

1 **Modelling Non-Ideal Bio-Physical-Chemical Effects on High-Solids**
2 **Anaerobic Digestion of the Organic Fraction of Municipal Solid Waste**

3

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14

15 **ABSTRACT**

16 This study evaluates the main effects of including ‘non-ideal’ bio-physical-chemical
17 corrections in high-solids anaerobic digestion (HS-AD) of the organic fraction of
18 municipal solid waste (OFMSW), at total solid (TS) between 10 and 40 %. As a novel
19 approach, a simple ‘non-ideal’ module, accounting for the effects of ionic strength (I)
20 on the main acid-base equilibriums, was coupled to a HS-AD model, to jointly evaluate
21 the effects of ‘non-ideality’ and the TS content dynamics on the HS-AD bio-physical-
22 chemistry. ‘Non-ideality’ influenced the pH, concentration of inhibitors (i.e. NH_3), and
23 liquid-gas transfer (i.e. CO_2), particularly at higher TS (i.e. ≥ 20 %). Meanwhile, fitting
24 the experimental data for batch assays at 15 % TS showed that HS-AD of OFMSW

25 might be operated at $I \geq 0.5$ M. Therefore, all HS-AD simulations should account for
26 ‘non-ideal’ corrections, when assessing the main inhibitory mechanisms (i.e. NH_3
27 buildup and acidification) potentially occurring in HS-AD of OFMSW.

28

29 **Keywords:** High-Solids Anaerobic Digestion Model; Non-Ideal Bio-Physical-Chemical
30 Corrections; Ionic Strength; Total Solids Dynamics; Ammonia Inhibition.

31

32

33 **1 INTRODUCTION**

34 Anaerobic digestion (AD) models enhance our understanding about the biogas
35 production dynamics and/or inhibitory mechanisms, while revealing potential
36 opportunities for bioprocess optimization (Lauwers et al., 2013; Steyer et al., 2006). The
37 Anaerobic Digestion Model No.1 (ADM1) is a structured model reproducing the main
38 bio-physical-chemical mechanisms in AD (Batstone et al., 2002). Biochemical
39 mechanisms include the disintegration, hydrolysis, acidogenesis, acetogenesis and
40 methanogenesis of organic substrates, expressed in chemical oxygen demand (COD)
41 units. Physical-chemical mechanisms include the liquid-gas transfer of CH_4 , CO_2 and
42 H_2 , and the ionic equilibriums of volatile fatty acids (VFA; i.e. acetic, propionic, butyric
43 and valeric), inorganic nitrogen (i.e. NH_3), and inorganic carbon (i.e. CO_2).

44

45 High-solids anaerobic digestion (HS-AD) is operated at total solid (TS) content ≥ 10 %,
46 in contrast to ‘wet’ AD (i.e. $\text{TS} < 10$ %) (Pastor-Poquet et al., 2019a). In HS-AD of the
47 organic fraction of municipal solid waste (OFMSW), a 30 - 80 % volatile solid (VS)
48 removal occurs due to the biogas production, modifying the reactor content mass

49 (M_{Global}) and/or volume (V_{Global}), but also the reactor content specific weight (ρ_{Global})
50 (Kayhanian & Tchobanoglous, 1996; Pastor-Poquet et al., 2018).

51

52 To account for the mass removal in HS-AD simulations, a HS-AD model based on
53 ADM1 was developed (Pastor-Poquet et al., 2018). The main difference between the
54 HS-AD model and the continuously-stirred tank reactor (CSTR) implementation of
55 ADM1 (Batstone et al., 2002) lies on the simulation of the M_{Global} , V_{Global} , TS, VS, and
56 ρ_{Global} dynamics by using an extended set of mass balances for homogenized HS-AD
57 reactors. For example, apart from the mass balance of soluble (“S”) and particulate
58 (“X”) substances in ADM1, the HS-AD model includes the mass balance of reactor
59 mass (M_{Global}), solvent ($M_{Solvent}$), and inert (M_{Inerts}) contents, allowing the dynamic
60 calculation of TS and VS. On the other hand, apparent concentrations (i.e. kg COD/m³
61 Solvent) were used in the bio-physical-chemical framework of the HS-AD model, to
62 account for the TS concentration effect on HS-AD solutes (i.e. VFA), and in contrast to
63 ADM1 that uses global concentrations (i.e. kg COD/m³ Total).

64

65 An important limitation of the physical-chemical framework of ADM1 is the absence of
66 corrections for the ‘non-ideal’ solution effects on AD (Batstone et al., 2012; Solon et
67 al., 2015; Tait et al., 2012). In solution, a global species concentration ($S_{T,i}$) includes the
68 corresponding dissociated ($S_i^{Z_i}$) and un-dissociated ($S_i^{Z_i=0}$) species concentrations, with
69 their associated ion charge (Z_i). Thus, the ‘ideal’ dissociated/un-dissociated species can
70 be obtained from $S_{T,i}$ once knowing the mass balance, the ‘ideal’ equilibrium constant
71 ($K_{a,i}$), and the solution pH. For example, the total ammonia/inorganic nitrogen (TAN,
72 S_{in}) in AD is mainly dissociated into ammonium ion (NH_4^+ , S_{nh4+}) and free ammonia

73 (NH₃, S_{nh3}), as a function of the equilibrium constant for inorganic nitrogen (K_{a,in}) and
 74 the proton concentration (H⁺, S_{h+}) [Equation 1]. Using the inorganic nitrogen mass
 75 balance [Equation 2] and the ‘ideal’ ammonia equilibrium [Equation 3], S_{nh4+} and S_{nh3}
 76 can be approximated for a given pH – S_{h+} concentration.

77



$$S_{in} = S_{nh4^+} + S_{nh3} \quad (2)$$

$$K_{a,in} = \frac{S_{nh3} \cdot S_{h^+}}{S_{nh4^+}} \quad (3)$$

78

79 Ionic strength (*I*) estimates the level of ionic interactions of an aqueous solution, and
 80 can be approximated from S_i^{Z_i} and Z_i [Equation 4] (Parkhurst & Appelo, 1999; Solon et
 81 al., 2015). Whether a solution is not infinitely diluted (i.e. ΣS_i^{Z_i} ≠ 0), the hypothesis of
 82 ‘ideality’ (i.e. *I* ~ 0) is not further valid, and all the ‘non-ideal’ equilibriums involved in
 83 the solution must be expressed in terms of activities, instead of molal concentrations
 84 (Batstone et al., 2012; Tait et al., 2012). The activity of a solute (a_i) is the product of the
 85 molal concentration (S_i^{Z_i}, kmol/kg Solvent) by the coefficient of activity (γ_i) [Equation
 86 5]. ‘Non-ideality’ corrections are required for AD solutions when *I* ≥ 0.2 M, being
 87 potentially important in HS-AD due to the high organic concentration used (Batstone et
 88 al., 2015; Solon et al., 2015; Tait et al., 2012).

