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► To cite this version:

Amel Abbassi, Doris Brockmann, Eric Trably, Claire Dumas, Jean-Philippe Delgenès, et al.. Total solids content drives high solid anaerobic digestion via mass transfer limitation. *Bioresource Technology*, 2012, 111, pp.55 - 61. 10.1016/j.biortech.2012.01.174 . hal-02647596

HAL Id: hal-02647596

<https://hal.inrae.fr/hal-02647596>

Submitted on 8 Aug 2023

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Total solids content drives high solid anaerobic digestion via mass transfer limitation

Amel Abbassi-Guendouz, Doris Brockmann, Eric Trably, Claire Dumas, Jean-Philippe Delgenès, Jean-Philippe Steyer, Renaud Escudie*

INRA, UR050, Laboratoire de Biotechnologie de l'Environnement, Avenue des Etangs, Narbonne, F-11100, France

*Corresponding author: escudie@supagro.inra.fr, (33) 468 215 173, fax: (33) 468 215 160.

Abstract:

The role of the total solids (TS) content on anaerobic digestion was investigated in batch reactors. A range of TS contents from 10 to 35% was evaluated, four replicates were performed. The total methane production slightly decreased with TS concentrations increasing from 10 to 25% TS. Two behaviors were observed at 30% TS: two replicates had similar performances to that at 25% TS; for the two other replicates, the methane production was inhibited as observed at 35% TS. This difference suggested that 30% TS content corresponded to a threshold of the solids content, above which methanogenesis was strongly inhibited. The Anaerobic Digestion Model No.1 (ADM1) was used to describe the experimental data. The effects of hydrolysis step and liquid/gas mass transfer were particularly investigated. The simulations showed that mass transfer limitation could explain the low methane production at high TS, and that hydrolysis rate constants slightly decreased with increasing TS.

Keywords

Dry anaerobic digestion; total solids content; mass transfer coefficient; hydrolysis; methanogenesis.

1. Introduction

The production of waste including municipal solid waste (MSW) has significantly increased in recent years. For example, in France, MSW generation has more than doubled in less than 50 years, from 175 kg year⁻¹ capita⁻¹ in 1960 to 354 kg year⁻¹capita⁻¹ in 2006 (ADEME, 2009). Different technologies are used for MSW treatment, such as incineration or composting, but anaerobic digestion (AD) processes are particularly interesting in terms of organic matter reduction by converting organic compounds into biogas. The methane content in biogas represents a source of renewable energy. Based on the total solids (TS) content of solid waste, three main types of technologies have been developed: wet ($\leq 10\%$ TS), semi-dry (10-20% TS) and dry ($\geq 20\%$ TS) processes. Dry technologies, also called “high-solid” anaerobic processes, are attractive because the quantity of water added to the raw waste is substantially reduced, and consequently, the digester size is minimized. However, difficulties in operating dry anaerobic digestion at both laboratory and industrial scales are related to the high concentration of total solids. Fernandez *et al.* (2008) showed that methane production started at day 14 in a reactor with 20% TS and at day 28 in a reactor with 30% TS in mesophilic dry anaerobic batch reactors treating the organic fraction of municipal solid waste. The total methane production was 17% lower at 30% than at 20% TS. This result is consistent with the one obtained by Forster-Carneiro *et al.*(2008), which showed better performance of anaerobic reactors operated at 20% TS compared to 25% and

30% TS. It was suggested that a high TS content could reduce substrate degradation and, therefore, biogas production (Fernandez *et al.*, 2008). Le Hyaric *et al.* (2011) used a microbial metabolic intermediate, propionate, as substrate to study specifically the methanogenic activity in dry reactors. The specific methanogenic activity increased linearly by a factor of 3.5 when the moisture content increased from 65% to 82% (corresponding to 35 to 18% TS, respectively).

A high TS content also affects the physical properties of the digested solid waste. Water distribution was investigated by Garcia-Bernet *et al.* (2011a) in biowastes and associated digestates sampled in industrial dry AD plants. Even if the proportion of the hydration and vicinal water fractions is small ($0.1 \text{ g}_{\text{water}} \text{ gDM}^{-1}$) compared to the total amount of water, the capillary water fractions of the digestates ranged from 2 to $2.5 \text{ g}_{\text{water}} \text{ gDM}^{-1}$: this fraction can represent up to 60% of the total water for a digestate having a TS = 20%. As a consequence, for dry AD systems, the high solids content strongly affects the rheological behavior of the digestates (Battistoni, 1993; Battistoni *et al.*, 1997; Garcia-Bernet *et al.*, 2011b). Digested media are visco-elastic materials characterized by high yield stress levels, and yield stress increases with TS content according to an exponential law (Garcia-Bernet *et al.*, 2011b). Digesters are thus difficult to mix and homogenize. Indeed, Karim *et al.* (2005) showed that, when the concentration of TS increases in reactors, mixing becomes more important for improving the production of methane. Nevertheless, under unmixed conditions, transport is likely governed by diffusion processes, which are strongly related to the porosity of the media and, thus, to the water content. Therefore, the diffusive transport resistance of soluble compounds (substrate or by-products) may have a strong influence on anaerobic digestion performance in dry systems.

The aim of this study is to assess the impact of the total solids content on anaerobic digestion of solid waste. Anaerobic batch reactor experiments were performed with TS concentrations ranging from 10 to 35%. The methane production performances were assessed. To better evaluate the impact of the water content on anaerobic digestion, the Anaerobic Digestion Model No. 1 (ADM1) was then used to describe the experimental data. The objective of the model application was to test some hypotheses in order to understand why the TS content affects the global anaerobic digestion performance. The effects of hydrolysis step and liquid/gas mass transfer were more particularly investigated.

