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1 **Total solids content drives high solid anaerobic digestion via mass transfer**
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3
4 **limitation**
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24 **Abstract:**

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26 The role of the total solids (TS) content on anaerobic digestion was investigated in
27
28 batch reactors. A range of TS contents from 10 to 35% was evaluated, four replicates
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30 were performed. The total methane production slightly decreased with TS
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32 concentrations increasing from 10 to 25% TS. Two behaviors were observed at 30%
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34 TS: two replicates had similar performances to that at 25% TS; for the two other
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36 replicates, the methane production was inhibited as observed at 35% TS. This difference
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38 suggested that 30% TS content corresponded to a threshold of the solids content, above
39
40 which methanogenesis was strongly inhibited. The Anaerobic Digestion Model No.1
41
42 (ADM1) was used to describe the experimental data. The effects of hydrolysis step and
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44 liquid/gas mass transfer were particularly investigated. The simulations showed that
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46 mass transfer limitation could explain the low methane production at high TS, and that
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48 hydrolysis rate constants slightly decreased with increasing TS.
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1 **Keywords**
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3 Dry anaerobic digestion; total solids content; mass transfer coefficient; hydrolysis;
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5 methanogenesis.
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10 **1. Introduction**
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12 The production of waste including municipal solid waste (MSW) has significantly
13 increased in recent years. For example, in France, MSW generation has more than
14 doubled in less than 50 years, from 175 kg year⁻¹ capita⁻¹ in 1960 to 354 kg year⁻¹capita⁻¹
15 ¹ in 2006 (ADEME, 2009). Different technologies are used for MSW treatment, such as
16 incineration or composting, but anaerobic digestion (AD) processes are particularly
17 interesting in terms of organic matter reduction by converting organic compounds into
18 biogas. The methane content in biogas represents a source of renewable energy.
19
20

21 Based on the total solids (TS) content of solid waste, three main types of technologies
22 have been developed: wet ($\leq 10\%$ TS), semi-dry (10-20% TS) and dry ($\geq 20\%$ TS)
23 processes. Dry technologies, also called “high-solid” anaerobic processes, are attractive
24 because the quantity of water added to the raw waste is substantially reduced, and
25 consequently, the digester size is minimized. However, difficulties in operating dry
26 anaerobic digestion at both laboratory and industrial scales are related to the high
27 concentration of total solids. Fernandez *et al.* (2008) showed that methane production
28 started at day 14 in a reactor with 20% TS and at day 28 in a reactor with 30% TS in
29 mesophilic dry anaerobic batch reactors treating the organic fraction of municipal solid
30 waste. The total methane production was 17% lower at 30% than at 20% TS. This result
31 is consistent with the one obtained by Forster-Carneiro *et al.*(2008), which showed
32 better performance of anaerobic reactors operated at 20% TS compared to 25% and
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1 30% TS. It was suggested that a high TS content could reduce substrate degradation
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3 and, therefore, biogas production (Fernandez *et al.*, 2008). Le Hyaric *et al.* (2011) used
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5 a microbial metabolic intermediate, propionate, as substrate to study specifically the
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7 methanogenic activity in dry reactors. The specific methanogenic activity increased
8
9 linearly by a factor of 3.5 when the moisture content increased from 65% to 82%
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11 (corresponding to 35 to 18% TS, respectively).
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15 A high TS content also affects the physical properties of the digested solid waste. Water
16
17 distribution was investigated by Garcia-Bernet *et al.* (2011a) in biowastes and
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19 associated digestates sampled in industrial dry AD plants. Even if the proportion of the
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21 hydration and vicinal water fractions is small ($0.1 \text{ g}_{\text{water}} \text{ gDM}^{-1}$) compared to the total
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23 amount of water, the capillary water fractions of the digestates ranged from 2 to 2.5
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25 $\text{g}_{\text{water}} \text{ gDM}^{-1}$: this fraction can represent up to 60% of the total water for a digestate
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27 having a TS = 20%. As a consequence, for dry AD systems, the high solids content
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29 strongly affects the rheological behavior of the digestates (Battistoni, 1993; Battistoni *et*
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31 *al.*, 1997; Garcia-Bernet *et al.*, 2011b). Digested media are visco-elastic materials
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33 characterized by high yield stress levels, and yield stress increases with TS content
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35 according to an exponential law (Garcia-Bernet *et al.*, 2011b). Digesters are thus
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37 difficult to mix and homogenize. Indeed, Karim *et al.* (2005) showed that, when the
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39 concentration of TS increases in reactors, mixing becomes more important for
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41 improving the production of methane. Nevertheless, under unmixed conditions,
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43 transport is likely governed by diffusion processes, which are strongly related to the
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45 porosity of the media and, thus, to the water content. Therefore, the diffusive transport
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47 resistance of soluble compounds (substrate or by-products) may have a strong influence
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49 on anaerobic digestion performance in dry systems.
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1 The aim of this study is to assess the impact of the total solids content on anaerobic
2 digestion of solid waste. Anaerobic batch reactor experiments were performed with TS
3 concentrations ranging from 10 to 35%. The methane production performances were
4 assessed. To better evaluate the impact of the water content on anaerobic digestion, the
5 Anaerobic Digestion Model No. 1 (ADM1) was then used to describe the experimental
6 data. The objective of the model application was to test some hypotheses in order to
7 understand why the TS content affects the global anaerobic digestion performance. The
8 effects of hydrolysis step and liquid/gas mass transfer were more particularly
9 investigated.

2. Materials and methods

2.1. Substrate characterization

2.1.1. Van Soest fractionation

10 The content of cellulose, hemicellulose and lignin-like fractions in the substrate was
11 analyzed according to the Van Soest procedure (Van Soest, 1963). After shredding and
12 sieving, 1g of cardboard was placed in a Fiberbag system (Gerhardt Germany). The
13 sequential fractionation procedure was performed for six samples as follows: (1) The
14 soluble compounds were obtained by extraction with a neutral detergent (30 g L^{-1}
15 $\text{C}_{12}\text{H}_{25}\text{NaO}_4\text{S}$; 18.61 g L^{-1} $\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8, 2\text{H}_2\text{O}$; 6.81 g L^{-1} $\text{Na}_2\text{B}_4\text{O}_7, 10\text{H}_2\text{O}$; 4.56 g L^{-1}
16 Na_2HPO_4 ; 10 mL L^{-1} $\text{C}_6\text{H}_{14}\text{O}_4$) at 100°C for 60 min; (2) the hemicellulose-like
17 compounds were extracted by an acid detergent (20 g L^{-1} $\text{C}_{19}\text{H}_{42}\text{NBr}$; 26.7 mL L^{-1}
18 $\text{H}_2\text{SO}_4, 95\text{-}97\%$) for 60 min at 100°C ; (3) the lignin-like compounds were obtained by
19 removing the cellulose-like compounds for 3 h with H_2SO_4 (72%). The remaining
20 fraction corresponds to lignin. At the end of each step, the extracted samples were

1 washed with deionized water and oven-dried at 100°C before the transition to the next
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3 step.
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8 *2.1.2. The biochemical methane potential*

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10 The biochemical methane potential (BMP) of the cardboard was assessed according to
11 Angelidaki and Sanders (2004). The assays were conducted in triplicate (and one blank)
12 in 600 mL serum bottles at 35° C, with a working volume of about 400 mL. The serum
13 bottles were filled with synthetic growth medium containing nutrients and trace
14 elements, and inoculated with granular sludge from a mesophilic anaerobic digester of a
15 sugar factory. The final sludge concentration in the bottles was 20 gVS L⁻¹. The bottles
16 were loaded with 1 g of cardboard (corresponding to 0.77 gVS). Biogas production and
17 composition were measured daily. The methane production is expressed under standard
18 condition and accounts for the variation of the gas content in the headspace of the
19 reactors. The calculated BMP accounts for the global methane production without the
20 residual (endogenous) methane production measured with the blank assay.
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38 **2.2. Batch preparation and operating conditions**

