor mass, ammonia and volatile fatty acids. By adequately simulating the reactor content mass/volume and the TS, the HS-AD model might bring further insight about potentially inhibitory mechanisms (i.e. NH_3 buildup and/or acidification) occurring in HS-AD of OFMSW.

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1. Introduction

Anaerobic digestion (AD) is a biochemical treatment technology for organic waste valorization yielding a high-methane-content biogas and a partially stabilized organic material with potential applications as soil amendment (Mata-Alvarez, 2003). High-solids anaerobic digestion (HS-AD) is a particular case of AD operated at a total solid (TS) content $\geq$ 10%, in contrast to 'wet' AD applications (i.e. TS < 10%) (Abbassi-Guendouz et al., 2012). Thus, HS-AD has the advantage of minimizing the reactor volume, as well as the need for water addition. On the other hand, HS-AD is normally associated with an important reduction of the total (TS) and volatile (VS) solid content, during the biological degradation of the organic matter. For example, HS-AD of the organic fraction of municipal solid waste (OFMSW) might lead to a TS removal of 30–80% (Cecchi et al., 2002; Mata-Alvarez, 2003; Pavan et al., 2000). However, some drawbacks limit the applicability of HS-AD as, for example, the reduced kinetics expected as a consequence of the hampered mass transfer, and the high risk of acidification due to organic overloading (Benbelkacem et al., 2015; De Baere, 2000).

Among the solid wastes used in HS-AD, the OFMSW is particularly suited for anaerobic treatment due to its elevated TS content (i.e. 25–30%), biodegradation potential and possibility to recover nutrients (i.e. nitrogen and phosphorous) from its composition (De Baere and Mattheeuws, 2013; Mata-Alvarez, 2003). However, HS-AD of OFMSW is normally associated with a high risk of inhibition due to the high protein content, leading to free ammonia nitrogen (NH_3), as one of the most important inhibitors (Chen et al., 2008; Kayhanian, 1999; Rajagopal et al., 2013).

Understanding the biochemical and physicochemical dynamics in HS-AD is crucial to ease the design and operation of HS-AD reactors, minimizing the risk of acidification/inhibition. Particularly important is the knowledge about the interactions between the main four phases – microorganisms, solids, liquids and gases – in HS-AD, since it might allow to increase the waste treatment capabilities and methane yield (Mata-Alvarez, 2003; Vavilin et al., 2004; Xu et al., 2015). In this line, an adapted mathematical model is required for the operational analysis and technology development of HS-AD, as some of the main applications for 'wet' AD of the anaerobic digestion model No.1 (ADM1) (Batstone, 2006; Batstone et al. 2002, 2015; Xu et al., 2015).

ADM1 is a structured model gathering together the main biochemical and physicochemical processes of AD (Batstone et al.

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2002, 2015). Biochemical processes include the disintegration, hydrolysis, acidogenesis, acetogenesis and methanogenesis of complex substrates composed of carbohydrates, proteins and lipids in chemical oxygen demand (COD) units. Physicochemical processes include the gas transfer and the equilibrium of the ionic species of the main inorganic compounds in AD (i.e. CO_2 and NH_3). However, the CSTR implementation of ADM1 was primarily conceived for 'wet' AD applications (i.e. TS $\ll$ 10%), while a more complex hydraulic and particulate component modelling is required for HS-AD (Batstone et al. 2002, 2015; Xu et al., 2015). Thus, modelling HS-AD might be particularly challenging due to the intrinsic complexity of the process (Batstone et al., 2015; Mata-Alvarez et al., 2000; Vavilin et al., 2004; Xu et al., 2015). For example, the (semi-)solid matrix might define the soluble/gaseous transport processes, as well as the capabilities of anaerobic biomass to access the substrates (Bollon et al., 2013; Vavilin and Angelidaki, 2005).

The mass balance modification, regarding the continuously stirred tank reactor (CSTR) implementation of ADM1 (Batstone et al., 2002), is required to account for the reactor content mass (M_{Global}) removal and the specific weight (ρ_{Global}) dynamics in HS-AD (Batstone et al., 2015; Kayhanian and Hardy, 1994; Richards et al., 1991; Vavilin et al., 2004). Noteworthy, the reactor content volume (V_{Global}) might describe important fluctuations during HS-AD, depending mainly on the substrate TS and biodegradability, in contrast to 'wet' AD. Furthermore, a given degree of gaseous porosity (ε) might be present in the HS-AD matrix, particularly at TS contents $\geq$ 25% (Batstone et al., 2015; Benbelkacem et al., 2013; Bollon et al., 2013; Vavilin et al., 2003). ADM1 was originally expressed in volumetric units (i.e. kg COD/m^3). Meanwhile, the most common measurements in HS-AD are normally expressed in mass units (i.e. kg COD/kg), since accounting for the specific weight of (semi-)solid samples – but also the specific weight dynamics in HS-AD – involves the complexity of the analytical techniques (Benbelkacem et al., 2013; Bollon et al., 2013; Kayhanian and Tchobanoglous, 1996). For example, the specific weight of a (semi-)solid sample can be approximated by the use of a water pycnometer, where the sample must be appropriately pretreated (i.e. dried/ground), the distilled water fully degassed and analyses performed under temperature-controlled conditions (ASTM, 2002). With all the above, HS-AD simulations need to be approached differently than in 'wet' AD, where ρ_{Global} and V_{Global} are normally assumed constant, as summarized in Fig. 1.

This study aimed at developing a mathematical tool based on the ADM1 biochemical framework, capable of simulating the solids and reactor content mass/volume dynamics in HS-AD of OFMSW, including the interrelationship between TS (and VS) removal and biogas production. By simulating adequately the global mass/volume and TS dynamics, the presented model might serve as a link between 'wet' AD and HS-AD, while it might help to explore potential inhibitory/acidification mechanisms occurring during HS-AD of OFMSW. Meanwhile, the proposed model was aimed to be as general as possible, since different HS-AD applications (i.e. organic substrate and/or reactor configuration) could be simulated, provided that the main hypotheses presented in the methodology section are fulfilled. Furthermore, the eventual model user is encouraged to further calibrate the model parameters and/or modify the model structure, in order to adapt the HS-AD model for any specific need.

2. Materials and methods

2.1. High-solids model implementation

The main basis for the dynamic model presented in this study was ADM1 (Batstone et al., 2002), including the modifications suggested by Blumensaat and Keller (2005) for closing nitrogen and carbon balances. The simulation of HS-AD for OFMSW treatment required four preliminary hypotheses in order to reduce the complexity of the model. Firstly, HS-AD was assumed to take place in a homogenized (i.e. completely mixed) reactor [Hypothesis 1]. Secondly, the effect of porosity and transport processes was assumed to be negligible [Hypothesis 2]. Then, the specific weight of solids and solvent was considered constant [Hypothesis 3]. Finally, the biochemical reactions were assumed to occur predominantly in water [Hypothesis 4].

With these hypotheses, ADM1 required some particular modifications in order to simulate the TS and mass/volume dynamics in HS-AD, while allowing the calibration of the proposed model. The main modifications implemented in ADM1 in order to simulate HS-AD were the inclusion of mass balances modifying the reactor mass and volume (needed to account for the organic solid removal in HS-AD) and the inclusion of apparent concentrations (as a link between 'wet' and high-solids applications).