89

$$I = \frac{1}{2} \sum S_i^{Z_i} \cdot Z_i^2 \quad (4)$$

$$a_i = \gamma_i \cdot S_i^{Z_i} \quad (5)$$

90

91 For an ‘ideal’ solution $\gamma_i = 1$, whereas for a ‘non-ideal’ solution $\gamma_i < 1$ for dissociate
 92 species (i.e. $Z_i \neq 0$) and $\gamma_i > 1$ for un-dissociated species (i.e. $Z_i = 0$). Thus, γ_i is mainly a
 93 function of I and, for a moderately concentrated solution (i.e. $I \leq 0.2$ M), the Davies
 94 equation [Equation 6] is commonly used for assessing the activity of ionic species
 95 (Allison et al., 1991; Parkhurst & Appelo, 1999). However, when $I > 0.2$ M, γ_i tends to
 96 unity with increasing I by using the Davies equation (Solon, 2016; Tait et al., 2012).
 97 Therefore, the WATEQ Debye-Hückel equation [Equation 7] is recommended for $0.2 \leq$
 98 $I \leq 1.0$ M, as γ_i progressively tends to zero with increasing I (Parkhurst & Appelo, 1999;
 99 Solon et al., 2015).

100

$$\log_{10}(\gamma_i) = -A \cdot Z_i^2 \cdot \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 \cdot I \right) \quad (6)$$

$$\log_{10}(\gamma_i) = -\frac{A \cdot Z_i^2 \cdot \sqrt{I}}{1 + B \cdot \alpha_i^0 \cdot \sqrt{I}} + b_i \cdot I \quad (7)$$

101

102 The liquid-gas transfer, ionic speciation, ion pairing and precipitation are the most
 103 important physical-chemical mechanisms affecting and being affected by ‘non-ideality’
 104 in AD (Batstone et al., 2015; Flores-Alsina et al., 2015). In particular, the ionic
 105 speciation determines the medium pH, as well as the concentration of soluble inhibitors
 106 (i.e. NH_3), being two of the most important parameters influencing the biogas
 107 production in ADM1 (Batstone et al., 2002; Rosén & Jeppsson, 2006; Xu et al., 2015).
 108 Therefore, failing to include ‘non-ideal’ corrections in ADM1-based models might
 109 result in an artificially high NH_3 concentration, subsequently influencing the parameter
 110 calibration related to NH_3 inhibition (Hafner & Bisogni, 2009; Nielsen et al., 2008;
 111 Patón et al., 2018).

112

113 With all the above, the ‘non-ideal’ approach may be particularly important to assess the
114 main inhibitory mechanisms in HS-AD of OFMSW, since HS-AD is easily subjected to
115 reactor inhibition by high levels of NH_3 , as a consequence of the high protein content of
116 OFMSW and the reduced free water available in the process (García-Bernet et al., 2011;
117 Kayhanian, 1999). For example, HS-AD of OFMSW can be operated at NH_3 content up
118 to 2.7 g N/kg (i.e. 0.19 mol N/kg), whereas NH_3 concentrations ≥ 1.0 g N/kg (i.e. 0.07
119 mol N/kg) are often reported inhibitory for methanogens (Pastor-Poquet et al., 2019a,
120 b). Thus, the NH_3 build-up in HS-AD may lead to VFA accumulation and eventual
121 reactor failure by acidification (i.e. $\text{pH} \leq 6.0$). On the other hand, acidification might be
122 also the result of substrate overload due to the imbalance between acidogenic-
123 methanogenic growth and/or the elevated organic content of HS-AD (Pastor-Poquet et
124 al., 2018; Staley et al., 2011). Noteworthy, the release of inorganic carbon (i.e.
125 $\text{CO}_2/\text{HCO}_3^-$) by acetoclastic methanogens is one of the main pH buffering agents in AD,
126 potentially counteracting reactor acidification (Steyer et al., 2006). Therefore, the risk of
127 acidification might be also affected by the ‘non-ideal’ effect on the CO_2 liquid-gas
128 transfer (Patón et al., 2018).

129

130 This study evaluates for the first time the main effects of including ‘non-ideal’ bio-
131 physical-chemical corrections in HS-AD simulations using OFMSW as substrate, at TS
132 contents from 10 to 40 %. With this aim, a relatively simple ‘non-ideal’ calculation
133 module, based on the Visual MINTEQ (Allison et al., 1991) and Phreeqc (Parkhurst &
134 Appelo, 1999) physical-chemical engines, was developed to assess the potential effects
135 of a high I (e.g. > 0.2 M) upon the main ionic equilibriums of HS-AD, while speeding-

136 up model simulations. Coupling the proposed ‘non-ideal’ module with the HS-AD
 137 model (Pastor-Poquet et al., 2018) permitted to explore some of the main inhibitory
 138 mechanisms (i.e. NH₃ buildup and acidification) in HS-AD of OFMSW, particularly at
 139 relatively high TS contents (i.e. $\geq 20\%$).

140

141

142 **2 METHODOLOGY**

143 **2.1 Activity Coefficients and Modified Equilibrium Constants**

144 In this study, the Extended Debye-Hückel (EDH) equation [Equation 8] was used to
 145 approximate the activity coefficients (γ_i) in HS-AD. EDH is a particular case of the
 146 WATEQ Debye-Hückel equation [Equation 7], whose parameters (A , B and a_i^0) are
 147 known for the main ionic species usually measured in AD (e.g. CH₃COO⁻,
 148 CH₃CH₂COO⁻, NH₄⁺ and Na⁺) (Ball & Nordstrom, 1991; Stumm & Morgan, 1996).
 149 Importantly, the activity coefficients for non-charged species (γ_0) in solution (i.e. NH₃,
 150 CO₂) were also calculated as a function of I [Equation 9], using $b_i = 0.1$ (Parkhurst &
 151 Appelo, 1999).

152

$$\log_{10}(\gamma_i) = -\frac{A \cdot Z_i^2 \cdot \sqrt{I}}{1 + B \cdot a_i^0 \cdot \sqrt{I}} \quad (8)$$

$$\log_{10}(\gamma_0) = -b_i \cdot I \quad (9)$$

153

154 To include ‘non-ideal’ effects in AD, the ‘ideal’ dissociation/equilibrium constants
 155 ($K_{a,i}$) were corrected in terms of activities (a_i) to obtain the modified equilibrium
 156 constants ($K_{a,i}'$) (Nielsen et al., 2008; Tait et al., 2012). For example, $K_{a,in}$ expressed in
 157 activity terms [Equation 10] can be reorganized to obtain the modified equilibrium

158 constant for inorganic nitrogen ($K_{a,in}$) [Equation 11]. Importantly, the proton activity
 159 (a_{h^+}) must be used for pH calculations [Equation 12] under ‘non-ideal’ conditions
 160 (Allison et al., 1991; Parkhurst & Appelo, 1999). Therefore, since the ‘non-ideal’ set of
 161 equations (i.e. Equations 2, 8, 9, 11 and 12) is implicit in S_{h^+} , the calculation of pH, I ,
 162 and $K_{a,i}$ must be solved iteratively, fulfilling both equilibriums and mass balances in an
 163 ionic solution.