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40 A compact cardboard with a density of 1.42 kg m⁻³, branded “Cartonnages Michel”, was
41 used as a substrate since cardboard represents usually the largest proportion of organic
42 compounds in municipal solid waste (21.5%) after putrescible waste (32.2%) (ADEME,
43 2009). The cardboard was shredded using a cutting mill SM-100 and sieved at 2 mm.
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45 Experiments were carried out in 600 mL batch flasks with a working volume of 100
46 mL. A mixture of cardboard, water, inoculum and oligo-elements was prepared to reach
47 six TS contents from “wet” to “dry” anaerobic conditions: TS = 10, 15, 20, 25, 30, 35
48 % . A substrate to biomass ratio S/X of 20 (w/w) was used to limit the influence of the
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1 inoculum composition on the degradation, S and X representing the initial TS contents
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3 of the substrate and the biomass, respectively. The inoculum corresponded to a leachate
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5 of pressed MSW digestate sampled in an industrial plant treating MSW. One mL of an
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7 oligo-element solution was added to the mixture. This oligo-element solution was
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9 composed of: $\text{FeCl}_2, 4 \text{H}_2\text{O}$ (2 g L^{-1}), $\text{CoCl}_2, 6 \text{H}_2\text{O}$ (0.5 g L^{-1}), $\text{MnCl}_2, 4 \text{H}_2\text{O}$ (0.1 g L^{-1}),
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11 $\text{NiCl}_2, 6 \text{H}_2\text{O}$ (0.1 g L^{-1}), ZnCl_2 (0.05 g L^{-1}), H_3BO_3 (0.05 g L^{-1}), Na_2SeO_3 (0.05 g L^{-1}),
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13 $\text{CuCl}_2, 2 \text{H}_2\text{O}$ (0.04 g L^{-1}), $\text{Na}_2\text{MoO}_4, 2 \text{H}_2\text{O}$ (0.01 g L^{-1}). The experiments were run
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15 over 298 days under mesophilic conditions (35°C) without mixing. Each TS condition
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17 was tested in four replicates.
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25 **2.3. Analytical methods**

26 *2.3.1 Biogas quantification and composition analysis*

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28 Biogas production and composition were determined daily during the first two months,
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30 and then once a week after the exponential phase of methane production.
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34 The biogas production was measured by the water displacement method and then
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36 normalized according to the ambient temperature. The biogas composition was
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38 determined using a gas chromatograph (Varian $\mu\text{GC-CP4900}$) by injecting a sample
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40 volume of 2 mL. This gas chromatograph was equipped with two columns: a Molsieve
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42 5A PLOT column for O_2 , N_2 , CH_4 and CO and a HayeSep A column for CO_2
43
44 quantification. The calibration was carried out with a standard gas composed of 25 %
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46 CO_2 , 2 % O_2 , 10 % N_2 and 63 % CH_4 . The temperatures were 30°C for the oven and
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48 100°C for the injector and the thermal conductivity detector. The gas carrier of the flow
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50 was Helium.
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2.3.2 VFA and pH analysis

1 Volatile fatty acids (VFA) were analyzed at the end of the batch test. After
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6 centrifugation (13000 rpm, 15 min), VFA concentrations were measured by a gas
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8 chromatograph (Varian μ GC-CP3900) equipped with a flame ionization detector (FID).
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10 The column used was a semi-capillar Econocap FFAP (Alltech). The gas carrier of the
11
12 flow was nitrogen. The rest of the assay technique is described in Ganesh *et al.* (2010).
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14 pH was measured directly on the digestate using a pH meter Eutech Instruments pH510
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16 with Mettler Toledo InLab® Expert Pt1000 pH electrodes.
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2.4. Mathematical model

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25 The Anaerobic Digestion Model No. 1 (ADM1) (Batstone *et al.*, 2002) was used to
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27 describe the experimental data. The characterization of the shredded cardboard with
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29 respect to ADM1 state variables, in particular carbohydrates and particulate inerts, was
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31 based on the results of the Van Soest fractionation and the degradable fraction of fibers
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33 (hemicellulose and cellulose). The degradable fraction of hemicellulose and cellulose
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35 (major degradable constituents of cardboard) was calibrated with the gas curve at 10%
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37 TS. The estimated value of 40% is of the same order of magnitude as the degradable
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39 fraction of fibers reported by Koch *et al.* (2010) for grass silage. In the model, the state
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41 variable for carbohydrates, X_{ch} , was considered to be composed of the biodegradable
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43 fraction of hemicellulose and cellulose, and the soluble organic fraction. The non-
44
45 degradable fraction of hemicellulose and cellulose, as well as the lignin fraction were
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47 considered as particulate inerts (X_I). Overall, $0.33 \text{ gCOD gTS}^{-1}$ were attributed to X_{ch}
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49 and $0.85 \text{ gCOD gTS}^{-1}$ to X_I . Simulations were run in Matlab/Simulink (Version 7.3.0).
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1 The model was calibrated to the experimental data of the batch experiments at 10% TS
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3 using a trial and error approach. Compared to the standard parameters proposed by
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5 Batstone and Keller (2003) for the anaerobic digestion of sludge, two main parameters
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7 were modified in order to account for the degradation of the specific substrate (i. e.,
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9 cardboard) at high total solids contents: the first-order hydrolysis rate constant for
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11 carbohydrates and the volumetric liquid/gas mass transfer coefficient.
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15 The default value of the first-order hydrolysis rate constant for carbohydrates ($k_{hyd,Xch}$)
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17 is 10 d^{-1} . For wet anaerobic digestion conditions and under mesophilic conditions,
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19 hydrolysis rate constants for cellulosic material (cellulose, office paper, cardboard,
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21 newsprint) reported in the literature are about 0.03 to 0.07 d^{-1} (Vavilin et al., 2008;
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23 Liebetrau et al., 2004; Vavilin et al., 2004). However, the present assays were
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25 conducted under semi-dry and dry conditions. At low moisture conditions, Pommier et
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27 al. (2007) observed a strong dependence on the moisture level for both kinetic rates and
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29 ultimate methane production from paper and cardboard waste samples. In a modeling
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31 work, Qu et al. (2009) used a value of 0.01 d^{-1} for the hydrolysis rate constant of office
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33 paper at TS contents of 40 and 66%. In the present work, the first-order hydrolysis rate
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35 constant for carbohydrates ($k_{hyd,Xch}$) was, thus, reduced from its default value to 0.01 d^{-1} .
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39 The volumetric liquid/gas mass transfer coefficient k_T (corresponding to the k_{La}
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41 variable in the model) was reduced from its default value (200 d^{-1} ; for wet anaerobic
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43 digestion of activated sludge) to 0.5 d^{-1} to account for a reduced gas transfer due the
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45 pasty texture of the substrate-biomass mixture. To our knowledge, the volumetric
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47 liquid/gas mass transfer coefficient has never been measured in dry anaerobic digestion
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49 processes. The volumetric mass transfer coefficient k_{La} depends on two parameters: k_L
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51 corresponding to the mass transfer coefficient, and a corresponding to the specific
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1 surface area. In dry and semi-dry anaerobic digestion processes, the volumetric mass
2 transfer coefficient k_{La} is drastically reduced because of two main reasons:
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6 (1) the solid-liquid/gas interface is low, because of the low biogas bubble
7 generation, and because of the unmixed conditions.
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10 (2) The mass transfer coefficient term is also affected by the low moisture
11 content. The following equation accounts for the difference between the
12 diffusivity coefficients of soluble compounds in the digestate $D_i (digestate)$
13 and in the water $D_i (water)$:
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$$20 \quad k_L (digestate) = k_L (water) \left(\frac{D_i (digestate)}{D_i (water)} \right)^{0.5} \quad (1)$$

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25 Diffusivity coefficients decrease drastically with the decrease of the porosity
26 (i. e., the water content) and the increase of viscosity, which is also strongly
27 related to the TS content (Battistoni, 1993; Battistoni *et al.*, 1997; Garcia-
28 Bernet *et al.*, 2011b).
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35 Based on these theoretical considerations, the order of magnitude of the volumetric
36 mass transfer coefficient is strongly affected by the TS content. A $k_T=0.5 \text{ d}^{-1}$ was
37 considered for the assay conducted at TS = 10%.
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45 **3. Results and Discussion**