2.1.1. Mass balances in high-solids anaerobic digestion reactors

The simulation of the reactor mass and TS/VS content of homogenized HS-AD reactors required the implementation of the global (M_{Global}) [Equation (1)], solid material (M_{Solids}) [Equation (2)], liquid-solvent content ($M_{Solvent}$) [Equation (3)] and inert material (M_{Inerts}) [Equation (4)] mass balances. In this study, the solvent was considered as only water, while the solid material included all the organic and inorganic compounds (i.e. particulates and soluble compounds, VFA, microorganisms) inside the reactor, except water. In mass balances, the mass content (M_i) – global or partial – dynamics were related to the corresponding mass fluxes (m_i), particularly the gases flowing out of the reactor as a consequence of methanogenesis. The implementation of reactor mass balances is crucial in HS-AD, since it accounts for the importance of mass and water removal due to biogas production, in contrast to 'wet' AD (Henze et al., 1997; Kayhanian and Tchobanoglous, 1996; Richards et al., 1991).

$$\frac{dM_{Global}}{dt} = m_{Influent,Global} - m_{Effluent,Global} - m_{Biogas} \quad (1)$$

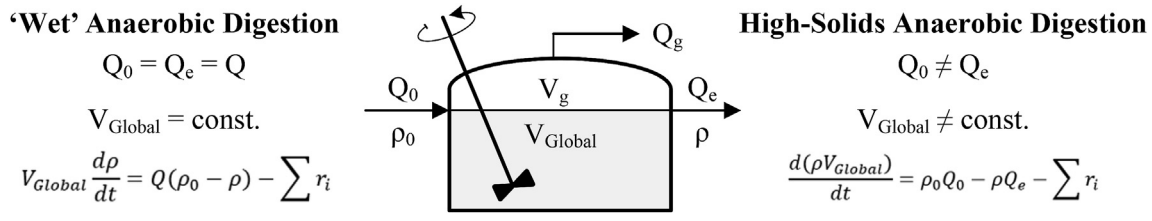


Fig. 1. High-solids vs. 'wet' anaerobic digestion.

$$\frac{dM_{Solids}}{dt} = m_{Influent,Solids} - m_{Effluent,Solids} - (m_{Biogas} - m_{Vapor}) \quad (2)$$

$$\frac{dM_{Solvent}}{dt} = m_{Influent,Solvent} - m_{Effluent,Solvent} - m_{Vapor} \quad (3)$$

$$\frac{dM_{Inerts}}{dt} = m_{Influent,Inerts} - m_{Effluent,Inerts} \quad (4)$$

The biogas (m_{Biogas}) [Equation (5)] and vapor (m_{Vapor}) [Equation (6)] outflows in the mass balances were calculated from the volumetric biogas flow (Q_g), obtained as shown in the CSTR implementation of ADM1 (Batstone et al., 2002), by using the molar gas composition (x_i) and the molecular weight (Mr_i) of each gaseous compound in the gas phase. The biogas was assumed to be composed of CH_4, CO_2, H_2, H_2O and NH_3. The reactor headspace was assumed to be vapor saturated, being vapor pressure (P_v) expressed as a function of temperature (T). On the other hand, an inert gas was added to account for the initial flushing in AD experiments (i.e. by N_2), assuming for it a negligible liquid solubility. Importantly, the inert gas was not included in m_{Biogas} calculations. Once knowing the M_{Global}, M_{Solids} and M_{Inerts}, the TS and VS contents were approximated in dynamic mode by using the corresponding definition (EPA, 2001) [Equations (7) and (8)]. Noteworthy, TS and VS in the proposed model were dimensionless (i.e. kg Solids/kg Total), varying from 0 to 1.

$$m_{Biogas} = \frac{P_T Q_g}{RT} \sum x_i Mr_i \quad (5)$$

$$m_{Vapor} = \frac{P_v Q_g}{RT} Mr_{H2O} \quad (6)$$

$$TS = \frac{M_{Solids}}{M_{Global}} \quad (7)$$

$$VS = \frac{M_{Solids} - M_{Inerts}}{M_{Global}} \quad (8)$$

The liquid-gas transfer of gaseous species in the CSTR implementation of ADM1 depends on the ratio between the reactor content volume (V_{Global}; 'V_{liq}' in ADM1) and the gas volume (V_g), while their sum yields the design/overall reactor volume ($V_{Reactor}$) (Batstone et al., 2002). Thus, since a considerable reduction of V_{Global} – alongside M_{Global} removal – can occur in HS-AD associated with methanogenesis, the reactor volume was approximated by the specific weigh of the reactor content (ρ_{Global}). Importantly, ρ_{Global} varies also in HS-AD, as it gathers together the individual dynamics of all the mass compounds in the system (Kayhanian and Tchobanoglous, 1996). Therefore, to simulate ρ_{Global}, it is necessary to know the specific weight of all the materials within HS-AD (ρ_i), but also their corresponding mass fraction (m_i) [Equation (9)]. For simplicity, the simulations in this study used a common specific weight for all the solid compounds (ρ_{Solids}) and a solvent specific weight ($\rho_{Solvent}$). With these simplifications, the V_{Global} dynamics could be approximated with Equation (10).

$$\frac{1}{\rho_{Global}} = \sum_i \frac{m_i}{\rho_i} \quad (9)$$

$$\frac{dV_{Global}}{dt} = \frac{1}{\rho_{Solids}} \cdot \frac{dM_{Solids}}{dt} + \frac{1}{\rho_{Solvent}} \cdot \frac{dM_{Solvent}}{dt} \quad (10)$$

The distinction between mass and volume in the proposed model for homogenized HS-AD reactors permitted the use of ADM1 volumetric units (i.e. kmol/m^3), while implementing the different influent and effluent mass and/or volumetric flows when operating HS-AD in (semi-)continuous mode. Finally, for illustrative purposes only, an adaptive volumetric effluent ($Q_{Effluent}$) was added to the model – in terms of a proportional controller – to maintain V_{Global} if required. This strategy permitted to compensate for the potential organic mass removal in (semi-)continuous HS-AD and, therefore, to stabilize the HS-AD system, as further discussed in section 3.1. A schematic diagram of the HS-AD model implementation for homogenized reactors is shown in Fig. 2.

2.1.2. Apparent concentrations – soluble species recalculation

The (soluble) apparent concentrations ($S_{T,i,App}$) were used in the HS-AD model biochemistry and physicochemistry to reproduce the effect of high TS in HS-AD, in contrast to 'wet' AD. This modification was related to the assumption that the main biochemical reactions might occur predominantly in the presence of water (Hypothesis 4). Similarly, the apparent concentrations served to link the global (i.e. kmol/kg Total) and liquid fraction (i.e. kmol/kg Solvent) measurements in HS-AD. The apparent concentrations were calculated for all the soluble species of ADM1 using TS, ρ_{Global} and $\rho_{Solvent}$ [Equation (11)]. Importantly, the long chain fatty acids (LCFA, S_{fa}) were not considered as soluble in HS-AD, due to their highly non-polar nature and reduced solubility in water (i.e. palmitic acid

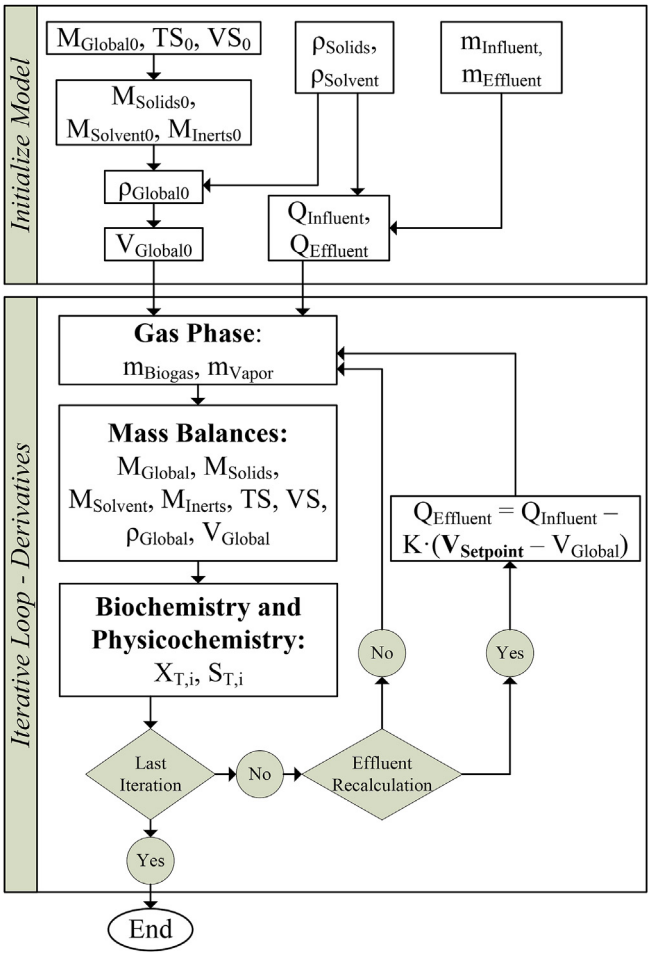


Fig. 2. Schematic representation of the high-solids anaerobic digestion model implementation.