164

$$K_{a,in} = \frac{a_{nh_3} \cdot a_{h^+}}{a_{nh_4^+}} = \frac{\gamma_{nh_3} \cdot S_{nh_3} \cdot \gamma_{h^+} \cdot S_{h^+}}{\gamma_{nh_4^+} \cdot S_{nh_4^+}} = \frac{\gamma_{nh_3} \cdot \gamma_{h^+}}{\gamma_{nh_4^+}} \cdot \frac{S_{nh_3} \cdot S_{h^+}}{S_{nh_4^+}} \quad (10)$$

$$K_{a,in}' = K_{a,in} \cdot \frac{\gamma_{nh_4^+}}{\gamma_{nh_3} \cdot \gamma_{h^+}} = \frac{S_{nh_3} \cdot S_{h^+}}{S_{nh_4^+}} \quad (11)$$

$$pH = -\log_{10}(a_{h^+}) = -\log_{10}(\gamma_{h^+} \cdot S_{h^+}) \quad (12)$$

165

166 For this study, the main global species used were acetate (S_{ac}), propionate (S_{pro}),
 167 butyrate (S_{bu}), valerate (S_{va}), inorganic carbon (S_{ic}), inorganic nitrogen (S_{in}), and mono-
 168 valent inorganic cations (S_{cat}) and anions (S_{an}), as originally proposed in ADM1
 169 (Batstone et al., 2002). The schematic representation of the iterative module for
 170 including the ‘non-ideality’ of an AD solution is shown in Figure 1. All the required
 171 equilibrium constants for an ‘ideal’ solution ($K_{a,i}$) and their temperature dependence
 172 using the van’t Hoff equation were extracted from Batstone et al. (2002) and Lide
 173 (2004).

174

175 To keep the physical-chemical module as simple as possible, the proposed calculation
 176 procedure did not consider ion-pairing or precipitation. Noteworthy, ion-pairing and
 177 precipitation are based on further ionic equilibriums, whereas the due kinetic rates of

178 nucleation and crystal growth phenomena must be adequately accounted also for
 179 precipitation (Huber et al., 2017; Vaneckhaute et al., 2018). Further information about
 180 those mechanisms and some potential strategies for their implementation in ADM1-
 181 based models can be found elsewhere (Flores-Alsina et al., 2015; Lizarralde et al., 2015;
 182 Mbamba et al., 2015; Parkhurst & Appelo, 1999; Vaneckhaute et al., 2018), as also
 183 mentioned in section 3.1.3.

184

185 The gaseous species used in this study were CH₄, H₂, CO₂, and NH₃. The addition of the
 186 NH₃ liquid-gas transfer in the HS-AD model was shown elsewhere (Pastor-Poquet et
 187 al., 2018). The Henry's constant ($K_{H,i}$) of each gaseous species was modified by the
 188 introduction of γ_0 , obtaining the modified Henry's constant ($K_{H,i}'$) [Equation 13]. The
 189 $K_{H,i}$ reference values and their dependence with temperature via the van't Hoff equation
 190 were extracted from Batstone et al. (2002) and Lide (2004).

191

$$K_{H,i}' \left(\frac{\text{kmol}}{\text{m}^3 \cdot \text{bar}} \right) = \frac{K_{H,i} \left(\frac{\text{kmol}}{\text{m}^3 \cdot \text{bar}} \right)}{\gamma_0} = \frac{S_{g,i} \left(\frac{\text{kmol}}{\text{m}^3} \right)}{P_i (\text{bar})} \quad (13)$$

192

193

194 **2.2 Model Implementation Verification**

195 **2.2.1 Model Comparison**

196 The 'non-ideal' calculation module [Figure 1] was used to upgrade the CSTR
 197 implementation of ADM1 as suggested by Rosén and Jeppsson (2006), and the HS-AD
 198 model proposed by Pastor-Poquet et al. (2018). Four different models were compared:
 199 standard ADM1 (ADM1); ADM1 using 'non-ideal' conditions (ADM1 Non-Ideal); the
 200 HS-AD model (HS-AD Model); and the HS-AD model using 'non-ideal' conditions

201 (HS-AD Model Non-Ideal). 365 days of continuous HS-AD operation were used in each
202 simulation. Apparent (i.e. kmol/m^3 Solvent) and global (i.e. kmol/m^3 Total)
203 concentrations were used to express exactly the same HS-AD results, since both
204 concentrations are related to each other by the TS, as well as global (ρ_{Global}) and solvent
205 (ρ_{Solvent}) specific weights (Pastor-Poquet et al., 2018). Particularly, apparent
206 concentrations were used in the HS-AD model to account for the TS concentration
207 effect on all the soluble species in a low water environment as HS-AD.

208

209 Importantly, simulation of a continuous HS-AD reactor using the HS-AD model
210 required the reduction of the volumetric effluent (Q_{Effluent}) compared to the influent
211 (Q_{Influent}) to maintain V_{Global} constant. With this aim, a proportional controller for
212 Q_{Effluent} was used as described by Pastor-Poquet et al. (2018), allowing also the
213 comparison between the steady-state results obtained with the CSTR implementation of
214 ADM1 and the HS-AD model. On the other hand, all the simulated TS and VS were
215 recalculated (i.e. $\text{TS}_{\text{Recalc}}$ and $\text{VS}_{\text{Recalc}}$, respectively) as shown by Pastor-Poquet et al.
216 (2018), to include the potential losses of volatile materials (i.e. CO_2 , NH_3 and VFA)
217 when drying a sample at 105°C (EPA, 2001). The organic loading rate (OLR) was
218 approximated as the daily influent COD per unit of V_{Global} (i.e. $\text{kg COD/m}^3 \cdot \text{d}$), while the
219 hydraulic retention time (HRT) was evaluated as the quotient between V_{Global} and
220 Q_{Effluent} (i.e. days). The overall biomass content (X_{biomass}) was the sum of all microbial
221 concentrations in ADM1: $X_{\text{biomass}} = X_{\text{su}} + X_{\text{aa}} + X_{\text{fa}} + X_{\text{c4}} + X_{\text{pro}} + X_{\text{ac}} + X_{\text{h2}}$.