46 **3.1. Impact of TS content on anaerobic digestion performance**

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48 Figure 1 shows the cumulated methane production for the reactors operated at six
49 different TS contents during the whole experiment. Each curve represents the average of
50 four replicates, except for TS = 30% where two distinguished behaviors were observed.
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57 On the first 7 days (shown in the insert in Figure 1), all the cumulated curves are
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1 similar. The initial rate of anaerobic degradation was, thus, identical for all TS contents,
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3 indicating that the intrinsic activity of the microbial consortium was the same for the
4
5 different conditions, with an average methane rate of about $0.48 \pm 0.05 \text{ mL gVS}^{-1} \text{ d}^{-1}$.
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8 After the first 7 days, the cumulated methane production was inversely proportional to
9
10 the TS content (the first 40 days in Figure 1).
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13 Then, from 30-40 days of operation, methane production rates increased for the
14
15 replicates having a TS content ranging from 10 to 25% (maximum methane rates are
16
17 shown in Figure 2a), indicating the beginning of the exponential growth phase. During
18
19 this phase, two different behaviors were observed at 30% TS. Two replicates followed a
20
21 similar trend to that of the experiments conducted at 35% TS (named 30%-a in Figure
22
23 1), whereas the two remaining replicates showed a behavior close to that at 25% TS
24
25 (named 30%-b in Figure 1). For 30%-b and 35% TS, the acceleration phase,
26
27 corresponding to the exponential growth phase, never started. The highest CH_4
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29 production was about 197 mL gVS^{-1} at 10% TS. Since the biochemical methane
30
31 potential (BMP) was about $214 \text{ mL CH}_4 \text{ gVS}^{-1}$, the biodegradation reaction was almost
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33 completed at 10% TS.
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40 Considering that the COD of the substrate was $1.44 \text{ gCOD gVS}^{-1}$, the BMP was, thus,
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42 $149 \text{ mL CH}_4 \text{ gCOD}^{-1}$ and corresponded to about 40% of the theoretical BMP value of
43
44 $350 \text{ mL CH}_4 \text{ gCOD}^{-1}$ (Buffière *et al.*, 2008). The low BMP value was probably due to
45
46 the composition of the substrate: indeed only 73% of the TS content of this cardboard
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48 corresponded to volatile solids, and the remaining 27% to a mineral non-biodegradable
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50 fraction. Among the volatile solids (VS), the organic matter was composed of only 4%
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52 of soluble fraction and 14% of hemicellulosic fraction: these two minor fractions
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55 represent the most degradable part of the organic matter. The two additional and most
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1 abundant fractions corresponding to cellulose and lignin represented 66% and 16% of
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3 the organic matter, respectively. These two fractions are resistant to biodegradation,
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5 especially under anaerobic conditions (Buffière *et al.*, 2008).
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10 11 3.1.1. Methane production rate

12 Methane production rates were estimated from the cumulative methane production
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14 curves. The maximum methane production rate is shown in Figure 2a for the different
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16 operating conditions. The maximum methane rate decreased with increasing TS
17
18 contents. This result is consistent with previous work of Fernandez *et al.* (2010) who
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20 showed that the maximum methane rate was higher at 20% than at 30% TS. In the
21
22 present work, the maximum methane rates were almost the same at 30%-b and 35% TS.
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24 However, the maximum methane rates were measured during the first seven days after
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26 the start-up of the experiment, corresponding therefore to the initial rate of anaerobic
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28 digestion. This initial rate was identical for all TS concentrations, because it
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30 corresponded to the intrinsic activity of the microbial consortium. For other TS
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32 concentrations, the maximum methane rates were observed between 40 to 80 days of
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34 experiment.
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45 3.1.2. Maximum methane yield

46 The cumulative methane yields measured after 298 days are shown in Figure 2b. They
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48 were clearly dependent on the TS content. Analyses of variance (ANOVA) were
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50 performed, distinguishing three groups: the first group (G1), which included all
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52 replicates of 10, 15, 20, 25% TS, was significantly different from the second group
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54 (G2), which included 30%-a replicates (*p = 0.0011); the third group (G3), which
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1 included replicates of 30%-b and 35% TS, was different from G1 and G2, with a very
2 significant***p of $2.2 \cdot 10^{-16}$ and $2.02 \cdot 10^{-6}$, respectively (*p < 0.05; **p < 0.005; ***p <
3 $5 \cdot 10^{-5}$; n.s., not significant (p >0.05)). The methane production was inversely correlated
4 to the TS concentration. The methane production was 176 ± 7 , 142 ± 1 and 30 ± 10 mL
5 gVS⁻¹ for the groups G1, G2 and G3, respectively. Concerning the replicates named
6 30%-a, the reduction of the cumulated methane production is consistent with previous
7 works. Indeed, Fernandez *et al.* (2008) observed a higher methane yield at 20% TS than
8 at 30% TS for mesophilic conditions in batch tests. Likewise, Forster-Carneiro *et al.*
9 (2008) reported a higher methane production in thermophilic batch tests at 20% TS
10 compared to 25% TS, and even higher than at 30% TS.

11 At 30%-b and 35% TS, lower methane productions of about 37 and 24 mL gVS⁻¹,
12 respectively, were observed. The difference in the behavior between the four replicates
13 at 30% TS suggested that 30% TS could be considered as a threshold concentration for
14 an inhibitory effect in high solids anaerobic digestion. This threshold could correspond
15 to an inhibition of anaerobic digestion at high solids content due to a higher
16 accumulation of metabolic by-products, such as volatile fatty acids.

3.1.3. pH and VFA concentration

17 For a better understanding of the failure of dry anaerobic digestion at TS >30%, volatile
18 fatty acids (VFA) and pH were analyzed at the end of the experiments (Figure 2c). For
19 batch experiments with a good anaerobic digestion performance (between 10% TS and
20 30%-a), there was no accumulation of VFA and the average pH was 7.43 ± 0.31 .

21 When anaerobic digestion was inhibited (30%-b and 35% TS), high VFA
22 concentrations were measured, with values ranging from 29 to 36 gVFA kgVS⁻¹. Under
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1 semi-dry anaerobic digestion conditions, Li *et al.* (2010) already observed an increase of
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3 the VFA concentration with increasing VS content (for TS contents of 16.0%, 13.5%
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5 and 11.0%, the maximum VFA value was 22.4 g L⁻¹, 6.8 g L⁻¹ and 4.2 g L⁻¹,
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7
8 respectively), and high concentrations of VFA inhibit the methane production (Ahring
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10 and Westermann, 1988). Mainly, total VFAs affect more specifically methanogens
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12 (Vedrenne, 2007). In addition, the average pH value was about 5.95 and 6.10 at 30%-b
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14 and 35% TS, respectively. These low pH values associated with VFA concentrations of
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16 29 and 36 g L⁻¹ might explain the inhibition of the anaerobic digestion process for these
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18 two TS contents, since VFA accumulation contributed to the decrease of pH. Moreover,
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20 at low pH, between 5 and 7, VFA are in their undissociated form, which is toxic for
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22 microorganisms (Zehnder, 1978).
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30 **3.2. Model results**