solubility = 1.2 mg/L at 60 °C). With this approach, the proposed model simulates the mass balance of dynamic variables ($C_{T,i}$) – either particulate ($X_{T,i}$) or soluble ($S_{T,i}$) – as a function of V_{Global} (i.e. kmol/m^3 Total) [Equation (12)], while the apparent concentrations ($S_{T,i,App}$) (i.e. kmol/m^3 Solvent) were used only for the soluble species included in the biochemical and physicochemical rates of ADM1 ($r_{i,ADM1}$) (i.e. uptake of acetate). It is important to mention that Equation (12) is the mass balance of an individual component in AD and, therefore, should be based in the chain rule in order to account for the V_{Global} dynamics, in contrast to the CSTR implementation of ADM1 (Batstone et al., 2002). On the other hand, it should be noted that the effect of apparent concentrations becomes negligible at low TS contents (i.e. TS < 5%) with ρ_{Global} tending to $\rho_{Solvent}$, as $S_{T,i,App}$ progressively approaches to $S_{T,i}$ in these conditions. With all the above, the sole implementation of the HS-AD mass balances and the use of apparent concentrations in this study may allow to simulate indistinctly 'wet' AD and HS-AD conditions, and/or the transition between these two AD regimes, for example, during a prolonged HS-AD operation.

$$S_{T,i,App}\left(\frac{kg\ or\ kmol}{m^3\ Solvent}\right) = \frac{S_{T,i}\left(\frac{kg\ COD\ or\ kmol}{m^3\ Total}\right)}{(1-TS)\left(\frac{kg\ Solvent}{kg\ Total}\right)} \cdot \frac{\rho_{Solvent}\left(\frac{kg\ Solvent}{m^3\ Solvent}\right)}{\rho_{Global}\left(\frac{kg\ Total}{m^3\ Total}\right)} \tag{11}$$

$$\frac{dC_{T,i}}{dt} = \frac{1}{V_{Global}} \cdot \left(Q_{Influent} \cdot C_{T,0} - \frac{m_{Effluent}}{\rho_{Global}} \cdot C_{T,i}\right) + \sum r_{i,ADM1} - \frac{C_{T,i}}{V_{Global}} \cdot \frac{dV_{Global}}{dt} \tag{12}$$

2.1.3. Kinetic rates

The ADM1 biochemical rates and inhibitions were used for the verification of the model implementation according to the protocol proposed by Rosén and Jeppsson (2006). The model verification aimed to test/assess the ADM1 implementation (code) alongside the adequate mathematical solution of the mass balances, determining the TS and organic removal both in 'wet' and high-solids AD applications. On the other hand, a slightly different set of biochemical rates was used for HS-AD model calibration. Thus, calibration aimed to test/assess the HS-AD model performance under real experimental conditions. The biochemical kinetics used in this study are shown in Table 1.

The biochemical rates used in the HS-AD model were associated with the inhibitory functions as originally proposed in ADM1 (Batstone et al., 2002; Rosén and Jeppsson, 2006) [Equations (13)–(16)]. However, all the soluble species terms included in the HS-AD biochemical rates – excluding S_{fa} – were expressed in terms of apparent concentrations, as mentioned in section 2.1.2.

$$I_{in} = \frac{S_{in,App}}{K_{S,Sin} + S_{in,App}} \tag{13}$$

$$I_{h2} = \frac{K_{i,Sh2}}{K_{i,Sh2} + S_{h2,App}} \tag{14}$$

$$I_{pH} = \frac{K_{pH}^{N_{pH}}}{K_{pH}^{N_{pH}} + S_{proton}^{N_{pH}}} \tag{15}$$

$$I_{nh3} = \frac{K_{i,Snh3}}{K_{i,Snh3} + S_{nh3,App}} \tag{16}$$

Regarding the HS-AD model implementation used for calibration [Table 1], the valerate uptake was assumed to be carried out by valerate degraders (X_{c5}), instead of butyrate and valerate being both degraded by butyrate degraders (X_{c4}), as proposed in ADM1 (Batstone et al., 2002). This last modification was used to account for the different dynamics observed for butyrate and valerate uptake in the experimental data. The valerate parameters and rates were maintained as in the original thermophilic (55 °C) implementation of ADM1, though the X_{c5} decay was included in the biochemical matrix. On the other hand, the microbial decay was assumed to yield particulate substances (i.e. carbohydrates and proteins) directly, avoiding the use of a composite material (X_c) and the associated disintegration kinetics (Batstone et al., 2015). The biomass decay COD fractioning (i.e. $f_{ch,xc}$) was maintained as proposed by Rosén and Jeppsson (2006). However, the inert materials (i.e. S_i and X_i) carbon content (C_i) was modified to 0.0405 kmol C/kg COD in order to close the biomass carbon balance, while the inert nitrogen content (N_i) was modified to 0.0144 kmol N/kg COD to close the biomass nitrogen balance. This last modification permitted to reduce the stiffness and speed up the model simulations in this study.

The degradation of the protein content of an organic waste determines the total ammonia nitrogen (TAN, S_{in}) in HS-AD (Kayhanian, 1999). In this line, the nitrogen balance has to be closed for the microorganisms in ADM1, while adding complex substrates implies the fulfilment of the corresponding nitrogen balances. For this study, two nitrogen balances were used for the biomass and substrate as shown in Equations (17) and (18), respectively, assuming a common nitrogen content for proteins/amino acids (N_{aa}). With this approach, two new inert variables ($S_{i,subs}$ and $X_{i,subs}$) were added to ADM1 in order to calibrate the initial protein content (X_{pr}) and/or the experimental TAN dynamics. The nitrogen balance for biomass [Equation (17)] remained closed as mentioned before, while the protein fraction of the substrate-inoculum mixture ($f_{pr,subs}$) could be adjusted by calibrating the inert nitrogen content of the substrate-inoculum mixture ($N_{i,subs}$), since all the remaining variables in the nitrogen balance (N_{subs}, $f_{si,subs}$ and $f_{xi,subs}$) [Equation (18)] could be obtained experimentally. For example, the anaerobic biodegradability (i.e. $COD_{removed}/COD_{substrate}$) of an organic substrate is equivalent to 1 - ($f_{si,subs} + f_{xi,subs}$), while the global nitrogen content of the substrate-inoculum mixture (N_{subs}) is the quotient between the total Kjeldahl nitrogen (TKN) and COD (i.e. $TKN_{substrate}/COD_{substrate}$).

$$N_{bac} = f_{pr,xc} \cdot N_{aa} + \left(f_{si,xc} + f_{xi,xc}\right) \cdot N_i \tag{17}$$

$$N_{subs} = f_{pr,subs} \cdot N_{aa} + \left(f_{si,subs} + f_{xi,subs}\right) \cdot N_{i,subs} \tag{18}$$

2.2. Verification of the model implementation

The proposed model implementation was verified for 'wet' AD according to Rosén and Jeppsson (2006). Similarly, the model was further tested for HS-AD conditions. In total, four different verification scenarios were simulated: A) 'wet' AD using the ADM1 implementation of Rosén and Jeppsson (2006); B) 'wet' AD using the HS-AD model implementation with a constant $Q_{Effluent}$; C) HS-AD using the HS-AD model and a constant $Q_{Effluent}$; and D) HS-AD considering the HS-AD model with an adaptive $Q_{Effluent}$. The HS-

Table 1
Biochemical kinetics used for model implementation verification and calibration.