2. Materials and methods

2.1. Substrate characterization

2.1.1. Van Soest fractionation

The content of cellulose, hemicellulose and lignin-like fractions in the substrate was analyzed according to the Van Soest procedure (Van Soest, 1963). After shredding and sieving, 1g of cardboard was placed in a Fiberbag system (Gerhardt Germany). The sequential fractionation procedure was performed for six samples as follows: (1) The soluble compounds were obtained by extraction with a neutral detergent ($30 \text{ g L}^{-1} \text{ C}_{12}\text{H}_{25}\text{NaO}_4\text{S}$; $18.61 \text{ g L}^{-1} \text{ C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8, 2\text{H}_2\text{O}$; $6.81 \text{ g L}^{-1} \text{ Na}_2\text{B}_4\text{O}_7, 10\text{H}_2\text{O}$; $4.56 \text{ g L}^{-1} \text{ Na}_2\text{HPO}_4$; $10 \text{ mL L}^{-1} \text{ C}_6\text{H}_{14}\text{O}_4$) at 100°C for 60 min; (2) the hemicellulose-like compounds were extracted by an acid detergent ($20 \text{ g L}^{-1} \text{ C}_{19}\text{H}_{42}\text{NBr}$; $26.7 \text{ mL L}^{-1} \text{ H}_2\text{SO}_4$, 95-97%) for 60 min at 100°C ; (3) the lignin-like compounds were obtained by removing the cellulose-like compounds for 3 h with H_2SO_4 (72%). The remaining 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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4 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)
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13 in 600 mL serum bottles at 35° C, with a working volume of about 400 mL. The serum
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15 bottles were filled with synthetic growth medium containing nutrients and trace
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17 elements, and inoculated with granular sludge from a mesophilic anaerobic digester of a
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19 sugar factory. The final sludge concentration in the bottles was 20 gVS L⁻¹. The bottles
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21 were loaded with 1 g of cardboard (corresponding to 0.77 gVS). Biogas production and
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23 composition were measured daily. The methane production is expressed under standard
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25 condition and accounts for the variation of the gas content in the headspace of the
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27 reactors. The calculated BMP accounts for the global methane production without the
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29 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
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42 used as a substrate since cardboard represents usually the largest proportion of organic
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44 compounds in municipal solid waste (21.5%) after putrescible waste (32.2%) (ADEME,
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46 2009). The cardboard was shredded using a cutting mill SM-100 and sieved at 2 mm.
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48 Experiments were carried out in 600 mL batch flasks with a working volume of 100
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50 mL. A mixture of cardboard, water, inoculum and oligo-elements was prepared to reach
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52 six TS contents from “wet” to “dry” anaerobic conditions: TS = 10, 15, 20, 25, 30, 35
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54 %. A substrate to biomass ratio S/X of 20 (w/w) was used to limit the influence of the
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inoculum composition on the degradation, S and X representing the initial TS contents of the substrate and the biomass, respectively. The inoculum corresponded to a leachate of pressed MSW digestate sampled in an industrial plant treating MSW. One mL of an oligo-element solution was added to the mixture. This oligo-element solution was 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}), $\text{NiCl}_2, 6 \text{ H}_2\text{O}$ (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}), $\text{CuCl}_2, 2 \text{ H}_2\text{O}$ (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 over 298 days under mesophilic conditions (35°C) without mixing. Each TS condition was tested in four replicates.

2.3. Analytical methods

2.3.1 Biogas quantification and composition analysis

Biogas production and composition were determined daily during the first two months, and then once a week after the exponential phase of methane production.

The biogas production was measured by the water displacement method and then normalized according to the ambient temperature. The biogas composition was determined using a gas chromatograph (Varian $\mu\text{GC-CP4900}$) by injecting a sample volume of 2 mL. This gas chromatograph was equipped with two columns: a Molsieve 5A PLOT column for O_2 , N_2 , CH_4 and CO and a HayeSep A column for CO_2 quantification. The calibration was carried out with a standard gas composed of 25 % CO_2 , 2 % O_2 , 10 % N_2 and 63 % CH_4 . The temperatures were 30°C for the oven and 100°C for the injector and the thermal conductivity detector. The gas carrier of the flow was Helium.

2.3.2 VFA and pH analysis

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

2.4. Mathematical model

The Anaerobic Digestion Model No. 1 (ADM1) (Batstone *et al.*, 2002) was used to describe the experimental data. The characterization of the shredded cardboard with respect to ADM1 state variables, in particular carbohydrates and particulate inerts, was based on the results of the Van Soest fractionation and the degradable fraction of fibers (hemicellulose and cellulose). The degradable fraction of hemicellulose and cellulose (major degradable constituents of cardboard) was calibrated with the gas curve at 10% TS. The estimated value of 40% is of the same order of magnitude as the degradable fraction of fibers reported by Koch *et al.* (2010) for grass silage. In the model, the state variable for carbohydrates, X_{ch} , was considered to be composed of the biodegradable fraction of hemicellulose and cellulose, and the soluble organic fraction. The non-degradable fraction of hemicellulose and cellulose, as well as the lignin fraction were considered as particulate inerts (X_i). Overall, $0.33 \text{ gCOD gTS}^{-1}$ were attributed to X_{ch} and $0.85 \text{ gCOD gTS}^{-1}$ to X_i . Simulations were run in Matlab/Simulink (Version 7.3.0).

The model was calibrated to the experimental data of the batch experiments at 10% TS using a trial and error approach. Compared to the standard parameters proposed by Batstone and Keller (2003) for the anaerobic digestion of sludge, two main parameters were modified in order to account for the degradation of the specific substrate (i. e., cardboard) at high total solids contents: the first-order hydrolysis rate constant for carbohydrates and the volumetric liquid/gas mass transfer coefficient.

The default value of the first-order hydrolysis rate constant for carbohydrates ($k_{hyd,Xch}$) is 10 d^{-1} . For wet anaerobic digestion conditions and under mesophilic conditions, hydrolysis rate constants for cellulosic material (cellulose, office paper, cardboard, newsprint) reported in the literature are about 0.03 to 0.07 d^{-1} (Vavilin et al., 2008; Liebetrau et al., 2004; Vavilin et al., 2004). However, the present assays were conducted under semi-dry and dry conditions. At low moisture conditions, Pommier et al. (2007) observed a strong dependence on the moisture level for both kinetic rates and ultimate methane production from paper and cardboard waste samples. In a modeling work, Qu et al. (2009) used a value of 0.01 d^{-1} for the hydrolysis rate constant of office paper at TS contents of 40 and 66%. In the present work, the first-order hydrolysis rate constant for carbohydrates ($k_{hyd,Xch}$) was, thus, reduced from its default value to 0.01 d^{-1} .

The volumetric liquid/gas mass transfer coefficient k_T (corresponding to the k_{La} variable in the model) was reduced from its default value (200 d^{-1} ; for wet anaerobic digestion of activated sludge) to 0.5 d^{-1} to account for a reduced gas transfer due the pasty texture of the substrate-biomass mixture. To our knowledge, the volumetric liquid/gas mass transfer coefficient has never been measured in dry anaerobic digestion processes. The volumetric mass transfer coefficient k_{La} depends on two parameters: k_L corresponding to the mass transfer coefficient, and a corresponding to the specific

surface area. In dry and semi-dry anaerobic digestion processes, the volumetric mass transfer coefficient $k_L a$ is drastically reduced because of two main reasons:

- (1) the solid-liquid/gas interface is low, because of the low biogas bubble generation, and because of the unmixed conditions.
- (2) The mass transfer coefficient term is also affected by the low moisture content. The following equation accounts for the difference between the diffusivity coefficients of soluble compounds in the digestate D_i (*digestate*) and in the water D_i (*water*):

$$k_L(\text{digestate}) = k_L(\text{water}) \left(\frac{D_i(\text{digestate})}{D_i(\text{water})} \right)^{0.5} \quad (1)$$

Diffusivity coefficients decrease drastically with the decrease of the porosity (i. e., the water content) and the increase of viscosity, which is also strongly related to the TS content (Battistoni, 1993; Battistoni *et al.*, 1997; Garcia-Bernet *et al.*, 2011b).

Based on these theoretical considerations, the order of magnitude of the volumetric mass transfer coefficient is strongly affected by the TS content. A $k_T=0.5 \text{ d}^{-1}$ was considered for the assay conducted at TS = 10%.