222

223 As a novel approach, the four model configurations presented above were used to assess
224 simultaneously the influence of the varying reactor content mass/volume, the effect of

225 the apparent concentrations, and the solution ‘non-ideality’ in HS-AD simulations. The
226 biochemical rates used for model verification are reported in Table 1. All the model
227 parameters were as in Rosén and Jeppsson (2006) for mesophilic (35°C) AD.
228 Continuous influent conditions were used at 10, 20 and 30 % TS [Supplementary
229 Information], together with a Q_{Influent} of 170 m³/d, a V_{Global} of 3400 m³, and a reactor
230 design volume (V_{Reactor}) of 3700 m³. With these specifications, all the simulations were
231 performed at an HRT of 20 d, while the OLR was proportionally increased for higher
232 TS influents. All the influent conditions simulated an OFMSW inflow with a relatively
233 high content of proteins (X_{pr}) at different dilutions, permitting to assess differently the
234 NH₃ inhibition on acetate uptake, particularly when reaching steady-state HS-AD.

235

236 **2.2.2 ‘Non-Ideal’ Calculations**

237 pH calculations were performed as shown in Rosén and Jeppsson (2006) and Volcke et
238 al. (2005). In order to implement ‘non-ideal’ conditions, the $K_{a,i}$ of all the ionic species
239 in ADM1 (i.e. S_{in} , S_{ic} , S_{ac}) were modified at each time-step, as shown in section 2.1. For
240 ‘non-ideal’ simulations, S_{cat} and S_{an} were entirely associated to Na⁺ and Cl⁻,
241 respectively. Importantly, apparent concentrations (i.e. kmol/m³ Solvent) were used in
242 the pH calculations – as well as in all the bio-physical-chemical dynamics – of the HS-
243 AD model, in contrast to the CSTR implementation of ADM1 that used global
244 concentrations (i.e. kmol/m³ Total).

245

246 In some HS-AD model simulations, the Phreeqc engine (Charlton & Parkhurst, 2011;
247 Parkhurst & Appelo, 1999) was used for pH, I and γ_i calculations, as an alternative to
248 the proposed ‘non-ideal’ module [Figure 1]. In these cases, precipitation was not used,

249 though ion pairing is one of the main features of Phreeqc. It must be mentioned that the
 250 proposed module for assessing ‘non-ideality’ in HS-AD simulations [Figure 1] is a
 251 simplification of more complex physical-chemical engines (i.e. Visual MINTEQ and
 252 Phreeqc). Nonetheless, the proposed ‘non-ideal’ module – instead of Phreeqc – served
 253 to compare ‘ideal’ and ‘non-ideal’ HS-AD simulations, using the same pH calculation
 254 routine in both cases, by only modifying the equilibrium constants ($K_{a,i}$) at each
 255 simulation time-step in the ‘non-ideal’ implementation.

256

257 To illustrate the existing link between ‘non-ideality’ and the main NH_3 inhibition
 258 parameters in structured HS-AD models, the NH_3 half-inhibition constant for
 259 acetoclastic methanogens ($K_{i,\text{Snh3},\text{Xac}}$) was slightly modified in some cases. Thus,
 260 simulations using the original $K_{i,\text{Snh3},\text{Xac}}$ for mesophilic (35°C) conditions (i.e. 0.0018
 261 kmol N/m^3) (Batstone et al., 2002) were compared with simulations using slightly
 262 different $K_{i,\text{Snh3},\text{Xac}}$ (i.e. 0.0008 and 0.0028 kmol N/m^3). To compare the different values
 263 for the soluble acetate concentration (S_{ac}) under ‘ideal’ ($S_{ac,\text{Ideal}}$) and ‘non-ideal’ ($S_{ac,\text{Non-}}$
 264 Ideal) conditions at the same influent TS, the relative acetate difference was used
 265 [Equation 14]. To compare the different values for the NH_3 concentration (S_{nh3}) under
 266 ‘ideal’ ($S_{\text{nh3},\text{Ideal}}$) and ‘non-ideal’ ($S_{\text{nh3},\text{Non-Ideal}}$) conditions, the relative NH_3 difference
 267 was used [Equation 15]. The Henry’s constant for CO_2 ($K_{\text{H},\text{co2}}$) reduction between
 268 ‘ideal’ ($K_{\text{H},\text{co2},\text{Ideal}}$) and ‘non-ideal’ ($K_{\text{H},\text{co2},\text{Non-Ideal}}$) conditions was also expressed as
 269 relative difference [Equation 16].

270

$$\text{Acetate Difference (\%)} = \frac{(S_{ac,\text{Non-Ideal}} - S_{ac,\text{Ideal}})}{S_{ac,\text{Ideal}}} \cdot 100 \quad (14)$$

$$NH_3 \text{ Difference (\%)} = \frac{(S_{nh3,Non-Ideal} - S_{nh3,Ideal})}{S_{nh3,Ideal}} \cdot 100 \quad (15)$$

$$K_{H,co2} \text{ Difference (\%)} = \frac{(K_{H,co2,Non-Ideal} - K_{H,co2,Ideal})}{K_{H,co2,Ideal}} \cdot 100 \quad (16)$$

271

272

273 **2.3 Experimental Data and Model Calibration**

274 A HS-AD batch experiment fed with OFMSW and using an inoculum-to-substrate ratio

275 (ISR) = 1.0 g VS/g VS at thermophilic (55°C) conditions was used for model

276 calibration. The batch experiment consisted of a sacrifice test with 15 replicates starting

277 at 15 % TS, where one replicate was opened – ‘sacrificed’ – periodically, and the main

278 physical-chemical analyses (e.g. TS, VFA) were performed. Experimental data included

279 the cumulative methane production, biogas composition (i.e. CH₄ and CO₂), TS and VS,

280 TAN, VFA, pH, and mono-valent ions (i.e. Na⁺, K⁺ and Cl⁻). The biogas production and

281 composition was the average ± standard deviation of all (remaining) replicates,

282 including that being subsequently emptied. The rest of analyses were performed in

283 triplicate for the punctually-emptied replicate. Manual agitation was only performed

284 while sampling the reactors. Further information about the experimental setup and the

285 physical-chemical analyses used can be found Pastor-Poquet et al. (2019a).

286

287 For calibration, the ‘non-ideal’ CSTR implementation of ADM1 (ADM1 Non-Ideal)

288 and the HS-AD model (HS-AD Model Non-Ideal) were compared, using the

289 biochemical rates reported in Table 1. Noteworthy, these rates were slightly different

290 than those used in the original ADM1 implementation (Batstone et al., 2002), since a

291 new population for valerate degraders (X_{c5}) was included, while the composite (X_c)

292 disintegration was disregarded, as shown by Pastor-Poquet et al. (2018). As an example,

293 a reversible (non-competitive) NH₃ inhibition function [Equation 17] was also used for
 294 propionate and valerate uptakes in model calibration [Table 1], to account for the
 295 potential methanogenic and/or acetogenic NH₃ inhibition observed in the experimental
 296 dataset (Pastor-Poquet et al., 2018). The initial conditions were recalculated based on
 297 the experimental data available. The biochemical parameters for thermophilic (55°C)
 298 conditions were extracted from Batstone et al. (2002). Meanwhile, some parameters
 299 were also modified aiming to fit adequately the experimental data [Table 2]. Parameter
 300 calibration and all the initial biomass concentrations (e.g. X_{ac}) were approximated by
 301 trial-and-error. The detailed methodology used for obtaining the initial conditions and
 302 for model calibration were described elsewhere (Pastor-Poquet et al., 2018).