Process	Rate (ρ_j, kg COD m^{-3} d^{-1})	
	Model Verification	Model Calibration
Disintegration	$k_{dis}*X_c$	–
Hydrolysis of Carbohydrates	$k_{h,ch}*X_{ch}$	$k_{h,ch}*X_{ch}$
Hydrolysis of Proteins	$k_{h,pr}*X_{pr}$	$k_{h,pr}*X_{pr}$
Hydrolysis of Lipids	$k_{h,li}*X_{li}$	$k_{h,li}*X_{li}$
Sugars Uptake	$k_{m,su}*S_{su,App}/(K_{S,Xsu}+S_{su,App})*X_{su}*I_{pH}*I_{in}$	$k_{m,su}*S_{su,App}/(K_{S,Xsu}+S_{su,App})*X_{su}*I_{pH}*I_{in}$
Aminoacids Uptake	$k_{m,aa}*S_{aa,App}/(K_{S,Xaa}+S_{aa,App})*X_{aa}*I_{pH}*I_{in}$	$k_{m,aa}*S_{aa,App}/(K_{S,Xaa}+S_{aa,App})*X_{aa}*I_{pH}*I_{in}$
LCFA Uptake	$k_{m,fa}*S_{fa}/(K_{S,Xfa}+S_{fa})*X_{fa}*I_{pH}*I_{in}*I_{h2}$	$k_{m,fa}*S_{fa}/(K_{S,Xfa}+S_{fa})*X_{fa}*I_{pH}*I_{in}*I_{h2}$
Valerate Uptake	$k_{m,c4}*S_{va,App}/(K_{S,Xc4}+S_{va,App})*X_{c4}*S_{va,App}/(1+S_{bu,App}+10^{-6})*I_{pH}*I_{in}*I_{h2}$	$k_{m,c5}*S_{va,App}/(K_{S,Xc5}+S_{va,App})*X_{c5}*I_{pH}*I_{in}*I_{h2}$
Butyrate Uptake	$k_{m,c4}*S_{bu,App}/(K_{S,Xc4}+S_{bu,App})*X_{c4}*S_{bu,App}/(1+S_{bu,App}+10^{-6})*I_{pH}*I_{in}*I_{h2}$	$k_{m,c4}*S_{bu,App}/(K_{S,Xc4}+S_{bu,App})*X_{c4}*I_{pH}*I_{in}*I_{h2}$
Propionate Uptake	$k_{m,pro}*S_{pro,App}/(K_{S,Xpro}+S_{pro,App})*X_{pro}*I_{pH}*I_{in}*I_{h2}$	$k_{m,pro}*S_{pro,App}/(K_{S,Xpro}+S_{pro,App})*X_{pro}*I_{pH}*I_{in}*I_{h2}$
Acetate Uptake	$k_{m,ac}*S_{acApp}/(K_{S,Xac}+S_{ac,App})*X_{ac}*I_{pH}*I_{in}*I_{nh3}$	$k_{m,ac}*S_{ac,App}/(K_{S,Xac}+S_{ac,App})*X_{ac}*I_{pH}*I_{in}*I_{nh3}$
Hydrogen Uptake	$k_{m,h2}*S_{h2,App}/(K_{S,Xh2}+S_{h2,App})*X_{h2}*I_{pH}*I_{in}$	$k_{m,h2}*S_{h2,App}/(K_{S,Xh2}+S_{h2,App})*X_{h2}*I_{pH}*I_{in}$
Sugar Degraders Decay	k_d*X_{su}	k_d*X_{su}
Aminoacids Degraders Decay	k_d*X_{aa}	k_d*X_{aa}
LCFA Degraders Decay	k_d*X_{fa}	k_d*X_{fa}
Valerate Degraders Decay	–	k_d*X_{c5}
Butyrate Degraders Decay	k_d*X_{c4}	k_d*X_{c4}
Propionate Degraders Decay	k_d*X_{pro}	k_d*X_{pro}
Acetate Degraders Decay	k_d*X_{ac}	k_d*X_{ac}
Hydrogen Degraders Decay	k_d*X_{h2}	k_d*X_{h2}

With
$I_{in} = S_{in,App}/(K_{S,Sin} + S_{in,App})$.
$I_{h2} = K_{i,Sh2}/(K_{i,Sh2} + S_{h2,App})$.
$I_{pH} = K_{pH}\hat{}N_{pH}/(K_{pH}\hat{}N_{pH} + S_{h+}\hat{}N_{pH})$.
$I_{nh3} = K_{i,Snh3}/(K_{i,Snh3} + S_{nh3,App})$.

Table 2
Influent and initial conditions used for model implementation verification and model calibration.

Name	Model Verification			Model Calibration	Units
	Simulation A	Simulation B	Simulations C & D		
S_{su}	0.010	0.010	0.010	13.557	kg COD m^{-3}
S_{aa}	0.001	0.001	0.001	2.207	kg COD m^{-3}
S_{fa}	0.001	0.001	0.001	1.393	kg COD m^{-3}
S_{va}	0.001	0.001	0.001	0.734	kg COD m^{-3}
S_{bu}	0.001	0.001	0.001	0.500	kg COD m^{-3}
S_{pro}	0.001	0.001	0.001	2.059	kg COD m^{-3}
S_{ac}	0.001	0.001	0.001	0.103	kg COD m^{-3}
S_{h2}	1.000E-08	1.000E-08	1.000E-08	1.000E-08	kg COD m^{-3}
S_{ch4}	1.000E-08	1.000E-08	1.000E-08	1.000E-08	kg COD m^{-3}
S_{ic}	0.040	0.040	0.040	0.029	kmol C m^{-3}
S_{in}	0.010	0.010	0.010	0.186	kmol N m^{-3}
S_i	0.020	0.020	0.020	0.000	kg COD m^{-3}
$S_{i,subs}$	–	–	–	32.227	kgCOD m^{-3}
X_c	2.000	2.000	2.000	–	kg COD m^{-3}
X_{ch}	5.000	5.000	120.000	40.671	kg COD m^{-3}
X_{pr}	20.000	20.000	20.000	30.902	kg COD m^{-3}
X_g	5.000	5.000	5.000	12.534	kg COD m^{-3}
X_{su}	0.010	0.010	0.010	0.050	kg COD m^{-3}
X_{aa}	0.010	0.010	0.010	0.050	kg COD m^{-3}
X_{fa}	0.010	0.010	0.010	0.001	kg COD m^{-3}
X_{c5}	–	–	–	0.010	kgCOD m^{-3}
X_{c4}	0.010	0.010	0.010	0.002	kg COD m^{-3}
X_{pro}	0.010	0.010	0.010	0.005	kg COD m^{-3}
X_{ac}	0.010	0.010	0.010	0.003	kg COD m^{-3}
X_{h2}	0.010	0.010	0.010	0.070	kg COD m^{-3}
X_i	25.000	25.000	250.000	0.000	kg COD m^{-3}
$X_{i,subs}$	–	–	–	80.567	kgCOD m^{-3}
S_{cat}	0.040	0.040	0.040	0.100	kmoleq m^{-3}
S_{an}	0.020	0.020	0.020	0.051	kmoleq m^{-3}
ρ_{Global}	–	1000.000	1100.000	1077.633	kg m^{-3}
TS	–	4.500	25.000	15.502	%
VS	–	3.500	23.000	12.942	%

AD model was coded in MATLAB® R2017a. The equation solver was ode15s; a variable-step, variable-order solver based on the numerical differentiation formulas of orders 1 to 5. The influent conditions used for model verification are shown in Table 2.

Noteworthy, the only difference between the influent conditions during simulations A and B was the introduction of the TS, VS and ρ_{Global} of the substrate in the last case [Table 2], permitting to excite the high-solids module of the proposed HS-AD model, in contrast

to the CSTR implementation of ADM1. On the other hand, for illustrative purposes only, a high-solids substrate was included using a different carbohydrate (X_{ch}) and particulate inert (X_i) content, but also TS, VS and ρ_{Global}, for simulations C and D [Table 2]. Thus, the high TS content of the influent conditions (i.e. 25%), associated predominantly with X_{ch} and X_i, permitted to test the model under HS-AD operation, while avoiding potential inhibitory states due to NH_3 accumulation.