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32 For better understanding of the origin of the limitation of anaerobic degradation at high
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34 solids contents, the Anaerobic Digestion Model No. 1 (ADM1) was used to describe
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36 this experimental data. Figure 3 presents exemplarily simulation results for 10% TS and
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38 the critical concentration of 30% TS. Model predictions closely followed the
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40 experimental data of cumulative methane production for a TS concentration of 10%,
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42 except for the first 50 days of the experiment. However, the model clearly over-
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44 predicted experimental data obtained for a TS concentration of 30%, using the same set
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46 of calibrated parameter values ($k_T=0.5\text{ d}^{-1}$ and $k_{\text{hyd},X_{\text{ch}}}=0.01\text{ d}^{-1}$). As the methane
47
48 production rate production rate decreased with increasing total solids content (see
49
50 section ‘3.1.1 Methane production rate’) and hydrolysis is the limiting step in methane
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52 production (Vavilin *et al.*, 2004), it was hypothesized that the first-order hydrolysis rate
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1 decreases with increasing TS concentration. Consequently, the first-order hydrolysis
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3 rate for carbohydrates, $k_{\text{hyd},X_{\text{ch}}}$, was decreased step by step with increasing TS
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5 concentration to fit simulation results, in particular the total cumulative methane
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7 production, to experimental data. The first-order hydrolysis rate needed to be reduced to
8
9 0.0045 d^{-1} in order to properly describe the final cumulative CH_4 production for the two
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11 experiments that were not inhibited by high VFA concentrations and low pH at 30% TS
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13 (Figure 3.b, solid line). The experimental results of the two experiments, in which
14
15 methane production stalled due to very high VFA concentrations and reactor
16
17 acidification, could not be described by further decreasing the hydrolysis rate (see
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19 section '3.2.1 Influence of the hydrolysis rate constant'). Thus, another mechanism must
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21 have been responsible for the inhibition of methane production.
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27 Due to the pasty texture of the substrate-biomass mixture, the initial value of the
28
29 liquid/gas transfer coefficient k_T was already reduced to 0.5 d^{-1} for a TS concentration
30
31 of 10% to account for reduced mass transfer. As the viscosity of the substrate-biomass
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33 mixture increased and the porosity decreased with increasing TS content, it was
34
35 hypothesized that the overall mass transfer decreases with increasing TS concentration.
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37 The overall mass transfer coefficient (k_T) was, therefore, decreased to match measured
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39 and simulated total cumulative methane production for the two inhibited batch
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41 experiments at 30% TS. Reducing the value of k_T from 0.5 d^{-1} to 0.02 d^{-1} resulted in an
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43 adequate representation of the final cumulative methane production for the two
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45 inhibited experiments (Figure 3.b, dashed line).
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51 Although the calibration of k_T and $k_{\text{hyd},X_{\text{ch}}}$ allowed for describing the final cumulative
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53 methane production, the ADM1 did not describe very well the initial phase of
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55 cumulative methane production. The ADM1 describes hydrolysis as a simple first-order
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1 process. According to Vavilin *et al.* (2008), hydrolysis of certain complex substrates
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3 can, however, be better represented by the Contois model, which considers that
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5 hydrolysis kinetics depends on both substrate and biomass concentration (concentration
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7 of the biomass that produces the enzymes for hydrolysis). The Contois model is a more
8
9 general model than the first-order hydrolysis kinetics and allows for better representing
10
11 the sigmoid-type curve of cumulative methane production (Vavilin *et al.*, 2008). Using
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13 the Contois model, however, has no impact on the prediction of the final cumulative
14
15 methane production (data not shown). As the aim of the modeling study was to find an
16
17 explanation for the general trend of the experimental data (inhibition of anaerobic
18
19 digestion of cardboard at high total solids contents), the first-order hydrolysis model is
20
21 the simplest approximation of the hydrolysis step. In addition, the more complex
22
23 structure of the Contois model makes it more difficult to identify and distinguish
24
25 mechanisms influencing anaerobic digestion at high TS concentrations. Thus, first-order
26
27 hydrolysis kinetics was used for deeper analysis of mechanisms affecting anaerobic
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29 digestion at high TS concentrations. Based on the simulation results presented above,
30
31 two different mechanisms were identified that have a considerable impact on anaerobic
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33 digestion at high TS concentrations: 1) the rate of hydrolysis of particulate substrates
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35 (here only carbohydrates), and 2) the transfer of produced gas from the liquid phase to
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37 the gas phase. The influence of both phenomena is now presented in more detail.
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50 *3.2.1 Influence of the hydrolysis rate constant*

51 For each TS concentration, the first-order hydrolysis rate constant for carbohydrates was
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53 calibrated for batch experiments that were not inhibited by high VFA concentrations
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55 and low pH to meet the total cumulative methane production at the end of each batch
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1 experiment. Figure 4 shows the calibrated hydrolysis rate constants for each TS
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3 concentration. The hydrolysis rate constants obtained for TS concentrations of 10% and
4
5 15% were similar. But the calibrated hydrolysis rate constants linearly decreased with
6
7 increasing TS concentration for $15\% \leq \text{TS} \leq 30\%$. This finding is in agreement with
8
9 results presented by Pommier *et al.* (2007), who observed a strong impact of the
10
11 moisture content on kinetic rates and maximum methane production in solid waste
12
13 anaerobic digestion. Extrapolation of the hydrolysis rate constant for a TS concentration
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15 of 35% using the linear relationship shown in Figure 4 gave a value of 0.00275 d^{-1} .
16
17
18 With this hydrolysis rate constant and a k_T value of 0.5 d^{-1} (as used for all non-inhibited
19
20 batch experiments), the ADM1 predicted a total cumulative methane production of 107
21
22 $\text{mL CH}_4 \text{ gVS}^{-1}$ and no VFA accumulation for $\text{TS} = 35\%$. The total cumulative methane
23
24 production predicted by the model was 4.5 times higher than that observed in the
25
26 experiment ($23.5 \text{ mL CH}_4 \text{ gVS}^{-1}$). Thus, a further decrease in the hydrolysis rate
27
28 constant could not explain why methane production stalled at a total solids
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30 concentration of 35%.
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37 In summary, a decreasing first-order hydrolysis rate constant with increasing TS content
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39 could well describe experimental methane production at different TS in non-inhibited
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41 batch experiments. But a decreasing hydrolysis rate constant could not explain
42
43 considerable VFA accumulation, reactor acidification, and limited methane production
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45 observed in two batch experiments at 30% TS and all batch experiments at 35% TS.
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52 3.2.2. Influence of the overall mass transfer coefficient