303

$$I_{nh3} = \frac{K_{i,Snh3}}{K_{i,Snh3} + S_{nh3,App}} \quad (17)$$

304

305 It must be stated that both the initial conditions and/or the biochemical model
 306 parameterization are tightly related to the model structure (Dochain & Vanrolleghem,
 307 2001; Donoso-Bravo et al., 2011; Poggio et al., 2016). Thus, in order to minimize the
 308 differences between the CSTR implementation of ADM1 and the HS-AD model, the
 309 same set of initial conditions [Supplementary Information] and thermophilic (55°C)
 310 parameters [Table 2] were used in both cases. The adjustment/fitting of the model
 311 implementations regarding the experimental data was evaluated by the weighted sum of
 312 squares, calculated as shown by Flotats et al. (2003). The weighted sum of squares
 313 included the cumulative methane production (V_{ch4} Cum.), gas composition (CH₄ +
 314 CO₂), pH, TAN (S_{in}), and VFA (S_{ac}, S_{pro}, S_{bu} & S_{va}).

315

316

317 **3 RESULTS AND DISCUSSION**318 **3.1 Verification of the ‘Non-Ideal’ Model Implementation**319 **3.1.1 Effects of ‘Non-Ideality’ on Standard ADM1**

320 The main difference between the ‘ideal’ ADM1 simulations using different influent TS
321 was the S_{in} and S_{ac} accumulation, but also the reduction of the acetoclastic methanogens
322 concentration (X_{ac}) along higher operating TS [Table 3]. These results are related to the
323 higher OLR used at higher influent TS, since the protein content (i.e. 0.22 kg COD/kg
324 COD), as well as the anaerobic biodegradability (i.e. 0.35 kg COD/kg COD) were set
325 equal for all the influent conditions. Meanwhile, the S_{ac} accumulation at higher influent
326 TS [Figure 2a] was also related to the NH_3 half-inhibition constant for acetoclastic
327 methanogens used in all simulations (i.e. $K_{i,S_{nh3},X_{ac}} = 0.0018 \text{ kmol N/m}^3$), since an
328 increasing S_{nh3} exacerbates inhibition [Table 1]. Thus, the $X_{ac}/X_{biomass}$ ratio was
329 observed to decrease from 20.6 to 16.6 % at 10 and 30 % influent TS, respectively
330 [Figure 2b]. Importantly, this last phenomenon might imply a greater risk of
331 methanogenic overloading at increasing OLR in HS-AD simulations under ‘ideal’
332 conditions, since a proportionally lower X_{ac} is available to counteract the S_{ac} buildup.

333

334 The CSTR implementation of ADM1 using ‘non-ideal’ conditions (ADM1 Non-Ideal)
335 showed an increasing I alongside the higher influent TS used, from 0.166 M at 10 % TS
336 up to 0.390 M at 30 % TS [Table 3]. These results suggest that the bio-physical-
337 chemistry in HS-AD of OFMSW might be considerably ‘non-ideal’ (i.e. $I \geq 0.2 \text{ M}$),
338 being the solution ‘non-ideality’ exacerbated at higher operating TS contents and/or by
339 the occurrence of inhibitory mechanisms (i.e. NH_3 build-up). Therefore, an adequate

340 ‘non-ideal’ methodology seems to be required to account for ionic speciation in HS-AD
341 simulations (Batstone et al., 2015; Tait et al., 2012), though the I range for HS-AD of
342 OFMSW should be better assessed by experimental data, as shown in section 3.3.

343

344 The ‘non-ideal’ ADM1 implementation affected practically all the simulated dynamics
345 (e.g. S_{ic} , S_{ac} and X_{ac}), in comparison to the ‘ideal’ ADM1 implementation [Table 3].
346 Particularly, S_{nh3} decreased by 3 - 45 % when using the ‘non-ideal’ in contrast to the
347 ‘ideal’ methodology at each operating TS (i.e. 10 - 30 %), substantially mitigating the
348 acetoclastic inhibition and S_{ac} accumulation [Figure 2a]. The potential alleviation of
349 NH_3 inhibition by using ‘non-ideal’ conditions was also suggested by Hafner and
350 Bisogni (2009) for AD digesters using cow/swine manure as substrate. In this study, the
351 implementation of ‘non-ideal’ ADM1 calculations also showed an 8 to 20 % increase in
352 the $X_{ac}/X_{biomass}$ ratio at higher TS (i.e. 20 - 30 %) compared to the ‘ideal’
353 implementation [Figure 2b]. Thus, ‘non-ideal’ conditions potentially allow a higher
354 operating OLR when simulating HS-AD of OFMSW, since the reduced S_{nh3} leads to a
355 relatively higher X_{ac} to counteract substrate overloading and S_{ac} accumulation.

356

357 It must be noted that, due to the inherent structure of both the biochemical (i.e. Monod
358 equation) and physical-chemical (i.e. charge balance) framework in ADM1, AD
359 simulations are highly non-linear (Donoso-Bravo et al., 2011; Solon, 2016; Volcke et
360 al., 2005). In other words, an increase in the influent conditions (i.e. OLR) of an
361 ADM1-based model might not lead to a proportional increase in the output dynamics
362 (e.g. S_{ac} and S_{nh3}) at steady-state. For example, the S_{ac} accumulation was observed to
363 increase exponentially alongside the S_{nh3} build-up both with the ‘ideal’ and ‘non-ideal’

364 implementations of ADM1 [Figure 2c]. This last effect is related to the Monod kinetics,
 365 as well as the reversible inhibition function used for acetoclastic methanogenesis in
 366 ADM1 [Table 1]. Therefore, the implementation of ‘non-ideal’ conditions may be
 367 crucial in HS-AD simulations, since minimal changes in S_{nh3} – associated to the ‘non-
 368 ideal’ physical-chemistry – might lead to considerable differences in the anaerobic
 369 kinetic rates and/or inhibition potential using structured HS-AD models.