3. Results and Discussion

3.1. Impact of TS content on anaerobic digestion performance

Figure 1 shows the cumulated methane production for the reactors operated at six different TS contents during the whole experiment. Each curve represents the average of four replicates, except for TS = 30% where two distinguished behaviors were observed.

On the first 7 days (shown in the insert in Figure 1), all the cumulated curves are

similar. The initial rate of anaerobic degradation was, thus, identical for all TS contents, indicating that the intrinsic activity of the microbial consortium was the same for the different conditions, with an average methane rate of about $0.48 \pm 0.05 \text{ mL gVS}^{-1} \text{ d}^{-1}$. After the first 7 days, the cumulated methane production was inversely proportional to the TS content (the first 40 days in Figure 1).

Then, from 30-40 days of operation, methane production rates increased for the replicates having a TS content ranging from 10 to 25% (maximum methane rates are shown in Figure 2a), indicating the beginning of the exponential growth phase. During this phase, two different behaviors were observed at 30% TS. Two replicates followed a similar trend to that of the experiments conducted at 35% TS (named 30%-a in Figure 1), whereas the two remaining replicates showed a behavior close to that at 25% TS (named 30%-b in Figure 1). For 30%-b and 35% TS, the acceleration phase, corresponding to the exponential growth phase, never started. The highest CH_4 production was about 197 mL gVS^{-1} at 10% TS. Since the biochemical methane potential (BMP) was about $214 \text{ mL CH}_4 \text{ gVS}^{-1}$, the biodegradation reaction was almost completed at 10% TS.

Considering that the COD of the substrate was $1.44 \text{ gCOD gVS}^{-1}$, the BMP was, thus, $149 \text{ mL CH}_4 \text{ gCOD}^{-1}$ and corresponded to about 40% of the theoretical BMP value of $350 \text{ mL CH}_4 \text{ gCOD}^{-1}$ (Buffière *et al.*, 2008). The low BMP value was probably due to the composition of the substrate: indeed only 73% of the TS content of this cardboard corresponded to volatile solids, and the remaining 27% to a mineral non-biodegradable fraction. Among the volatile solids (VS), the organic matter was composed of only 4% of soluble fraction and 14% of hemicellulosic fraction: these two minor fractions represent the most degradable part of the organic matter. The two additional and most

abundant fractions corresponding to cellulose and lignin represented 66% and 16% of the organic matter, respectively. These two fractions are resistant to biodegradation, especially under anaerobic conditions (Buffière *et al.*, 2008).

3.1.1. Methane production rate

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

3.1.2. Maximum methane yield

The cumulative methane yields measured after 298 days are shown in Figure 2b. They were clearly dependent on the TS content. Analyses of variance (ANOVA) were performed, distinguishing three groups: the first group (G1), which included all replicates of 10, 15, 20, 25% TS, was significantly different from the second group (G2), which included 30%-a replicates (*p = 0.0011); the third group (G3), which

included replicates of 30%-b and 35% TS, was different from G1 and G2, with a very significant***p of $2.2 \cdot 10^{-16}$ and $2.02 \cdot 10^{-6}$, respectively (*p < 0.05; **p < 0.005; ***p < $5 \cdot 10^{-5}$; n.s., not significant (p > 0.05)). The methane production was inversely correlated to the TS concentration. The methane production was 176 ± 7 , 142 ± 1 and 30 ± 10 mL gVS⁻¹ for the groups G1, G2 and G3, respectively. Concerning the replicates named 30%-a, the reduction of the cumulated methane production is consistent with previous works. Indeed, Fernandez *et al.* (2008) observed a higher methane yield at 20% TS than at 30% TS for mesophilic conditions in batch tests. Likewise, Forster-Carneiro *et al.* (2008) reported a higher methane production in thermophilic batch tests at 20% TS compared to 25% TS, and even higher than at 30% TS.

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

3.1.3. pH and VFA concentration

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

When anaerobic digestion was inhibited (30%-b and 35% TS), high VFA concentrations were measured, with values ranging from 29 to 36 gVFA kgVS⁻¹. Under

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

3.2. Model results

For better understanding of the origin of the limitation of anaerobic degradation at high solids contents, the Anaerobic Digestion Model No. 1 (ADM1) was used to describe this experimental data. Figure 3 presents exemplarily simulation results for 10% TS and the critical concentration of 30% TS. Model predictions closely followed the experimental data of cumulative methane production for a TS concentration of 10%, except for the first 50 days of the experiment. However, the model clearly over-predicted experimental data obtained for a TS concentration of 30%, using the same set 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 production rate decreased with increasing total solids content (see section '3.1.1 Methane production rate') and hydrolysis is the limiting step in methane production (Vavilin *et al.*, 2004), it was hypothesized that the first-order hydrolysis rate

decreases with increasing TS concentration. Consequently, the first-order hydrolysis rate for carbohydrates, $k_{\text{hyd},X_{\text{ch}}}$, was decreased step by step with increasing TS concentration to fit simulation results, in particular the total cumulative methane production, to experimental data. The first-order hydrolysis rate needed to be reduced to 0.0045 d^{-1} in order to properly describe the final cumulative CH_4 production for the two experiments that were not inhibited by high VFA concentrations and low pH at 30% TS (Figure 3.b, solid line). The experimental results of the two experiments, in which methane production stalled due to very high VFA concentrations and reactor acidification, could not be described by further decreasing the hydrolysis rate (see section '3.2.1 Influence of the hydrolysis rate constant'). Thus, another mechanism must have been responsible for the inhibition of methane production.

Due to the pasty texture of the substrate-biomass mixture, the initial value of the liquid/gas transfer coefficient k_T was already reduced to 0.5 d^{-1} for a TS concentration of 10% to account for reduced mass transfer. As the viscosity of the substrate-biomass mixture increased and the porosity decreased with increasing TS content, it was hypothesized that the overall mass transfer decreases with increasing TS concentration. The overall mass transfer coefficient (k_T) was, therefore, decreased to match measured and simulated total cumulative methane production for the two inhibited batch experiments at 30% TS. Reducing the value of k_T from 0.5 d^{-1} to 0.02 d^{-1} resulted in an adequate representation of the final cumulative methane production for the two inhibited experiments (Figure 3.b, dashed line).