53 The influence of the overall mass transfer coefficient k_T was evaluated by varying its
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55 value between 0.001 d^{-1} and 100 d^{-1} for each studied TS concentration. The default
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1 value (named k_{La} in the original ADM1) is 200 d^{-1} for modeling anaerobic digestion of
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3 activated sludge (wet digestion) (Rosen and Jeppsson, 2006). The first-order hydrolysis
4
5 rate constant for carbohydrates was kept constant at 0.01 d^{-1} for all simulations to focus
6
7 on the effect of the overall mass transfer coefficient. Figure 5 shows the final
8
9 cumulative methane production obtained for different values of k_T and different TS
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11 contents. A sudden and steep decrease in the cumulative methane production can be
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13 observed for k_T values between 0.04 d^{-1} and 0.18 d^{-1} depending on the TS content.
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15 Above a critical k_T value, methane production was not influenced by overall mass
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17 transfer and the cumulative methane production remained almost constant
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19 independently of the k_T value. In this case, no VFA accumulation was observed. Below
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21 the critical k_T value, limited overall mass transfer clearly affected methane production
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23 and resulted in considerably lower cumulative methane production. Methane production
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25 was more sensitive to overall mass transfer limitations at high TS concentrations as the
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27 methane production dropped already at higher k_T values (at 0.18 d^{-1} for 35% TS
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29 compared to 0.04 d^{-1} for 10% TS). Low methane production always went along with
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31 accumulation of VFA and reactor acidification (data not shown).
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33 The different behaviors in the batch experiments at 30% TS content might be related to
34
35 slightly different actual total solids contents in the serum bottles as a result of minor
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37 inaccuracies in the preparation of the bottles, including measurement errors. In
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39 simulations, methane production at 30% TS content dropped from $174.5 \text{ mL CH}_4 \text{ gVS}^{-1}$
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41 to $51.9 \text{ mL CH}_4 \text{ gVS}^{-1}$ when the mass transfer coefficient was reduced from 0.16 d^{-1} to
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43 0.15 d^{-1} . At 35% TS, the methane production dropped already between $k_T = 0.18 \text{ d}^{-1}$ and
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45 $k_T = 0.17 \text{ d}^{-1}$ from $174.5 \text{ mL CH}_4 \text{ gVS}^{-1}$ to $32.8 \text{ mL CH}_4 \text{ gVS}^{-1}$. In addition, the lines for
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47 TS 30% and 35% in Figure 5 are very close to each other. Thus, a small increase in the
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1 actual TS concentration at a desired TS content of 30% can have already a significant
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3 impact on the cumulative methane production.
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6 According to model results, overall mass transfer limitation resulted in an accumulation
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8 of inorganic carbon (CO₂), dissolved methane, and dissolved hydrogen, and can have an
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10 inhibitory effect on methanogenesis. Indeed, the CO₂ produced during methanogenesis
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12 remains trapped in the matrix since the release of dissolved compounds is low in the
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14 digestate: therefore, the local CO₂ concentration can increase, which may cause a local
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16 acidification, and hence inhibition of methanogenesis from the beginning of the
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18 experiment implicating VFA accumulation. The accumulation of dissolved hydrogen
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20 can also cause inhibition of valerate, butyrate, and propionate degradation and generate
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22 an accumulation of these VFA. “Obligated Hydrogen-Producing Acetogens” bacteria
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24 convert VFA and high molecular weight long-chain fatty acids to acetate, carbon
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26 dioxide and hydrogen. These β -oxidation reactions are thermodynamically not possible
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28 under standard conditions ($\Delta G^\circ > 0$). In fact, β -oxidation occurs only at very low
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30 hydrogen partial pressure. Thus, produced hydrogen needs to be locally consumed (e.g.,
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32 syntrophic association between hydrogen producing species and methanogenic species)
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34 (Ahring, 2003), or to be removed from the liquid phase through liquid/gas mass
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36 transfer.
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45 An effect of a limitation of the overall mass transfer on hydrolysis cannot be reported as
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47 the ADM1 does not consider inhibition of hydrolysis. Overall, the simulation results
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49 clearly show that overall mass transfer limitation can explain limited methane
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51 production at 30% and 35% TS. But the decreasing cumulative methane production for
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53 TS concentrations between 15% and 30% cannot be attributed to mass transfer
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55 limitation.
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3 **4. Conclusion**
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6 Based on experimental observations and ADM1 simulations, it was shown that the TS
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8 content affects the global anaerobic digestion performance of solids through (i)
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10 reduction of the microbial hydrolysis rate for $10\% \leq TS \leq 25\%$ and (ii) physical
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12 limitation related to liquid/gas mass transfer for $TS \geq 30\%$. Further investigations need
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14 to be done to understand the role of the TS content on the behavior of the microbial
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16 community structure involved in the anaerobic digestion degradation of solids from wet
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18 to dry technologies.
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26

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35
36 Sweden, for providing the Matlab implementation of ADM1.
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Figure captions

Figure 1: Cumulated methane production from cardboard according to the TS content.

The insert corresponds to the first 40 days of the experiment.

Figure 2: Influence of TS content on anaerobic digestion performance.

a) Maximum methane production rate.

b) Final methane yield (at the end of the experiment).

c) pH and VFA concentration at the end of the experiment.

Figure 3: Experimental and simulated cumulative CH₄ production.

a) At 10% TS, with calibrated values for k_T and $k_{hyd,Xch}$.

b) At 30% TS, with calibrated values for k_T and $k_{hyd,Xch}$.

Figure 4: Influence of the first-order hydrolysis rate constant for carbohydrates on anaerobic digestion of cardboard for unlimited mass transfer as predicted by the ADM1.

Figure 5: Influence of the overall mass transfer coefficient k_T on anaerobic digestion of cardboard as predicted by the ADM1.

Figure 1

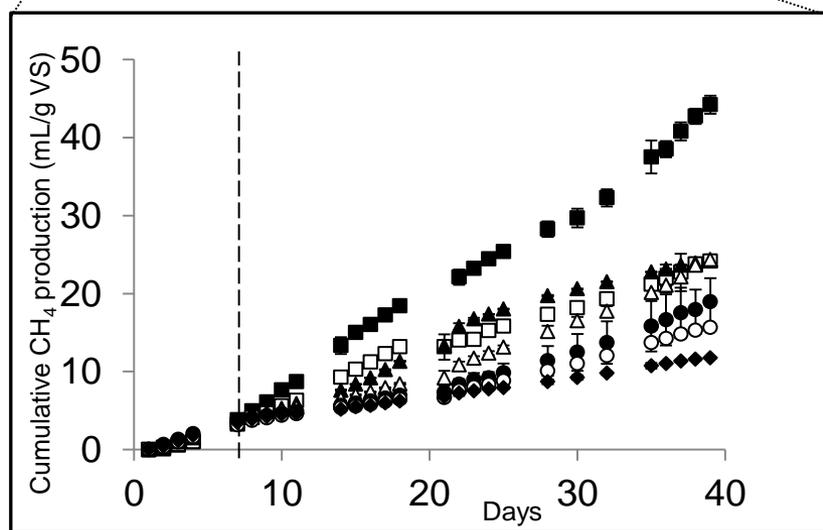
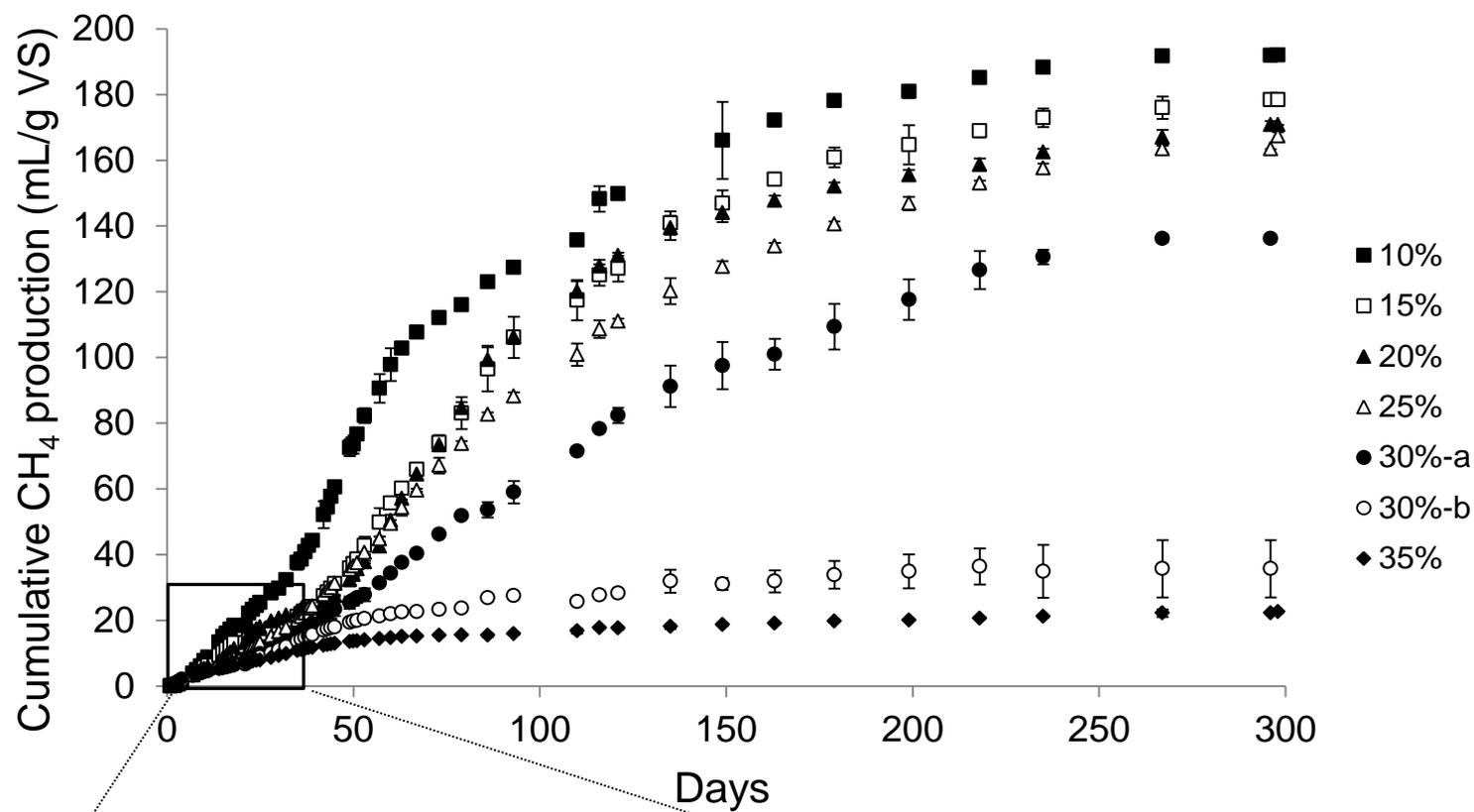