370

371 Finally, $K_{H,i}$ for gaseous species (i.e. CH_4 and CO_2) decreased linearly alongside
 372 increasing I by using ‘non-ideal’ conditions in HS-AD. For example, K_{H,CO_2} showed a
 373 8.6 % reduction at an I of 0.39 M using ADM1 Non-Ideal [Equation 16], corresponding
 374 to a 30 % influent TS [Table 3 and Figure 2d]. Similarly, a linear relationship was also
 375 obtained for the K_{H,CO_2} reduction at increasing TS contents from 10 to 40 %: K_{H,CO_2}
 376 *Difference (%) = - 0.242 · TS (%) - 1.343, $r^2 = 1.000$* – data not shown. The $K_{H,i}$
 377 reduction with increasing TS strongly influences the liquid-gas transfer in HS-AD
 378 simulations. For example, the K_{H,CO_2} reduction exacerbates the CO_2 volatilization in HS-
 379 AD, potentially reducing the available inorganic carbon content (S_{ic}, HCO_3^-), as an
 380 important source of buffering capacity and resistance against organic overloading
 381 (Patón et al., 2018; Poggio et al., 2016; Steyer et al., 2006). Therefore, ‘non-ideal’
 382 conditions are also needed to evaluate the liquid-gas transfer (i.e. CO_2) in HS-AD
 383 simulations, as a potential trigger for reactor acidification.

384

385 **3.1.2. ‘Non-Ideal’ Implementation of the HS-AD Model**

386 The main difference between the CSTR implementation of ADM1 and the HS-AD
 387 model lies on the simulation of M_{Global} , V_{Global} , TS, VS, and ρ_{Global} dynamics by the HS-

388 AD model (Pastor-Poquet et al., 2018). Moreover, Q_{Effluent} had to be reduced compared
389 to Q_{Influent} when using the HS-AD model, as mentioned in section 2.2.1. Therefore, all
390 simulations using the HS-AD model resulted in noticeable differences in the values of
391 these operational variables (i.e. TS, VS and Q_{Effluent}) at steady-state [Table 3], in
392 comparison to the corresponding influent conditions. On the other hand, the use of
393 apparent concentrations (i.e. $S_{\text{ac,App}}$, kg COD/m³ Solvent) increased relatively the
394 soluble global species concentrations (i.e. S_{ac} , kg COD/m³ Total) at higher operating TS
395 [Table 3], due to the lower amount of free water in HS-AD (Pastor-Poquet et al., 2018).

396

397 The previous conclusions about the NH₃ inhibition alleviation and the increasing liquid-
398 gas transfer (i.e. CO₂) using ADM1 Non-Ideal – section 3.1.1 – are also valid for HS-
399 AD Model Non-Ideal. In particular, S_{ac} was from 48 to 93 % lower for ‘non-ideal’ than
400 ‘ideal’ HS-AD model simulations [Table 3 and Figure 2a]. However, it must be
401 highlighted that ‘non-ideal’ conditions were further exacerbated using the HS-AD
402 model, likely due to the inclusion of apparent concentrations in the bio-physical-
403 chemical framework. Thus, HS-AD Model Non-Ideal showed a 5 - 32 % increase on I
404 compared to ADM1 Non-Ideal [Table 3]. Meanwhile, the $K_{\text{H,co2}}$ reduction [Equation 16]
405 at influent TS contents from 10 to 40 % showed a more pronounced slope than that
406 obtained with ADM1: $K_{\text{H,co2}} \text{ Difference (\%)} = -0.400 \cdot \text{TS (\%)} + 0.565$, $r^2 = 0.991$ –
407 data not shown.

408

409 Interestingly, when using HS-AD Model Non-Ideal, some seemingly contradictory
410 results were observed regarding the NH₃ inhibition between the ‘ideal’ and ‘non-ideal’
411 simulations at steady-state: At 30 % influent TS, the apparent NH₃ concentration

412 ($S_{nh3,App}$) was 0.00867 and 0.00868 kmol N/m³ Solvent (i.e. 0.12 % difference), while
413 S_{ac} was 19.5 and 10.0 kg COD/m³ Total, for the ‘ideal’ and ‘non-ideal’ HS-AD model
414 implementations, respectively [Table 3]. In other words, the steady-state S_{ac} was
415 substantially lower at an equivalent $S_{nh3,App}$. Meanwhile, the steady-state S_{ac} vs. S_{nh3} still
416 fulfilled the Monod inhibition framework [Figure 2c].

417

418 To emphasize these last results, the relative differences in the acetate [Equation 14] and
419 NH₃ [Equation 15] concentrations were used. Thus, $S_{ac,Non-Ideal}$ was lower than $S_{ac,Ideal}$ –
420 the acetate difference was negative – at any influent TS [Table 3 and Figure 3a].

421 Nevertheless, the NH₃ difference between $S_{nh3,Non-Ideal}$ and $S_{nh3,Ideal}$ at 30 % TS was
422 positive, in contrast to 10 and 20 % TS influent conditions [Table 3 and Figure 3b].

423 Similar ‘contradictory’ results were also observed at higher influent TS contents (i.e. 35
424 - 40 % TS), where S_{ac} was lower (i.e. 26 - 35 %), while S_{nh3} was higher (i.e. 1 - 3 %),
425 for the ‘non-ideal’ in contrast to the ‘ideal’ HS-AD model implementation [Figure 3].

426

427 Summarizing, results above seemed to contradict the expected trend for acetoclastic
428 inhibition in HS-AD simulations at steady-state: a higher S_{nh3} concentration should lead
429 to a higher S_{ac} accumulation. However, these seemingly contradictory results on NH₃
430 inhibition were only related to the direct comparison of two strongly non-linear model
431 implementations (i.e. ‘ideal’ vs. ‘non-ideal’). More in particular, during the initial 40
432 days of HS-AD model simulations using a 30 % influent TS, the X_{ac} growth was
433 promoted by the ‘non-ideal’ in contrast to the ‘ideal’ model implementation, due to a
434 lower operating $S_{nh3,App}$, as further discussed in section 3.1.3.

435

436 All the above simulations were performed using $K_{i,S_{nh3},X_{ac}} = 0.0018 \text{ kmol N/m}^3$.
 437 Importantly, when shifting $K_{i,S_{nh3},X_{ac}}$ towards lower/higher values in HS-AD Model
 438 Non-Ideal, the TS threshold where $S_{ac,Ideal} > S_{ac,Non-Ideal}$ for $S_{nh3,Ideal} < S_{nh3,Non-Ideal}$
 439 ('inversion' threshold) also shifted [Figure 3]. For example, using $K_{i,S_{nh3},X_{ac}} = 0.0008$
 440 kmol N/m^3 , the 'inversion' threshold occurred at around 20 % influent TS, while using
 441 $K_{i,S_{nh3},X_{ac}} = 0.0028 \text{ kmol N/m}^3$, the 'inversion' threshold occurred between 35 and 40 %
 442 TS. Similar acetoclastic inhibition results were also obtained between the 'ideal' and
 443 'non-ideal' ADM1 implementations, though the 'inversion' thresholds shifted towards
 444 slightly higher operating TS regarding the HS-AD model [Figure 3]. For example, using
 445 $K_{i,S_{nh3},X_{ac}} = 0.0018 \text{ kmol N/m}^3$, the 'inversion' threshold using ADM1 was 40 % influent
 446 TS, instead of 30 % influent TS. All these results indicate that 'non-ideality' is tightly
 447 related to the NH_3 inhibition parameters, but also to the overall HS-AD model structure.