Although the calibration of k_T and $k_{\text{hyd},X_{\text{ch}}}$ allowed for describing the final cumulative methane production, the ADM1 did not describe very well the initial phase of cumulative methane production. The ADM1 describes hydrolysis as a simple first-order

process. According to Vavilin *et al.* (2008), hydrolysis of certain complex substrates can, however, be better represented by the Contois model, which considers that hydrolysis kinetics depends on both substrate and biomass concentration (concentration of the biomass that produces the enzymes for hydrolysis). The Contois model is a more general model than the first-order hydrolysis kinetics and allows for better representing the sigmoid-type curve of cumulative methane production (Vavilin *et al.*, 2008). Using the Contois model, however, has no impact on the prediction of the final cumulative methane production (data not shown). As the aim of the modeling study was to find an explanation for the general trend of the experimental data (inhibition of anaerobic digestion of cardboard at high total solids contents), the first-order hydrolysis model is the simplest approximation of the hydrolysis step. In addition, the more complex structure of the Contois model makes it more difficult to identify and distinguish mechanisms influencing anaerobic digestion at high TS concentrations. Thus, first-order hydrolysis kinetics was used for deeper analysis of mechanisms affecting anaerobic digestion at high TS concentrations. Based on the simulation results presented above, two different mechanisms were identified that have a considerable impact on anaerobic digestion at high TS concentrations: 1) the rate of hydrolysis of particulate substrates (here only carbohydrates), and 2) the transfer of produced gas from the liquid phase to the gas phase. The influence of both phenomena is now presented in more detail.

3.2.1 Influence of the hydrolysis rate constant

For each TS concentration, the first-order hydrolysis rate constant for carbohydrates was calibrated for batch experiments that were not inhibited by high VFA concentrations and low pH to meet the total cumulative methane production at the end of each batch

experiment. Figure 4 shows the calibrated hydrolysis rate constants for each TS concentration. The hydrolysis rate constants obtained for TS concentrations of 10% and 15% were similar. But the calibrated hydrolysis rate constants linearly decreased with increasing TS concentration for $15\% \leq \text{TS} \leq 30\%$. This finding is in agreement with results presented by Pommier *et al.* (2007), who observed a strong impact of the moisture content on kinetic rates and maximum methane production in solid waste anaerobic digestion. Extrapolation of the hydrolysis rate constant for a TS concentration of 35% using the linear relationship shown in Figure 4 gave a value of 0.00275 d^{-1} . With this hydrolysis rate constant and a k_T value of 0.5 d^{-1} (as used for all non-inhibited batch experiments), the ADM1 predicted a total cumulative methane production of $107 \text{ mL CH}_4 \text{ gVS}^{-1}$ and no VFA accumulation for $\text{TS} = 35\%$. The total cumulative methane production predicted by the model was 4.5 times higher than that observed in the experiment ($23.5 \text{ mL CH}_4 \text{ gVS}^{-1}$). Thus, a further decrease in the hydrolysis rate constant could not explain why methane production stalled at a total solids concentration of 35%.

In summary, a decreasing first-order hydrolysis rate constant with increasing TS content could well describe experimental methane production at different TS in non-inhibited batch experiments. But a decreasing hydrolysis rate constant could not explain considerable VFA accumulation, reactor acidification, and limited methane production observed in two batch experiments at 30% TS and all batch experiments at 35% TS.

3.2.2. Influence of the overall mass transfer coefficient

The influence of the overall mass transfer coefficient k_T was evaluated by varying its value between 0.001 d^{-1} and 100 d^{-1} for each studied TS concentration. The default

value (named k_{La} in the original ADM1) is 200 d^{-1} for modeling anaerobic digestion of activated sludge (wet digestion) (Rosen and Jeppsson, 2006). The first-order hydrolysis rate constant for carbohydrates was kept constant at 0.01 d^{-1} for all simulations to focus on the effect of the overall mass transfer coefficient. Figure 5 shows the final cumulative methane production obtained for different values of k_T and different TS contents. A sudden and steep decrease in the cumulative methane production can be observed for k_T values between 0.04 d^{-1} and 0.18 d^{-1} depending on the TS content. Above a critical k_T value, methane production was not influenced by overall mass transfer and the cumulative methane production remained almost constant independently of the k_T value. In this case, no VFA accumulation was observed. Below the critical k_T value, limited overall mass transfer clearly affected methane production and resulted in considerably lower cumulative methane production. Methane production was more sensitive to overall mass transfer limitations at high TS concentrations as the methane production dropped already at higher k_T values (at 0.18 d^{-1} for 35% TS compared to 0.04 d^{-1} for 10% TS). Low methane production always went along with accumulation of VFA and reactor acidification (data not shown). The different behaviors in the batch experiments at 30% TS content might be related to slightly different actual total solids contents in the serum bottles as a result of minor inaccuracies in the preparation of the bottles, including measurement errors. In simulations, methane production at 30% TS content dropped from $174.5\text{ mL CH}_4\text{ gVS}^{-1}$ to $51.9\text{ mL CH}_4\text{ gVS}^{-1}$ when the mass transfer coefficient was reduced from 0.16 d^{-1} to 0.15 d^{-1} . At 35% TS, the methane production dropped already between $k_T = 0.18\text{ d}^{-1}$ and $k_T = 0.17\text{ d}^{-1}$ 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 TS 30% and 35% in Figure 5 are very close to each other. Thus, a small increase in the

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
23
24 convert VFA and high molecular weight long-chain fatty acids to acetate, carbon
25
26 dioxide and hydrogen. These β -oxidation reactions are thermodynamically not possible
27
28 under standard conditions ($\Delta G^\circ > 0$). In fact, β -oxidation occurs only at very low
29
30 hydrogen partial pressure. Thus, produced hydrogen needs to be locally consumed (e.g.,
31
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
46
47 the ADM1 does not consider inhibition of hydrolysis. Overall, the simulation results
48
49 clearly show that overall mass transfer limitation can explain limited methane
50
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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4. Conclusion

Based on experimental observations and ADM1 simulations, it was shown that the TS content affects the global anaerobic digestion performance of solids through (i) reduction of the microbial hydrolysis rate for $10\% \leq TS \leq 25\%$ and (ii) physical limitation related to liquid/gas mass transfer for $TS \geq 30\%$. Further investigations need to be done to understand the role of the TS content on the behavior of the microbial community structure involved in the anaerobic digestion degradation of solids from wet to dry technologies.

Acknowledgements

This research was supported by the French National Research Agency through the BIOENERGIES 2008 program (n° ANR-08-BIOE-009-03). The authors acknowledge Valorga International for their assistance in supplying the anaerobic inoculum. The authors also thank Dr. Ulf Jeppsson and Dr. Christian Rosen from Lund University, 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 CH_4 production.

- a) At 10% TS, with calibrated values for k_T and $k_{\text{hyd},X_{\text{ch}}}$.
- b) At 30% TS, with calibrated values for k_T and $k_{\text{hyd},X_{\text{ch}}}$.

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.