Figure2a

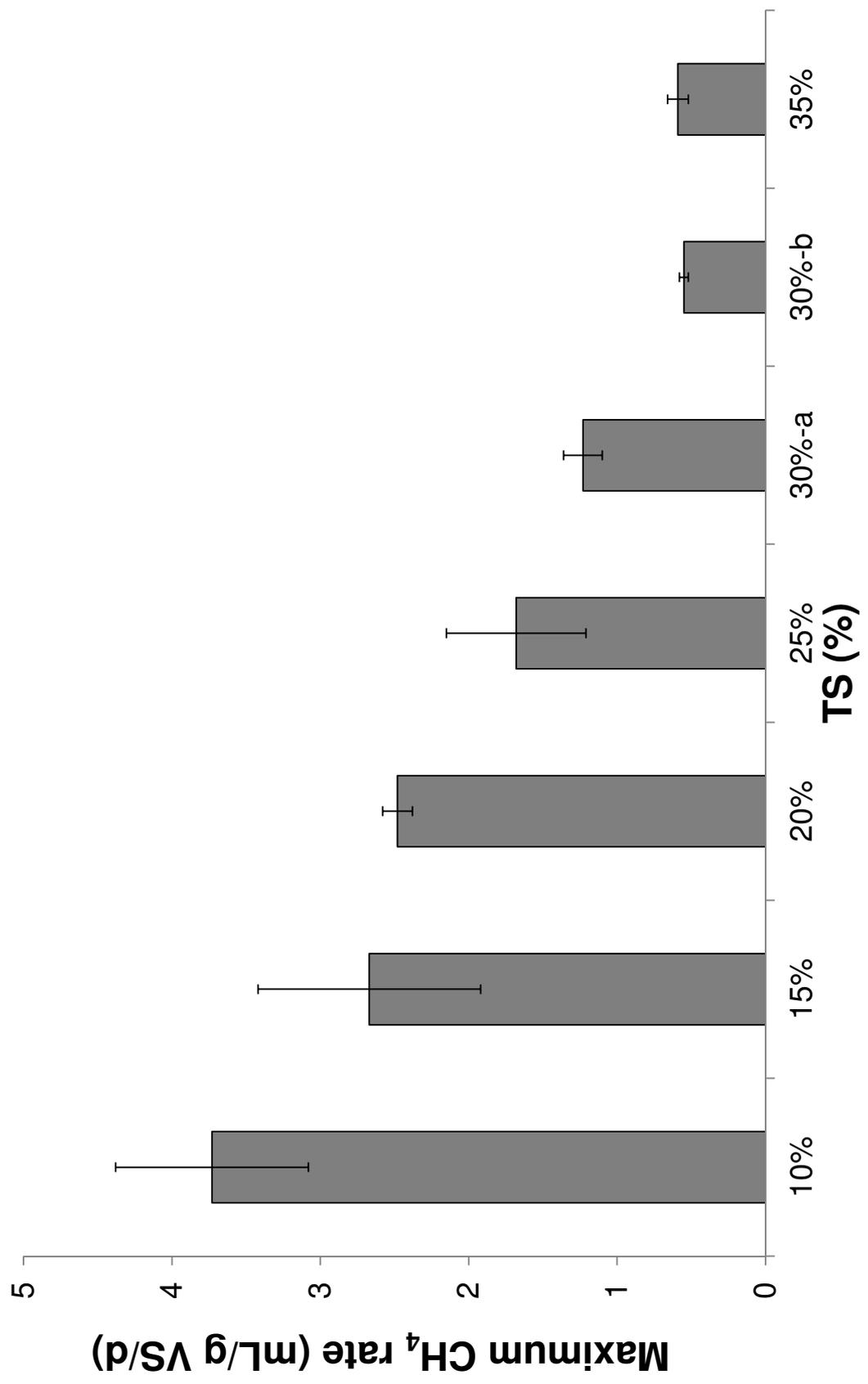


Figure2b

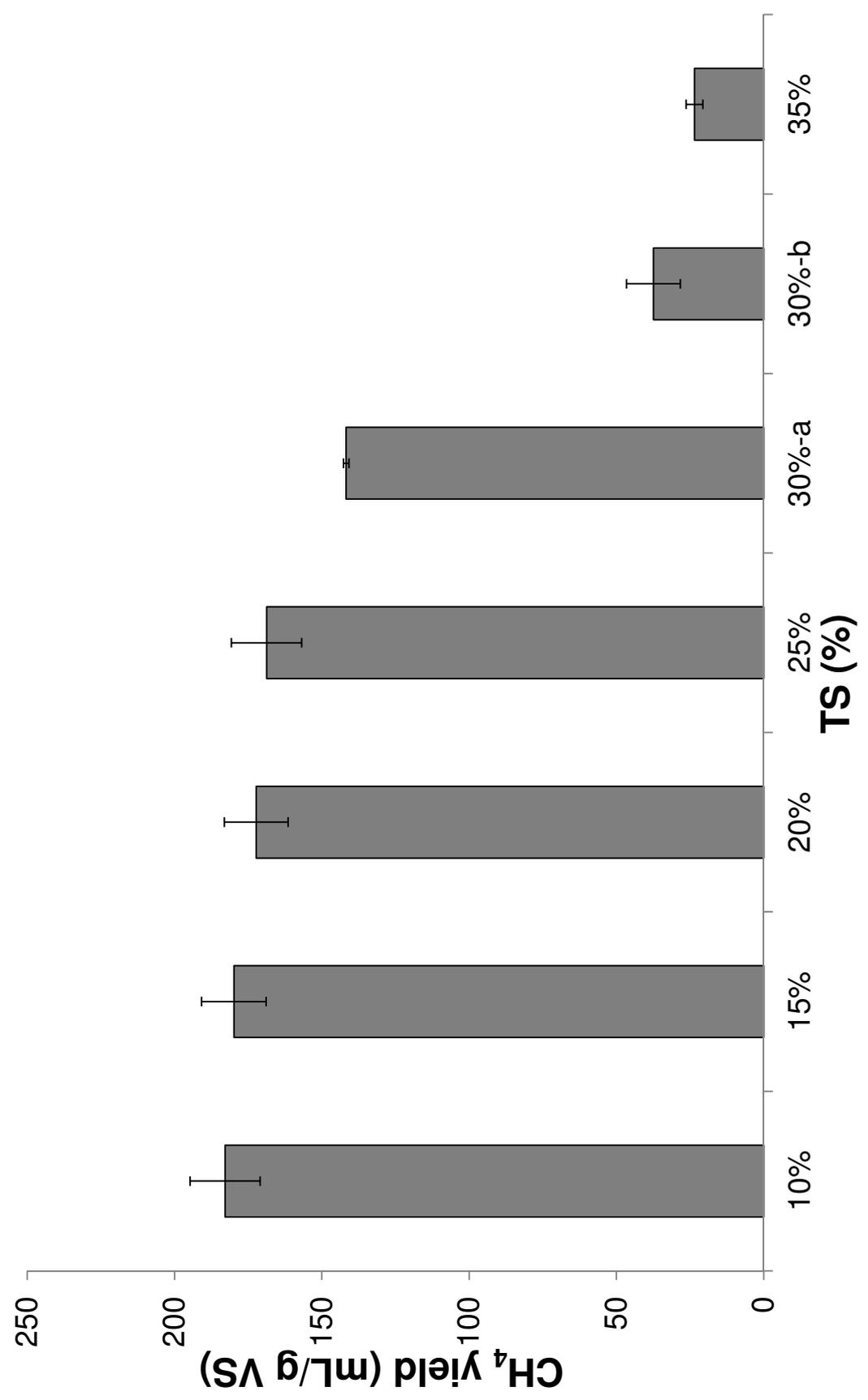


Figure 2c