448

449 **3.1.3 The Effects of 'Non-Ideality' during the Initial Days of HS-AD Simulations**

450 During the initial 20 days of HS-AD simulations using 30 % influent TS, X_{ac} was
 451 observed to increase considerably faster under 'non-ideal' than 'ideal' conditions
 452 [Figure 4a], explaining the lower S_{ac} buildup under 'non-ideal' conditions [Figure 4b].
 453 pH was equivalent during the initial 10 days of 'ideal' and 'non-ideal' simulations,
 454 though pH for 'non-ideal' simulations was up to 0.27 units higher from day 10 [Figure
 455 4c and Table 3]. Meanwhile, a lower $S_{nh3,App}$ was observed along the initial 40 days of
 456 'non-ideal' simulations [Figure 4d], despite the apparent TAN ($S_{in,App}$) was equivalent
 457 in both the 'ideal' and 'non-ideal' model implementations [Figure 4e]. Therefore, the
 458 'non-ideal' bio-physical-chemistry of HS-AD at 30 % influent TS led to a lower
 459 $S_{nh3,App}$, mitigating the NH_3 inhibition and promoting the X_{ac} growth, as previously

460 observed for 10 and 20 % influent TS. Nonetheless, the steady-state results [Table 3]
461 prevented observing the overall effect of ‘non-ideality’ in HS-AD simulations.
462

463 With all the above, the ‘inversion’ threshold on the NH_3 concentration at steady-state
464 [Figure 3b] is the consequence of comparing two strongly non-linear model
465 implementations (i.e. ‘ideal’ vs. ‘non-ideal’) at steady-state, being non-linearity
466 associated to the complexity of the biochemical and physical-chemical framework of
467 ADM1-based models, as mentioned before. Importantly, the occurrence of the NH_3
468 ‘inversion’ threshold further stresses the fact that ‘ideal’ ADM1-based models should
469 not be applied to HS-AD (i.e. $\text{TS} \geq 10\%$), since the equation non-linearities might lead
470 to important differences in both the dynamics and the steady state results (i.e. pH , X_{ac} ,
471 S_{nh_3} , S_{ac}) of HS-AD simulations. The ‘inversion’ threshold on the NH_3 inhibition at
472 steady-state was also observed when using slightly different initial conditions (i.e. $X_{\text{pr},0}$,
473 $S_{\text{in},0}$, $S_{\text{ac},0}$, $S_{\text{cat},0}$, $X_{\text{su},0}$ and/or $X_{\text{aa},0}$ – data not shown), since steady-state AD simulations
474 should not depend on the initial conditions used (Donoso-Bravo et al., 2011). Thus, all
475 the above results indicate that a high I (i.e. $\geq 0.2\text{ M}$) strongly influenced the bio-
476 physical-chemistry of HS-AD simulations, particularly the NH_3 inhibition dynamics
477 during the initial days of reactor operation at high TS contents (i.e. $\geq 20 - 30\%$).
478

479 To assess ‘non-ideal’ effects on AD, some of the most complete physical-chemical
480 engines for ‘non-ideal’ characterizations are Visual MINTEQ (Allison et al., 1991) and
481 Phreeqc (Parkhurst & Appelo, 1999) software, including the direct ADM1
482 implementation in Phreeqc (C code) described by Huber et al. (2017), the generic
483 nutrient recovery model of Vaneeckhaute et al. (2018), but also the physical-chemical

484 module developed by Flores-Alsina et al. (2015) and Solon et al. (2015) for plant-wide
485 wastewater treatment. Indeed, the high organic content in HS-AD might strongly
486 determine the precipitation, ion-pairing and ion-surface interactions (Batstone et al.,
487 2012; Huber et al., 2017), requiring even further complexity of the HS-AD bio-
488 physical-chemical framework than for ‘wet’ AD applications (i.e. TS < 10 %). On the
489 other hand, more simple ‘non-ideal’ modules for AD solutions have been also used by
490 Patón et al. (2018) and Nielsen et al. (2008). In this line, the model complexity depends
491 on the model objectives and experimental data available, being always recommended to
492 keep the model as simple as possible, though well suited for addressing the envisaged
493 objectives (Eberl et al., 2006).

494

495 To validate the ‘non-ideal’ module proposed in this study [Figure 1], ‘non-ideal’
496 simulations of the HS-AD model were also performed coupling the Phreeqc engine
497 (Charlton & Parkhurst, 2011). In spite of the higher complexity of Phreeqc, both ‘non-
498 ideal’ modules yielded practically the same HS-AD dynamics (i.e. S_{ac} , S_{in} , X_{ac}) using 30
499 % influent TS [Figure 3], being the 2 - 6 % higher I the most noticeable difference when
500 Phreeqc was used as ‘non-ideal’ module [Figure 3f]. The Phreeqc engine coupling to
501 the HS-AD model also yielded closely-matching results to the proposed ‘non-ideal’
502 module under all the HS-AD simulations presented in section 3.1.2 – data not shown.
503 Importantly, due to the reduced complexity of the proposed ‘non-ideal’ module [Figure
504 1] and/or the coupling of an ‘external’ software, the simulation speed increased
505 considerably (i.e. 7 - 8 times faster) compared to when using the Phreeqc engine as
506 ‘non-ideal’ module.

507

508 3.2 HS-AD Calibration under ‘Non-Ideal’ Conditions

509 The calibration in this study was not aimed to be exhaustive due to the great number of
510 parameters (i.e. > 15) and initial conditions (i.e. > 10) involved in an ADM1-based
511 model, as well as the reduced number of experimental data available (Dochain &
512 Vanrolleghem, 2001; Donoso-Bravo et al., 2011; Poggio et al., 2016). Instead, the
513 calibration aimed to assess the operative levels of I in HS-AD of OFMSW. Moreover,
514 real data calibration could also serve to evaluate the influence of the model complexity
515 (i.e. mass balances) regarding the need for ‘non-ideal’ calculations in HS-AD.

516

517 For the calibration of ADM1 Non-Ideal and HS-AD Model Non-Ideal, the same initial
518 conditions and biochemical parameters [Table 2] were used, yielding a similar degree of
519 adjustment regarding the experimental data (i.e. weighted sum of squares = 2.2 - 2.5)
520 [Supplementary Information]. Nonetheless, HS-AD Model Non-Ideal outperformed
521 ADM1 Non-Ideal in terms of simulating the TS, VS, and M_{Global} dynamics due to the
522 use of a more extended set of mass balances. Moreover, HS-AD Model Non-Ideal
523 adjustment improved considerably towards the end of the experiment, in contrast to the
524 ADM1 Non-Ideal simulations [Figure 5]. For example, the experimental matching in
525 S_{in} , S_{pro} , S_{va} , and gas composition improved from day 15 - 20 onwards, as M_{Global} and/or
526 V_{Global} reduction by methanogenesis occurred in the system. In this line, HS-AD Model
527 Non-Ideal predicted 1.6 g of M_{Global} were removed, equivalent to a 4.4 % of the initial
528 reactor content, during 92 days of batch operation.