Figure1

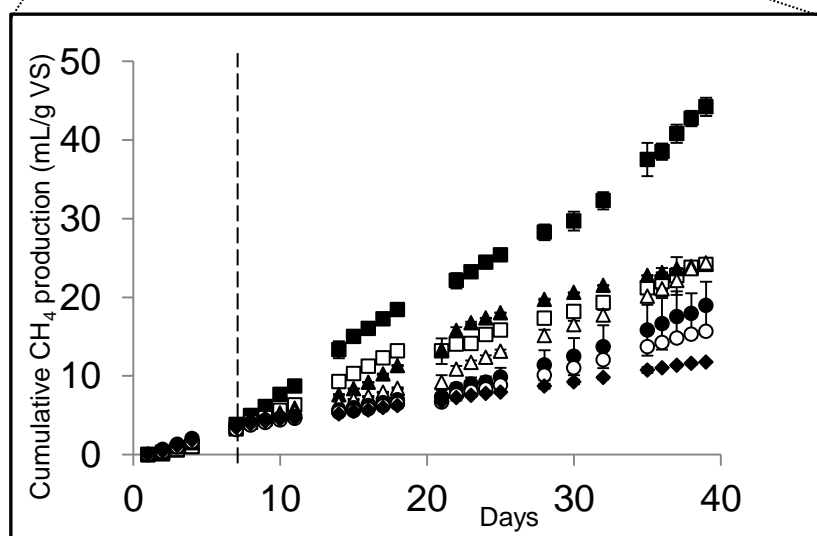
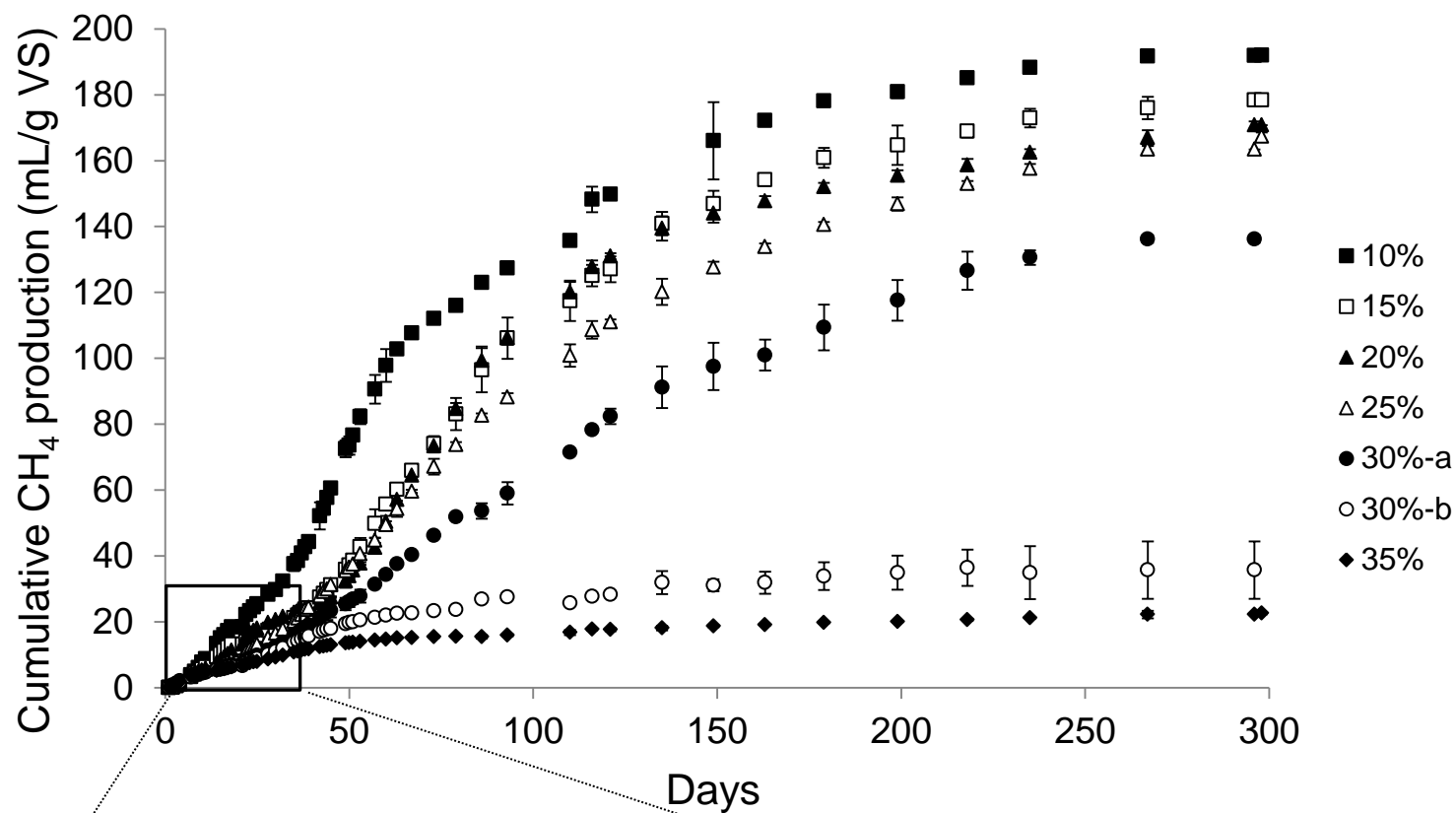