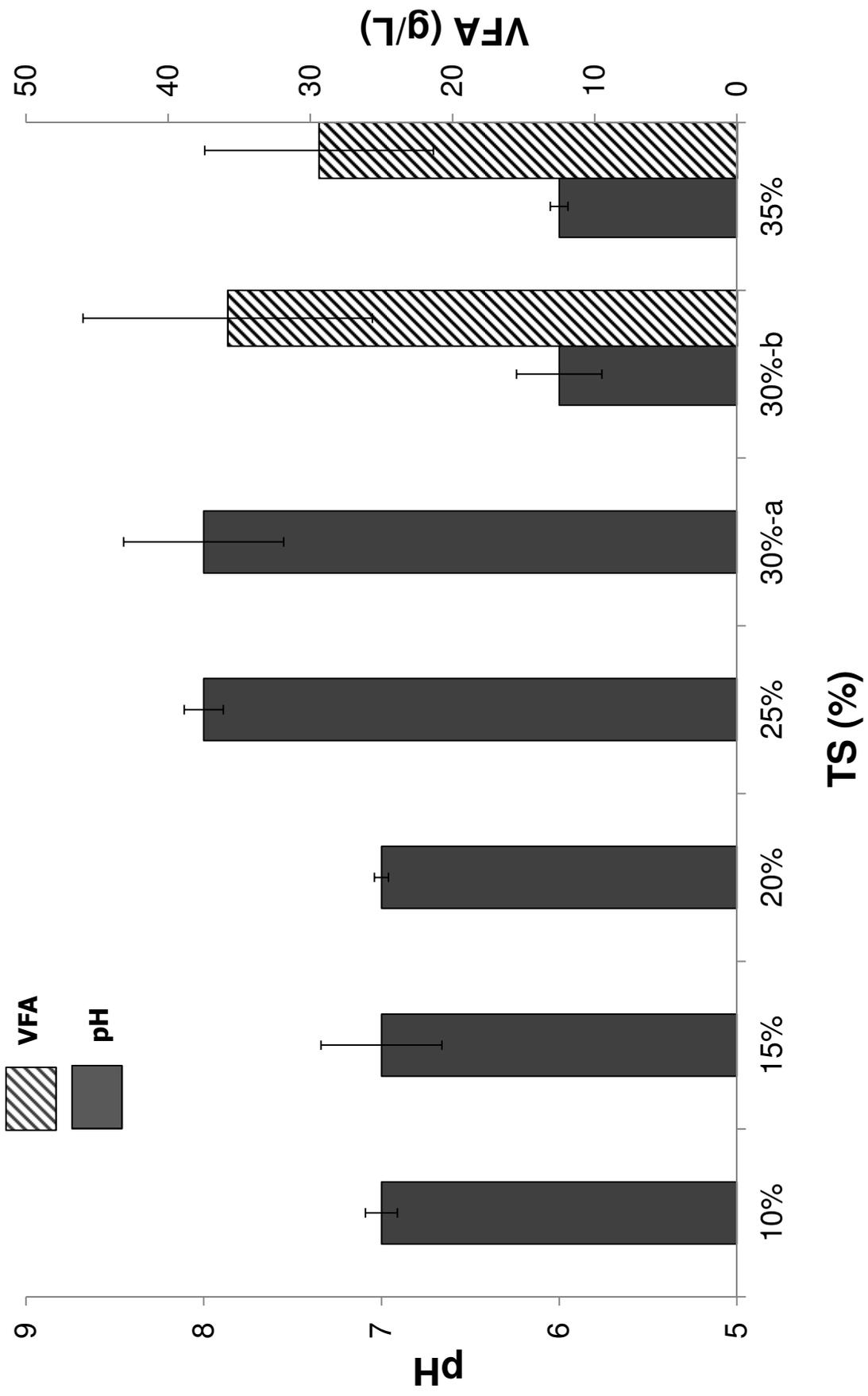


Figure3a

TS 10%

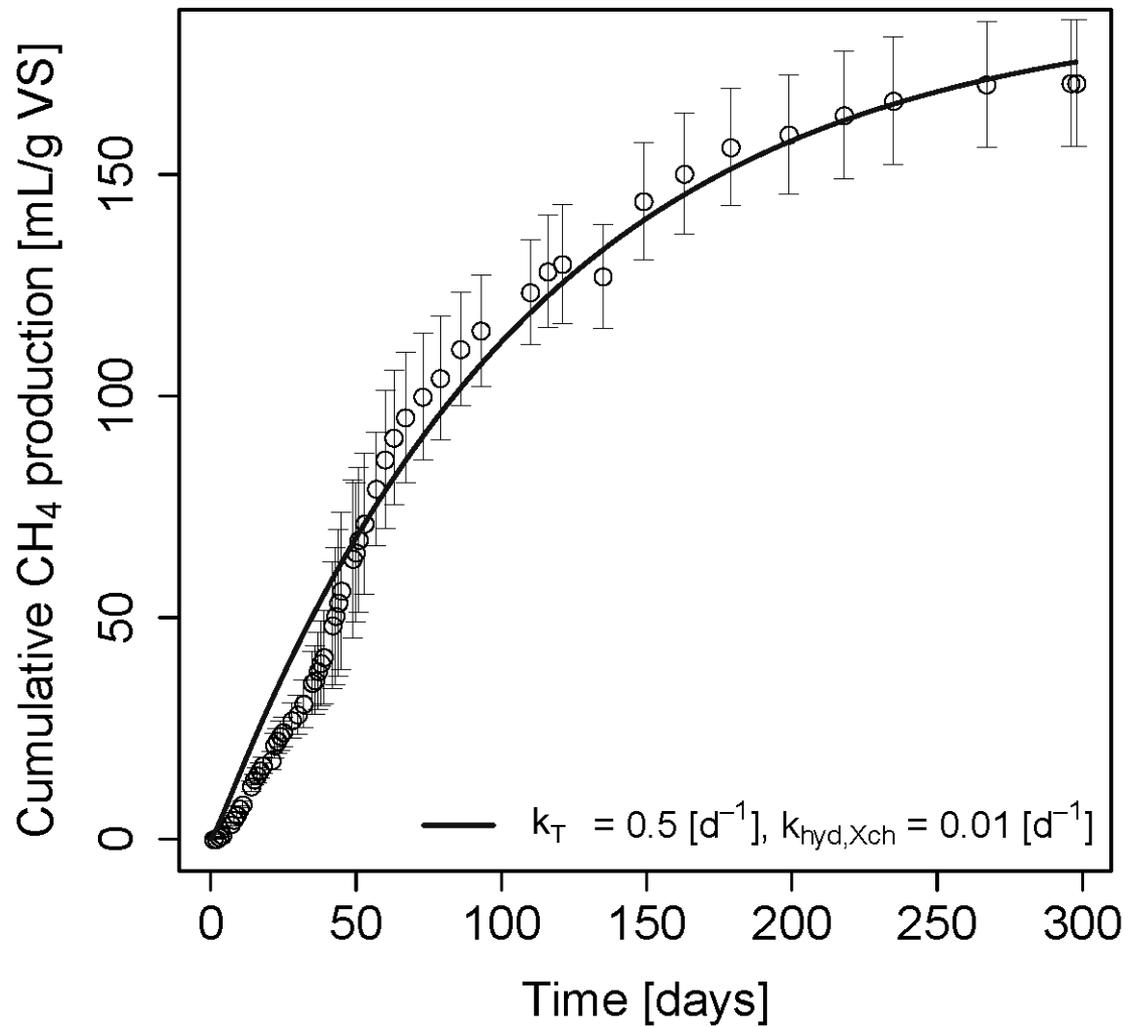