During the verification of the model implementation, all the ADM1 parameters were used as proposed by Rosén and Jeppsson (2006) for mesophilic (35 °C) AD operation, though the original hydrolysis constant for carbohydrates ($k_{h,ch}$) had to be reduced to 0.10 days in the HS-AD verification only (simulations C and D), in order to avoid reactor overloading and acidification (i.e. $pH \leq 6.0$) during the initial days of simulation. 200 days of 'wet' AD or HS-AD operation were simulated for each verification scenario. The organic loading rate (OLR) was evaluated as the daily substrate addition in COD units divided by V_{Global}, while the hydraulic retention time (HRT) was evaluated as the quotient between V_{Global} and $Q_{Effluent}$.

2.3. Experimental data and data recalculation

The experimental data used to calibrate the HS-AD model consisted in a batch-sacrifice test fed with dried OFMSW and centrifuged inoculum at TS of 15% operated under thermophilic (55 °C) conditions. In the sacrifice test, 15 replicates were implemented in 280 mL serum bottles. Thus, after measuring the biogas volume and composition, a single replicate was opened, and the HS-AD content thoroughly analyzed for the main physicochemical variables. The experimental results included the TS, VS, ρ_{Global}, COD, TKN, TAN, pH, volatile fatty acids (VFA; valeric, butyric, propionic and acetic acids), mono-valent ions (Na^+, K^+ and Cl^-), biogas composition (CH_4, CO_2 and H_2) and methane yield. The serum bottles were agitated only on those days when the biogas production was measured. Further information about the experimental setup, substrate, inoculum and physicochemical analyses is presented as Supplementary Information.

Importantly, an experimental bias might exist on TS measurements whether volatile compounds (i.e. NH_3, CO_2 and VFA) are lost when drying at 105 °C (Angelidaki et al., 2009; EPA, 2001). For this study, the mass of volatile substances at 105 °C ($M_{Volatiles}$) was assumed to be equivalent to the total mass of VFA (S_{ac}, S_{pro}, S_{bu} and S_{va}), TAN (S_{in}) and inorganic carbon (S_{ic}) [Equation (19)]. Thus, the simulated TS and VS were recalculated *a posteriori* (TS_{Recalc} and VS_{Recalc}) [Equations (20) and (21)] in order to compare them with the experimental values.

$$M_{Volatiles} = \left(S_{ac}\cdot\frac{60}{64} + S_{pro}\cdot\frac{74}{112} + S_{bu}\cdot\frac{88}{160} + S_{va}\cdot\frac{102}{208} + S_{in}\cdot 17 + S_{ic}\cdot 44\right)\cdot V_{Global} \quad (19)$$

$$TS_{Recalc} = \frac{M_{Solids} - M_{Volatiles}}{M_{Global}} \quad (20)$$

$$VS_{Recalc} = \frac{M_{Solids} - M_{Inerts} - M_{Volatiles}}{M_{Global}} \quad (21)$$

2.4. Model calibration

The calibration of some of the main biochemical parameters in this study aimed to obtain the best fitting with the experimental data for a homogenized HS-AD laboratory-scale reactor, in order to assess the correct simulations of the TS and reactor content dynamics. The model calibration was carried out by trial and error, mainly for the hydrolysis (i.e. $k_{h,ch}$) and maximum growth rate (i.e. $k_{m,su}$) constants, aiming to maintain as close as possible the parameters proposed for thermophilic (55 °C) AD in ADM1 (Batstone et al., 2002). Noteworthy, the initial composition (i.e. S_{ac}, S_{in}) was chosen based on the evaluation of the experimental data available (i.e. VFA, TAN), while all the initial microorganisms concentrations (i.e. X_{ac}, X_{su}) were calibrated also by trial and error, alongside the main biochemical parameters, as further discussed in section 3.2.1.

3. Results and discussion

3.1. Model implementation verification

3.1.1. 'Wet' AD verification

The model verification for 'wet' AD operating in a CSTR (simulation A) showed minimal differences (i.e. 4^{th}-5^{th} significant digit) compared to the results suggested by Rosén and Jeppsson (2006) [Table 3], being these differences likely associated with the slightly different equation resolution method used [U. Jeppsson, Personal Communication]. Importantly, when using the HS-AD model implementation for 'wet' AD (simulation B), the results were again very close to the original 'wet' ADM1 verification, though some differences could be observed for all the dynamic variables [Table 3]. For example, the acetic acid (S_{ac}) predicted with the HS-AD model implementation (simulation B) was around 39% higher than that in the original ADM1 (simulation A). The TS concentration effect of apparent concentrations might define some differences among all the soluble species during 'wet' AD (i.e. S_{ac}, S_{h2}, S_{nh3}), though the apparent concentrations effect in 'wet' applications was relatively small in simulation B due to the low TS content (i.e. < 5%) [Equation (11)].

It is important to mention that the differences between simulations A and B were related to the fact that the 'wet' AD simulation using the HS-AD model (simulation B) did not reach steady-state. Thus, a steady-state operation in simulation B was not reached even after 200 days, particularly due to the implementation of a common volumetric influent/effluent (i.e. $Q_{Influent} = Q_{Effluent}$). In this line, simulation B showed an overall 37% reduction in the TS content after 200 days, as well as a 13% reduction in V_{Global} (but also HRT), and a 0.5% reduction in ρ_{Global} [Table 3]. Therefore, a daily-averaged 0.06% V_{Global} modification occurred in 'wet' AD using the HS-AD model, which might be considered negligible for short operation periods, but increasingly important for longer operation (Henze et al., 1997; Richards et al., 1991). The progressive reduction of HRT during simulation B led to a proportional increase in OLR from 2.85 to 3.27 kg COD/m^3·d [Fig. 3a], explaining the differences between simulations A and B (i.e. S_{ac}) mentioned before. Interestingly, the reduction in ρ_{Global} (i.e. 0.994 kg/L) below $\rho_{Solvent}$ (i.e. 1.000 kg/L) suggests that the influent conditions (i.e. $\rho_{Global0} = \rho_{Solvent}$) and/or the model simplifications (i.e. $\rho_{Solids} = \text{const.}$) required further testing.

The specific weight of a complex sample (ρ_{Global}) depends on all the compounds involved [Equation (9)]. Since the measurement of all the variables ρ_i in an AD sample is rarely available, the ρ_i of each compound needs to be known/assumed for simulations. In this line,

Table 3
Summary of steady-state results for model implementation verification.

Variable	ADM1 Implementation		HS-AD Model Implementation			Units
	Rosén and Jeppsson (2006)	'Wet' AD	'Wet' AD Const. Effluent[b]	HS-AD Const. Effluent[b]	HS-AD Variable Effluent	
S_{su}	0.01195	0.01195	0.01269	0.01692	0.01000	kg COD m^{-3}
S_{ac}	0.19763	0.19721	0.27484	0.16339	0.05707	kg COD m^{-3}
S_{ic}	0.15268	0.15270	0.15232	0.11377	0.11028	kmole C m^{-3}
S_{in}	0.13023	0.13023	0.13129	0.08451	0.07803	kmole N m^{-3}
X_{ch}	0.02795	0.02795	0.03183	60.73693	41.21685	kg COD m^{-3}
X_{su}	0.42017	0.42017	0.43628	5.38786	6.15898	kg COD m^{-3}
X_{ac}	0.76056	0.76058	0.78837	2.35994	2.52894	kg COD m^{-3}
$Q_{Effluent}$	170	170	170	170	160	m^3 d^{-1}
pH	7.47	7.46	7.48	7.20	7.16	m^3 d^{-1}
S_{co2}	0.0099	0.0099	0.0096	0.0128	0.0134	kmol C m^{-3}
S_{nh3}	0.0041	0.0041	0.0042	0.0015	0.0012	kmol N m^{-3}
P_T	1.069	1.069	1.069	1.180	1.220	bar
Q_g	2956	2956	2939	9752	12472	Nm^3 d^{-1}
$\%CH_4$	61[a]	60.9	60.8	50.6	49.9	%
$\%CO_2$	34[a]	33.9	34.0	44.7	45.5	%
V_{Global}	3400	3400	2967	1717	3400	m^3
$\rho_{Global0}$	–	1000	1000	1100	1100	kg m^{-3}
ρ_{Global}	–	1000	995	1082	1077	kg m^{-3}
HRT	20[a]	20	20	20	20	d
HRT_{real}	–	20	17	10	20	d
OLR	–	2.85	2.85	19.85	19.85	kg COD m^{-3} d^{-1}
OLR_{real}	–	2.85	3.27	39.32	19.86	kg COD m^{-3} d^{-1}
TS_0	4.5[a]	–	4.5	25.0	25.0	%
TS	–	–	2.9	20.4	19.0	%
TS_{Recalc}	–	–	1.9	19.8	18.5	%
VS_0	–	–	3.5	23.0	23.0	%
VS	–	–	1.8	18.2	16.9	%
VS_{Recalc}	–	–	0.9	17.6	16.3	%