Figure2a

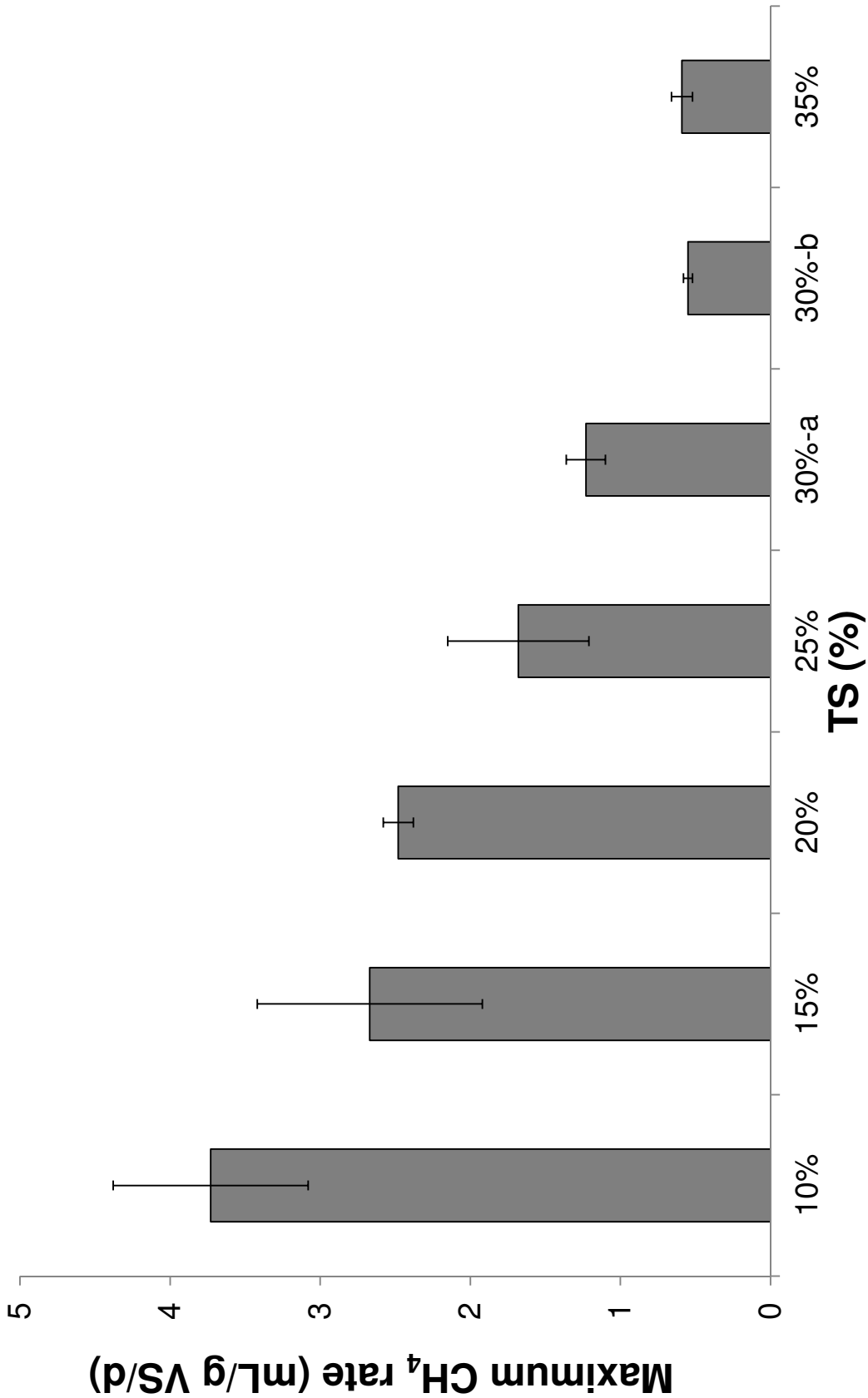


Figure2b

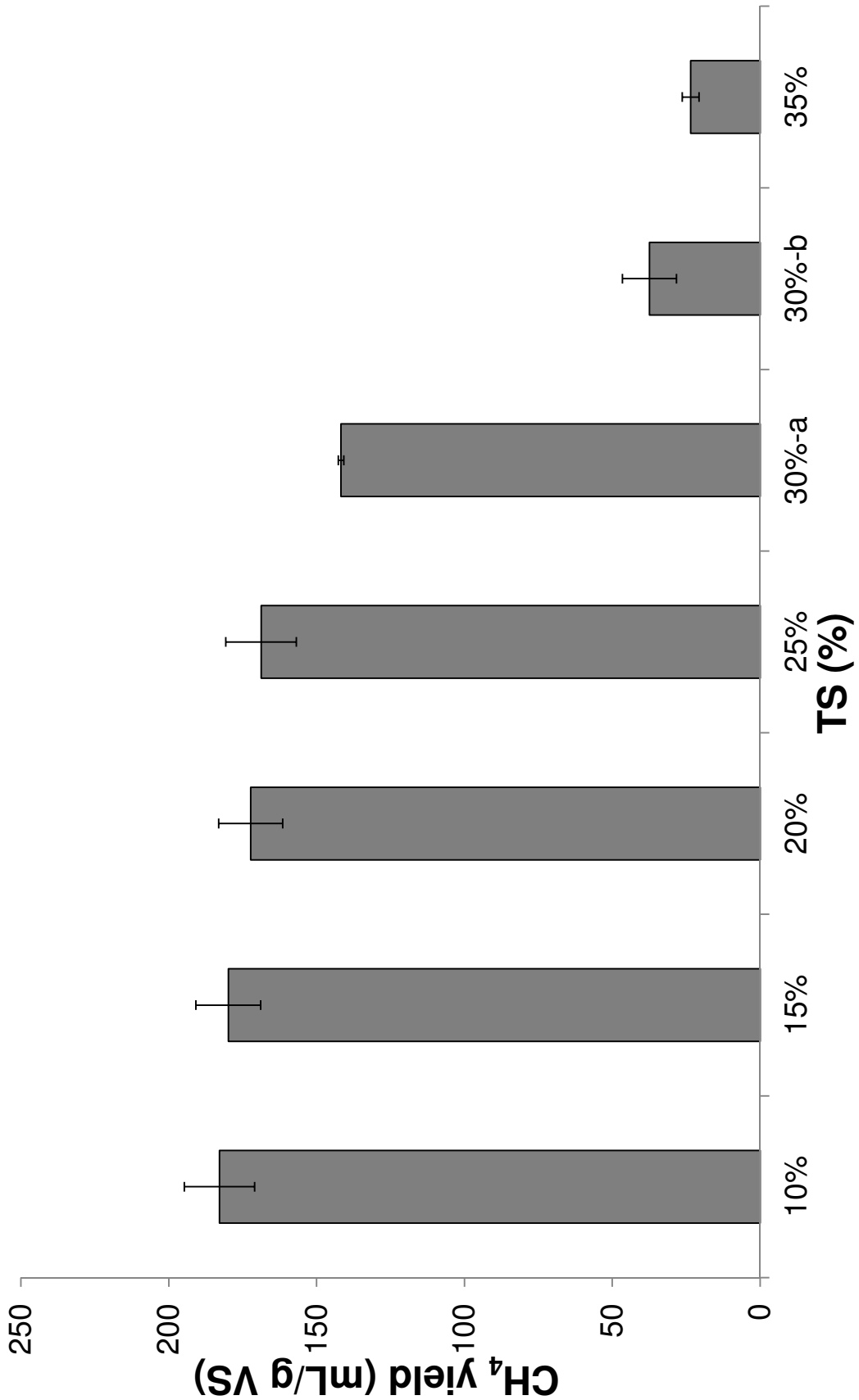