Figure 3b

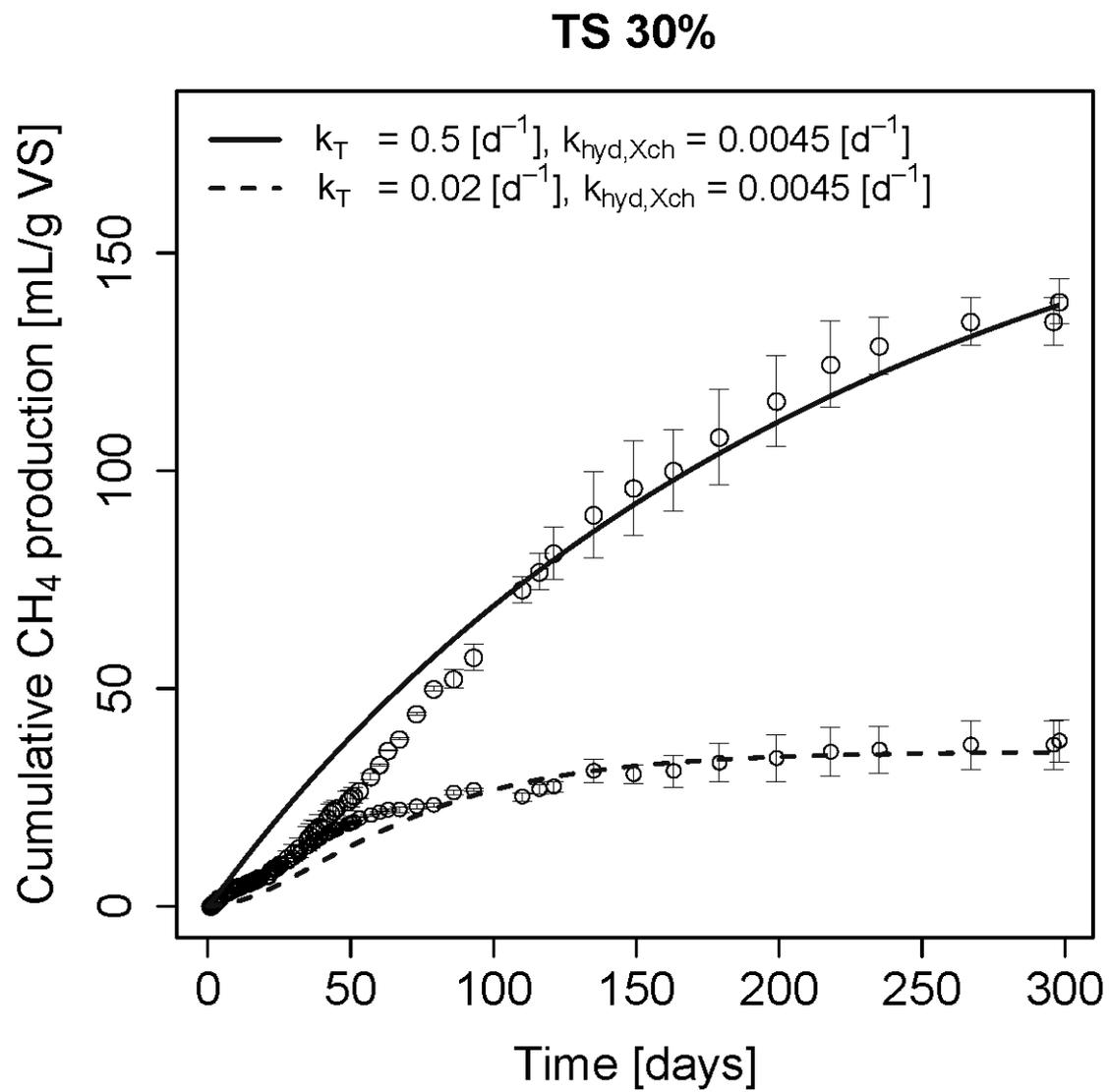


Figure4

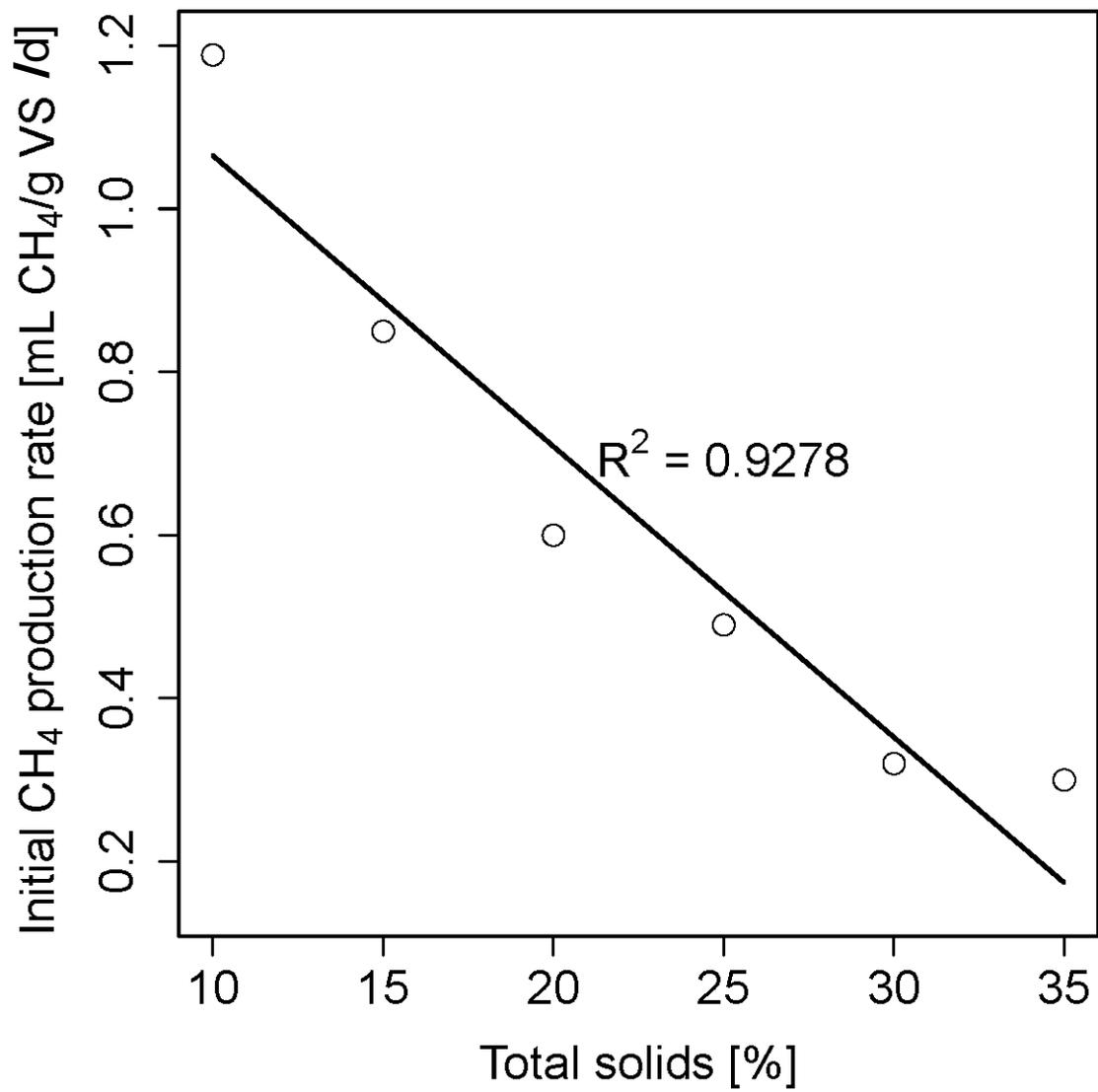


Figure5