[a] Mentioned Only.
[b] No Steady-State Reached.

the specific weight of a sample solid fraction (ρ_{Solids}) can be approximated by knowing the specific weight of the solvent ($\rho_{Solvent}$), though $\rho_{Solvent}$ is again function of all the different compounds in solution, as well as a function of temperature and pressure (Lide, 2004). As a preliminary approach, $\rho_{Solvent}$ was assumed to be close to the specific weight (density) of water at 0 °C and 1 bar (i.e. $\rho_{Solvent} = 1$ kg/L), since the density of water is 999.84 kg/m^3 at 0 °C, 993.64 kg/m^3 (0.63% error) at 35 °C, and 985.19 kg/m^3 (1.48% error) at 55 °C (Kell, 1975; Lide, 2004), thus being approximately constant at any of these temperatures. With this strategy, the specific weights obtained for the overall sample (ρ_{Global}) and/or the solid fraction (ρ_{Solids}) were considered relative regarding the specific weight of solvent ($\rho_{Solvent}$). Meanwhile, $\rho_{Solvent}$ (but also ρ_{Solids}) could be set to any value, or modified by any expression (i.e. as a function of temperature), without modifying the structure of the model. Thus, once knowing the $\rho_{Solvent}$, the ρ_{Global} and TS of a (semi-)solid sample, ρ_{Solids} could be approximated by using the mass balance [Equation (9)].

Previous research indicated that ρ_{Solids} ranges from 1.3 kg/L in lignocellulosic materials to 1.5 kg/L in OFMSW and 2.5 kg/L for inorganic inert solids (i.e. sand). On the other hand, the specific weight of microorganisms is reported between 0.8 and 1.4 kg/L (van Veen and Paul, 1979), though this fraction might be a negligible part (i.e. 5%) of the whole reactor mass content. Therefore, a compromise value of $\rho_{Solids} = 1.5$ kg/L was chosen for the preliminary model verification/calibration, though further testing must be devoted to this particular variable, since it could influence other aspects of the HS-AD simulations (i.e. V_{Global}), as mentioned before.

3.1.2. HS-AD verification

Regarding the HS-AD model verification with constant $Q_{Effluent}$ (simulation C), the HS-AD simulation did not reach the steady state after 200 days, while longer simulations (i.e. 365 days) yielded reactor acidification (i.e. pH ≤ 6.0) – data not shown. This is due to a progressive reduction of V_{Global} in HS-AD when maintaining a volumetric outflow equal to the volumetric inflow (i.e. $Q_{Influent} = Q_{Effluent}$) (Kayhanian and Tchobanoglous, 1996; Richards et al., 1991). Thus, HRT decreases – and OLR increases – proportionally to the V_{Global} reduction in HS-AD until the 'washout' of methanogens occurs and the reactor acidifies. For example, a 50% reduction in HRT was observed with the influent conditions tested in simulation C [Fig. 3b], showing an approximately daily-averaged V_{Global} reduction of 0.25%.

Meanwhile, a rapid stabilization of the HS-AD process was obtained when choosing a constant reactor volume as a set point (i.e. $V_{Setpoint} = V_{Global0}$) and recalculating $Q_{Effluent}$ [Table 3 and Fig. 3b]. Noteworthy, the $Q_{Effluent}$ recalculation operation yielded a reduction of around 5.6% of the steady-state value regarding $Q_{Influent}$, and a 24% TS removal compared to the substrate TS (i.e. from 25 to 19%). These results condense the importance of reducing the effluent compared to the influent (i.e. $Q_{Influent} > Q_{Effluent}$) to reach steady-state HS-AD, in order to compensate the organic removal by methanogenesis (Kayhanian and Hardy, 1994; Kayhanian and Tchobanoglous, 1996; Richards et al., 1991). Furthermore, the use of apparent concentrations might be also crucial for HS-AD simulations, since practically all the biochemical rates were affected (i.e. speeded-up/slowed-down) by the TS concentration effect on soluble substrates (i.e. S_{ac}) and/or inhibitors (i.e. S_{nh3}) [Table 1]. For example, a 26% increase in all the soluble concentrations (i.e. S_{su} and S_{h2}) was obtained by the tested HS-AD conditions in steady-state operation – data not shown.

The water/solvent in this study was assumed to be conservative, since the same water entering leaves the system as a liquid effluent ($m_{Effluent,Solvent}$) or vapor (m_{Vapor}), but is not produced/consumed. Importantly, production/consumption of water in the biochemical processes (i.e. hydrolysis to methanogenesis) might occur, linking

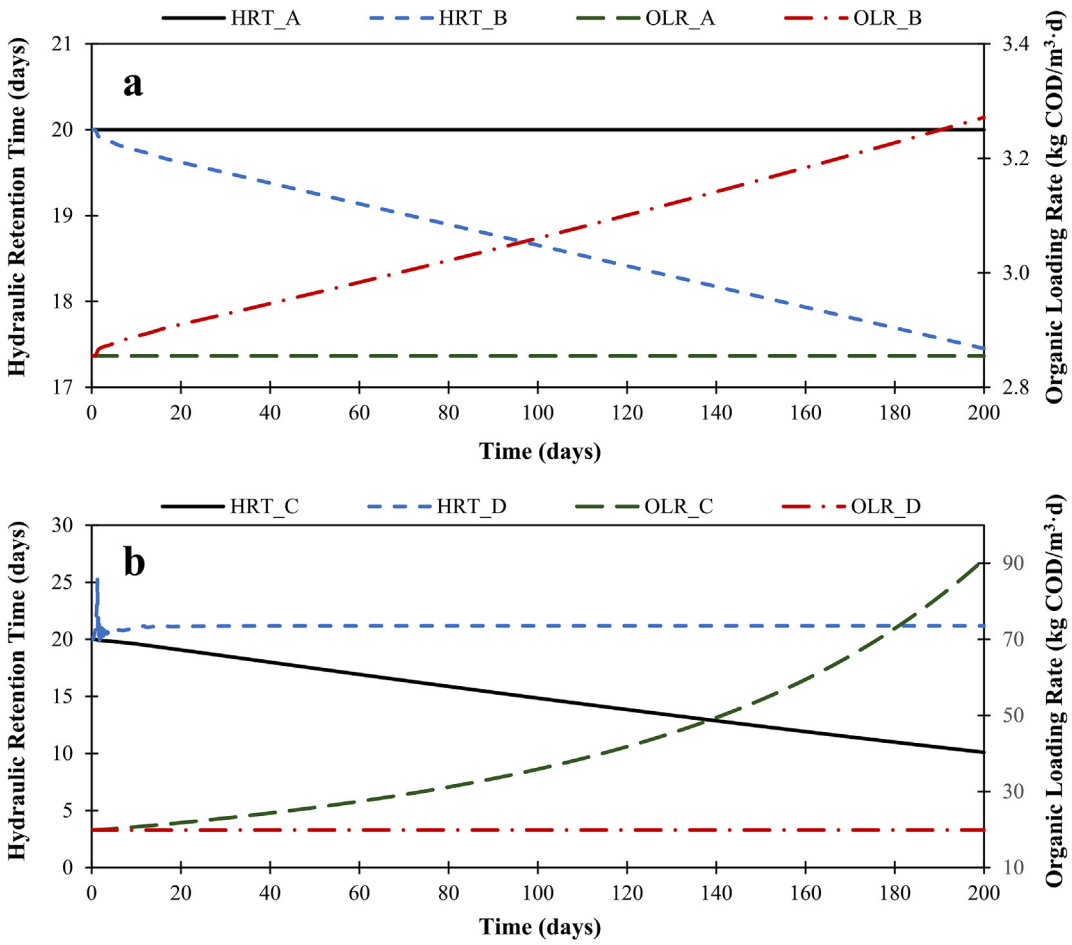


Fig. 3. Hydraulic retention time and organic loading rate in model implementation verification: a) 'wet' anaerobic digestion (simulations A and B); and b) high-solids anaerobic digestion (simulations C and D).