Figure 2c

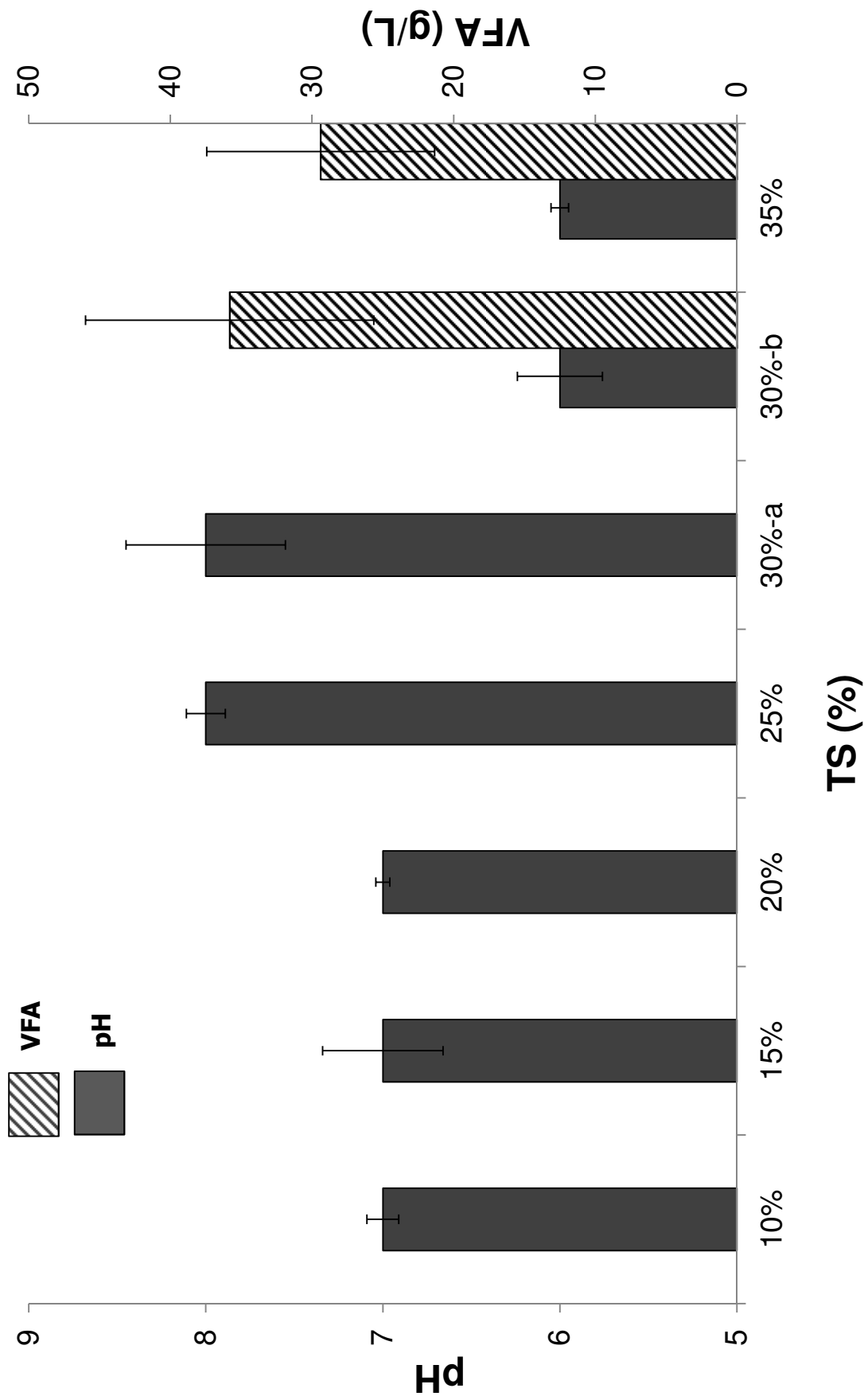


Figure3a

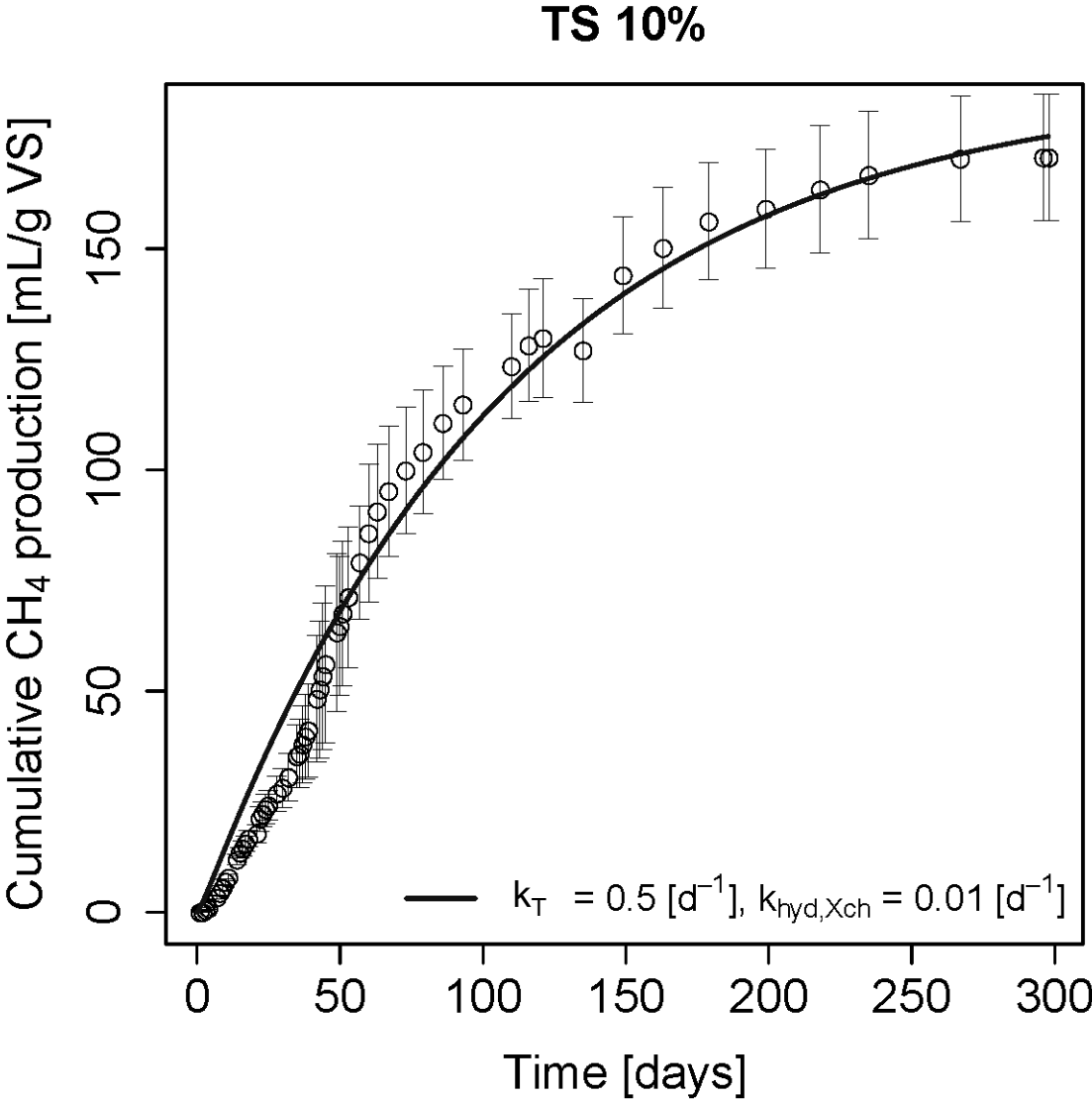


Figure 3b