529

530 Both ADM1 Non-Ideal and HS-AD Model Non-Ideal simulations showed $I \geq 0.5$ M
531 from day 50 [Figure 5d], associated to the accumulation of S_{in} and VFA, with I being

532 around 5 - 10 % higher in HS-AD Model, due to the use of apparent concentrations.
533 These results confirm that I might be considerably higher than 0.2 M in HS-AD of
534 OFMSW, strongly suggesting the implementation of ‘non-ideal’ conditions at high TS
535 contents (i.e. $\geq 10\%$) to improve the simulations of pH, biochemical inhibition (i.e.
536 NH_3), VFA accumulation (i.e. acetate), and liquid-gas transfer (i.e. CO_2). Furthermore,
537 taking into account the high I observed (i.e. ≥ 0.5 M), the Davies equation [Equation 6]
538 might not be appropriated for HS-AD simulations due to the increasing errors in γ_i at $I \geq$
539 0.2 M. For example, a 20 to 25 % higher $\gamma_{\text{NH}_4^+}$ is obtained at I of 0.5 and 0.6 M,
540 respectively, by using the Davies instead of the EDH equation [Equation 8].

541

542 With all the above, the influence of ‘non-ideality’ on the bio-physical-chemistry of HS-
543 AD simulations strongly depends on the model configuration used. Therefore, the HS-
544 AD model (Pastor-Poquet et al., 2018) may be well suited to assess ‘non-ideal’ effects
545 in HS-AD using OFMSW as a substrate, and particularly the TS concentration effect on
546 the soluble species by using apparent concentrations. Noteworthy, the implementation
547 of apparent concentrations (i.e. kmol/kg Solvent) is in line with the fact that the bio-
548 physical-chemistry of HS-AD occurs predominantly in water. Thus, using apparent
549 concentrations might enhance the predictive capabilities of the ‘non-ideal’ calculation
550 procedure, while influencing both the kinetic rates and inhibition of anaerobic
551 microorganisms in HS-AD simulations (Pastor-Poquet et al., 2018). On the other hand,
552 an adequate mass balance implementation in HS-AD models is needed when using
553 relatively long simulations (i.e. ≥ 20 days), as the effect of reactor mass/volume removal
554 by methanogenesis becomes gradually more important to capture all the bio-physical-
555 chemical mechanisms in HS-AD.

556

557 To end up, further calibration/optimization alongside a thorough sensitivity analysis is
558 needed for the main biochemical parameters of the HS-AD model, in order to draw
559 adequate conclusions about some of the inhibitory mechanisms (i.e. NH_3 buildup and
560 acidification) potentially occurring in HS-AD of OFMSW. In this line, the faster HS-
561 AD model resolution obtained when coupling the proposed ‘non-ideal’ module might be
562 particularly suited to speed up the calibration process, where a great number of
563 simulations are usually required to match appropriately the experimental data (Dochain
564 & Vanrolleghem, 2001; Donoso-Bravo et al., 2011; Flotats et al., 2006). Alongside,
565 further bio-physical-chemical mechanisms as precipitation, ion pairing and ion-surface
566 interactions should be also evaluated in future model implementations, to adequately
567 address the inherent complexity of HS-AD using OFMSW as substrate.

568

569

570 **4 CONCLUSIONS**

571 HS-AD of OFMSW might be operated at $I \geq 0.5$ M. Therefore, the bio-physical-
572 chemistry of all HS-AD simulations needs to account for the ‘non-ideal’ effects on the
573 pH, soluble inhibitors (i.e. NH_3), and liquid-gas transfer (i.e. CO_2), particularly at higher
574 TS contents (i.e. ≥ 20 %). In this study, coupling a HS-AD model to a simplified ‘non-
575 ideal’ module yielded adequate simulations regarding the NH_3 inhibition in HS-AD,
576 both in batch and continuous mode. Using an appropriate set of parameters, the HS-AD
577 model using ‘non-ideal’ conditions might bring further insights about the main
578 inhibitory mechanisms in HS-AD of OFMSW.

579

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584

585

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709 **TABLE CAPTIONS**

710

711 **Table 1:** Biochemical rates used for model implementation verification and model
712 calibration.

713

714 **Table 2:** Biochemical parameters modified for model calibration at thermophilic (55°C)
715 conditions.

716

717 **Table 3:** Summary of steady-state results (i.e. day 365) for model implementation
718 verification at different influent total solid (TS) contents.

719

720

721 **FIGURE CAPTIONS**

722

723 **Figure 1:** Schematic representation of the ‘ideal’ or ‘non-ideal’ physical-chemical
724 implementation used for all ADM1-based models in this study.

725

726 **Figure 2:** Summary of results for model implementation verification as a function of
727 influent total solids (TS). Comparison between standard ADM1, ADM1 Non-Ideal, HS-
728 AD Model and HS-AD Model Non-Ideal outputs: a) Total acetate concentration (S_{ac})
729 vs. initial TS; b) total acetoclastic methanogens to biomass ratio ($X_{ac}/X_{biomass}$) vs. initial
730 TS; c) total acetate concentration (S_{ac}) vs. total NH_3 concentration (S_{nh3}); and d) Henry’s
731 constant difference for CO_2 ($K_{H,co2}$) vs. ionic strength.

732

733 **Figure 3:** Contour plots for the relative difference between the ‘ideal’ and ‘non-ideal’
734 implementations of both ADM1 and the HS-AD model at different influent total solid
735 (TS) contents: a) Acetate (S_{ac}) difference [Equation 14]; and b) NH_3 (S_{nh3}) difference
736 [Equation 15].

737

738 **Figure 4:** Effect of ‘non-ideality’ during the initial 40 days of HS-AD model
739 simulations at 30 % influent TS. Comparison between ‘ideal’ and ‘non-ideal’
740 conditions, including the Phreeqc engine: a) Acetoclastic methanogens concentration
741 (X_{ac}); b) total acetate concentration (S_{ac}); c) pH; d) apparent NH_3 concentration
742 ($S_{nh3,App}$); e) total ammonia nitrogen concentration ($S_{in,App}$); and f) ionic strength (I).

743

744 **Figure 5:** Model calibration results. Comparison between ADM1 Non-Ideal and HS-
745 AD Model Non-Ideal: a) Total ammonia nitrogen (TAN); b) total propionate (S_{pro}) and
746 valerate (S_{va}) concentrations; c) gas composition; and d) ionic strength.

747