Equations (2) and (3). However, the production/consumption of water is tightly linked to the stoichiometry of all the reactions occurring in HS-AD, while the stoichiometry of all the biochemical reactions in ADM1 requires further development (De Gracia et al., 2006; Kleerebezem and van Loosdrecht, 2006; Rodríguez et al., 2006). Therefore, using Equations (1)–(4) is a reasonable hypothesis that can be modified, once the global stoichiometry of HS-AD is well-defined. In this last case, the Petersen matrix originally proposed for ADM1 would need to account for water as another dynamic variable. For example, De Gracia et al. (2006) included water (i.e. S_{h2o}) in the Petersen matrix of ADM1, though the AD stoichiometry was partially assumed (i.e. particulate compounds elemental composition). Furthermore, in order to use Equations (1)–(4) in this study, it was also assumed that the organic solid destruction only proceeds when biogas production occurs. In other words, whether hydrolysis, acidogenesis and/or acetogenesis occur, but not biogas production (i.e. CH_4, CO_2 and/or H_2), complex substrates (i.e. carbohydrates) are just transformed into more simple substrates (i.e. sugars, VFA), being both of them jointly included in the term $m_{Effluent,Solids}$. With these two last assumptions, the hydrolysis to acidogenesis steps were not included in Equations (1)–(4). However, the mass volatile compounds at 105 °C ($M_{Volatiles}$) needed to be accounted in the TS and VS calculations, as shown in Equations (19)–(21).

Due to the considerably higher COD of the influent conditions [Table 2], the OLR was around 7 times higher for HS-AD than for 'wet' AD simulations [Table 3], which directly relates to the higher chances of HS-AD acidification, and the necessity to reduce considerably the $k_{h,ch}$ for HS-AD simulations. In either case, HS-AD experimental data are required to calibrate biochemical parameters (i.e. $k_{h,ch}$).

3.2. Model calibration

3.2.1. Comparison between simulated and experimental values

The HS-AD simulation of OFMSW in batch conditions at 15% TS closely matched all the experimental variables [Fig. 4], though slight disagreements were also observed between the experimental data and the simulated values. The initial conditions and modified parameters used are shown in Tables 2 and 4, respectively. Firstly, the cumulative methane production was 830 NmL CH_4 [Fig. 4a], coinciding to that obtained experimentally, while the biogas composition was also well simulated – data not shown. Importantly, the overall biogas production was associated with 1.7 g M_{Global} removal (i.e. 4.6%), in agreement with the 1.5–2.0 g that could have been removed according to the experimental biogas flow/composition. Noteworthy, the simulation suggested that ρ_{Global} was reduced from 1078 to 1064 kg/m^3 (i.e. 1.2% reduction) along the whole experimental period (data not shown), though the ρ_{Global} modification should be further validated with experimental data, as discussed before. The M_{Global} and ρ_{Global} modification yielded a V_{Global} reduction of 3.5% – data not shown.

The initial composition in the batch experiment [Table 2] was based on the availability of experimental data (i.e. COD, TS and CH_4

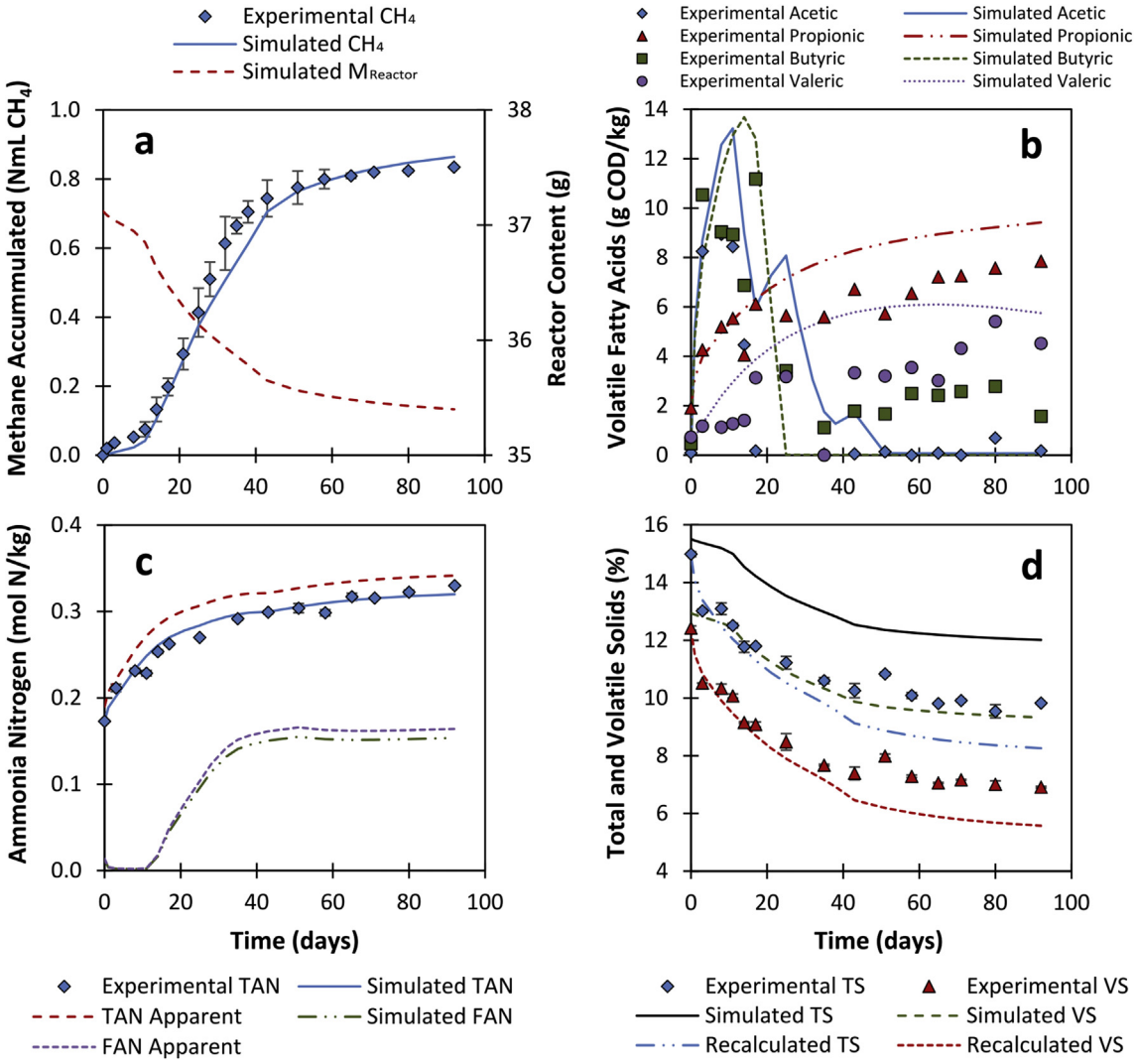


Fig. 4. Batch mono-digestion of OFMSW at 15% total solids: a) accumulated methane production and reactor mass content; b) volatile fatty acids; c) total and free ammonia nitrogen; and d) total and volatile solids.

Table 4
Main parameters modified for model calibration.