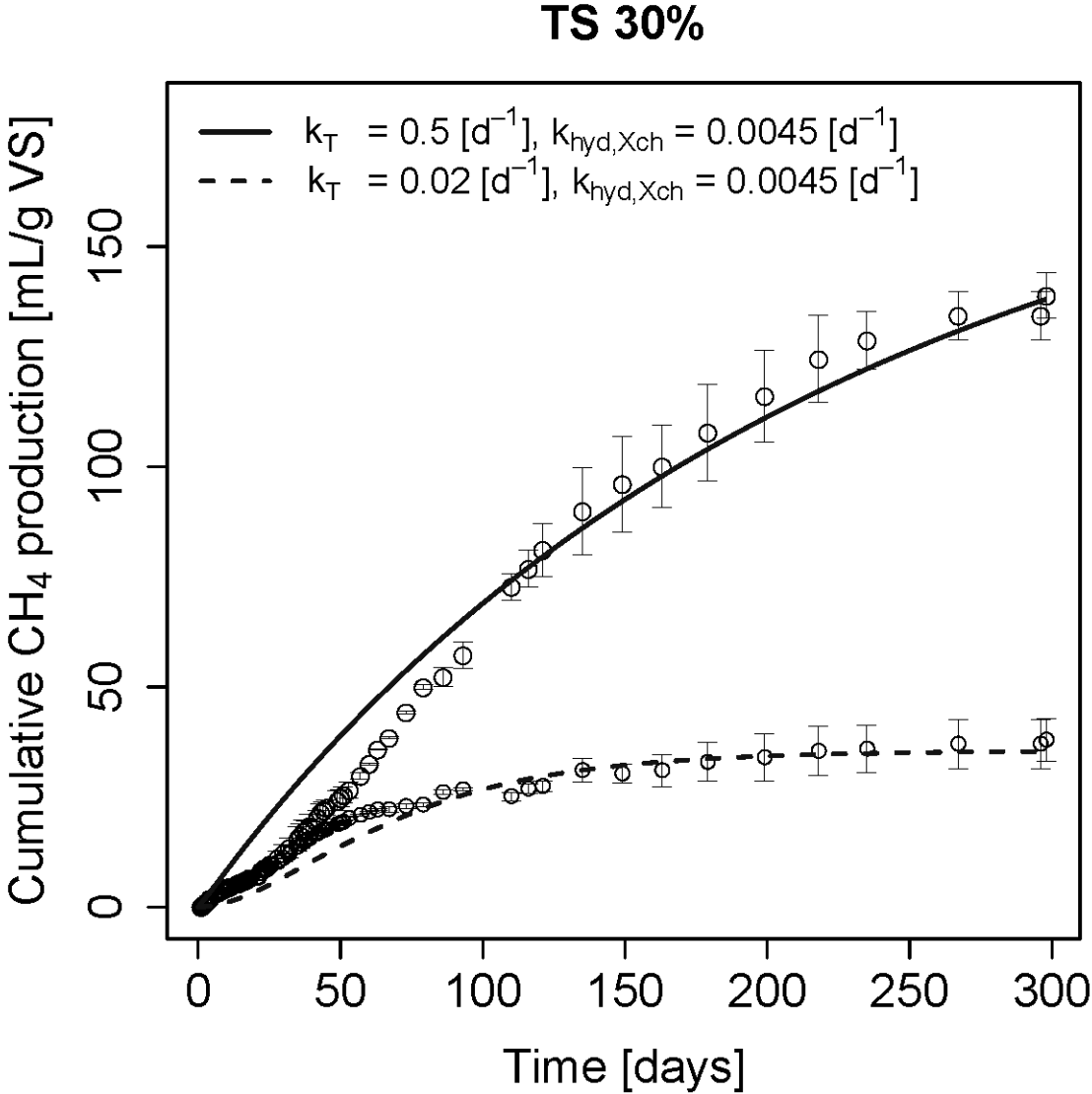


Figure4

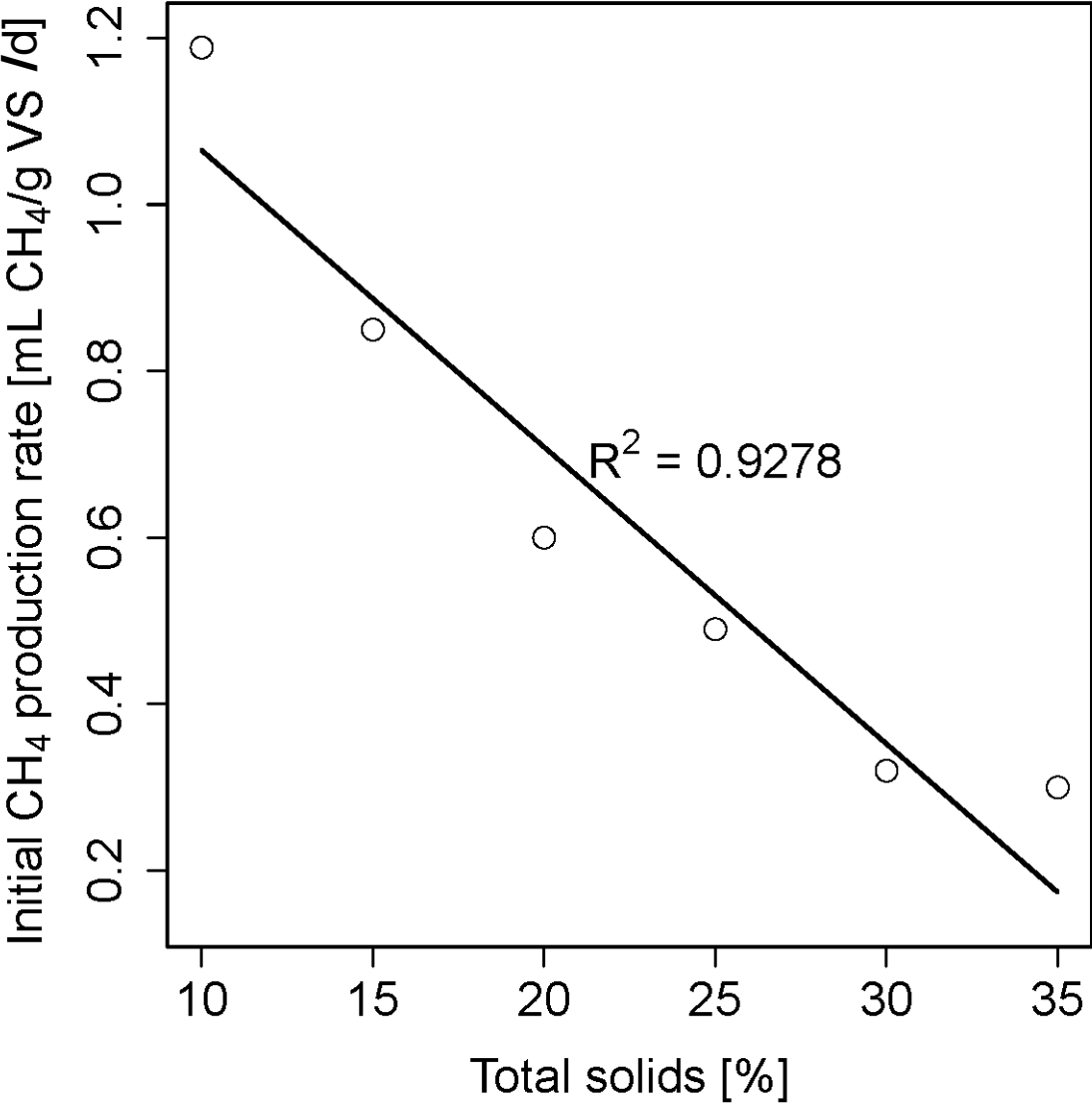


Figure5