Parameter	ADM1	This Study	Units
$k_{h,ch}$	10	0.05	d^{-1}
$k_{h,pr}$	10	0.05	d^{-1}
$k_{h,li}$	10	0.07	d^{-1}
$k_{m,su}$	70	35	d^{-1}
$k_{m,fa}$	10	4	d^{-1}
$k_{m,c5}$	30	1	d^{-1}
$k_{m,c4}$	30	6	d^{-1}
$k_{m,pro}$	20	1	d^{-1}
$pH_{LL,ac}$	6	5.8	
$pH_{UL,ac}$	7	6.8	
$f_{bu,su}$	0.13	0.37	
$f_{pro,su}$	0.27	0.11	
$f_{ac,su}$	0.41	0.40	
$f_{h2,su}$	0.19	0.12	
$N_{i,subs}$	–	0.001	kmol N m^{-3}

yield), but also on a reasoned assessment of the substrate and/or inoculum composition. For example, the protein content of the substrate/inoculum mixture (i.e. $X_{pr} + S_{aa}$) was adjusted according to the nitrogen content of proteins and amino acids (N_{aa}) [Table 4] and the inert materials (i.e. $X_i + S_i$) to simulate the TAN (S_{in}) dynamics, as mentioned in section 2.1.3. Unfortunately, apart from the CH_4 yield and COD of the initial mixture, no data were available regarding the remaining complex substances (i.e. particulates) involved in the biochemical framework of the model. Therefore, the distinction between the initial carbohydrate/sugars (X_{ch}/S_{su}) and lipids/LCFA (X_g/S_{fa}) had to be tuned alongside the biochemical parameters to simulate the initial days of the batch setup.

During the initial 20 days of experiment, pH was observed to drop from 7.3 to 6.3 – data not shown – due to VFA accumulation [Fig. 4b]. Thus, the initial VFA and pH dynamics were simulated by a plausible set of microorganism concentrations, hydrolysis constants and initial substrate/inoculum fractionation [Tables 2 and 4]. The initial microbial concentrations are crucial in the simulation of AD batch experiments, though they are normally unknown due to the difficulties for measuring the populations involved (Donoso-Bravo et al., 2011; Flotats et al., 2010). Importantly, the hydrolysis constants (k_h) were considerably reduced compared to the original values proposed in ADM1 for thermophilic (55 °C) operation (i.e. $k_{h,ch} = 0.05$ d^{-1} vs. 10 d^{-1}, respectively), though the calibrated values were in accordance with reported hydrolysis rates for simulation of OFMSW (Batstone et al., 2002; Kayhanian, 1995;

Mata-Alvarez, 2003; Vavilin and Angelidaki, 2005).

In order to obtain the best fitting between the simulated and experimental VFA dynamics from day 20, the maximum growth rate (k_m) of some microbial populations was also considerably reduced. For example, the maximum growth rate of propionate degraders ($k_{m,pro}$) was reduced to 1 d^{-1}, in contrast to the 20 d^{-1} proposed by ADM1 for thermophilic (55 °C) operation [Table 4]. Noteworthy, the extremely low k_m used for model calibration, in contrast to the original values of ADM1, might be suggesting that some inhibition in the VFA uptake was occurring in the experiment. Thus, NH_3 reached particularly high contents in the reactor (i.e. 0.16 mol N/kg) [Fig. 4c] mainly due to the high pH observed (i.e. ≥ 8.0), while NH_3 is a well-known inhibitor of acetoclastic and hydrogenotrophic methanogens (Angelidaki and Ahring, 1993; Gallert and Winter, 1997; Jokela and Rintala, 2003). In this line, the implementation of reversible NH_3 inhibition [Equation (16)] in hydrogen uptake could match adequately all the VFA, since valerate and propionate degraders are inhibited by H_2 buildup in ADM1 (Batstone et al., 2002). However, this last strategy led to H_2 accumulation in the gas phase (i.e. 2–5%, data not shown), though no H_2 was detected experimentally. Therefore, all the VFA-degrading populations might be affected in some degree by NH_3 accumulation, as suggested by Poggi-Varaldo et al. (1997).

The model suggested a 5–15% difference between the simulated and experimental TS and VS contents, despite the experimental trends were well approximated in both cases [Fig. 4d]. Therefore, since the simulated M_{Global}, CH_4 yield and COD showed good simulations, an experimental bias was suspected in the experimental TS/VS measurement. Noteworthy, the recalculated TS and VS [Equations (19)–(21)] improved considerably the matching of the TS and VS simulations with the values observed experimentally, though some differences were also observed from day 20 onwards. Meanwhile, the TS and VS recalculation is supported by the fact that some organic material (i.e. VFA), ammonia nitrogen (i.e. NH_3) and/or inorganic carbon (i.e. CO_2) might volatilize when drying the samples at 105 °C for prolonged periods of time (i.e. 24 h) (Angelidaki et al., 2009; EPA, 2001). With all the above, the observed differences between the TS and VS recalculated and experimental values [Fig. 4d] were likely related to the differences in the propionate and valerate simulations [Fig. 4b] during the same period. Therefore, the model calibration might require further improvement as also discussed in next section.

3.2.2. Need for further calibration

The model calibration in this study was aimed to be minimal because of: 1) the complexity of HS-AD vs. the assumptions taken (i.e. homogenized reactor); 2) the little data available regarding solids mass dynamics (i.e. TS/VS); 3) the high number of biochemical parameters involved (i.e. > 10); and 4) the 'strong' interrelationship between parameters and the initial conditions in structured AD models (Batstone et al., 2015; Donoso-Bravo et al., 2011; Flotats et al., 2010; Vanrolleghem et al., 1995). Thus, the calibration in this study was mainly addressed to the simultaneous fitting of the overall dynamics of TS/VS removal, reactor mass, biogas production, VFA and pH, in order to assess the potentiality of the proposed model to simulate a homogenized HS-AD matrix.

The parameter modification compared to ADM1 values [Table 4] was needed to obtain an adequate fitting of the overall set of experimental data for the sacrifice test in this study. Importantly, most of the biochemical parameters modified were within the recommended range suggested in ADM1, with the exception of the maximum propionate and valerate growth rates (i.e. $k_{m,pro}$ and $k_{m,va}$) that could be associated to NH_3 inhibition, as mentioned in section 3.2.1. For example, the lower and upper pH levels for acetate uptake ($pH_{LL,ac}$ and $pH_{UL,ac}$, respectively) might vary around 30% from the values proposed in ADM1 (i.e. $pH_{LL,ac} = 6.0$ and $pH_{UL,ac} = 7.0$) (Batstone et al., 2002). However, it must be highlighted that the implementation of a single experimental dataset was not enough to calibrate a large number of parameters since, for example, different combinations of biochemical parameters and/or initial conditions (i.e. microorganisms) could yield practically the same agreement between experimental and simulated results (Girault et al., 2011; Jablonski and Lukaszewicz, 2014; Vanrolleghem et al., 1995; Vavilin et al., 2008). Therefore, more experimental datasets (i.e. laboratory and/or large scale applications) are needed to refine the calibration of the proposed parameters for HS-AD of OFMSW. Meanwhile, a sensitivity analysis and an adequate parameter optimization strategy might reveal important aspects about the main biochemical and physicochemical processes occurring in HS-AD of OFMSW.

With all the above, the minimal model calibration showed the potentiality of using adequately the mass balances alongside the biochemical framework of ADM1 to simulate HS-AD of OFMSW. Thus, the HS-AD model simulates particularly well the TS, VS, and M_{Global} dynamics of HS-AD, provided the four preliminary hypotheses proposed are fulfilled. Meanwhile, further studies are needed in order to improve the biochemical calibration of the HS-AD model, with the aim to explore the different acidification/inhibitory mechanisms of HS-AD fed with OFMSW. Further calibration will be also helpful to double check the hypotheses used, assess the HS-AD model performance and/or highlight potential areas requiring further model development. Summarizing, the user could calibrate the model parameters and/or readapt the HS-AD model structure as required for any particular HS-AD application.

4. Conclusions

In this study, a novel ADM1-based model was developed to simulate the solids and reactor mass/volume dynamics of homogenized HS-AD reactors. An adequate mass balance implementation condensed the effects of biogas production on HS-AD mass/volume, being critical to simulate relatively long operations. Apparent concentrations accounted for the TS concentration effect on soluble species. The model was verified for 'wet' AD and HS-AD, serving as a link between both operational regimes. The model simulated particularly well HS-AD of OFMSW in batch, including the TS and reactor mass, while further model calibration might serve to assess inhibitory mechanisms in HS-AD of OFMSW.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.watres.2018.06.016.

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