ADM1 modelling of large-scale covered in-ground anaerobic reactor treating sugarcane vinasse

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ABSTRACT

In this paper, we demonstrate in a clear procedure the application of ADM1 to model a large-scale covered in-ground anaerobic reactor (Cigar), processing sugarcane vinasse from a biorefinery in Brazil. The biochemical make-up (carbohydrates, proteins, and lipids) of the substrate was analysed based on the food industry standards. Two distinct subsets of data, based on the sugarcane harvest season for bioethanol and sugar production in 2012 and 2014, were used to direct and cross validate the model, respectively. We fitted measured data by estimating two key parameters against biogas flow rate: the degradation extent (f_d) and the first order hydrolysis rate coefficient (k_{hyd}). By cross-validation we show that the fitted model can be generalised to represent the behaviour of the reactor under study. Therefore, motivated by practical and industrial application of ADM1, for both different reactors types and substrates, we show aspects on the implementation of ADM1 to a specific large-scale reactor for anaerobic digestion of sugarcane vinasse.

Keywords ADM1, anaerobic digestion, biogas; simulation, sugarcane vinasse

INTRODUCTION

Sugarcane bioethanol has been produced in many countries/regions, such as Brazil, the USA and the European Union and is regarded as one of the most promising alternatives to replace fossil fuels. However, such interest has led to bioethanol expansion and the saying “what goes in must come out”, is especially true for the sugar-bioethanol industry, which produces huge amounts of residues, including sugarcane vinasse (SV), a dark brown wastewater after bioethanol distillation. The projections by the Agricultural Trade Office (ATO/São Paulo) of total bioethanol production in Brazil’s marketing year (MY) 2017/18 were 26.65 billion litres (11.83 billion litres of anhydrous bioethanol and 14.82 billion litres of hydrated bioethanol) (GAIN 2017). On average Brazilian biorefineries produce 12 L of SV for each litre of bioethanol. The trade-off between the concentration of alcohol and the viability of yeast limits the reduction of SV volumes.

SV has been extensively worldwide used as fertilizer in the sugarcane fields given the presence of rich minerals, such as potassium, calcium, magnesium, phosphorus, and nitrogen. SV can also be

applied onto so-called "sacrifice areas" in Brazil when not used as fertilizer. However, in both cases there is a great risk of environmental contamination. The emission and degradation of SV in the terrestrial and aquatic environment can cause severe impacts, such as eutrophication of rivers and lakes, ground water contamination and GHG (greenhouse gas) emissions (Moraes et al. 2015). Nevertheless, effective and economic biological treatment of SV, such as anaerobic digestion (AD) has been often cited as an option for mitigating the environmental impacts (Leite et al. 2015, Moraes et al. 2015).

AD arises as a sustainable bioprocess to unlock the value of SV as an energy feedstock. It is a biological engineering solution that improves the attractiveness of bioethanol as an alternative fuel, both as a means of pollution potential reduction and through recovery of biogas for renewable bioenergy generation (Barrera et al. 2015, Leite et al. 2015). Moreover, biogas produced by AD can replace the burning of bagasse, which is a by-product from the first-generation bioethanol production, to encourage second-generation bioethanol production from bagasse (Moraes et al. 2015). However, the industrial exploitation of SV has been hampered by inefficient reactors and/or their improper operation. An experimental approach coupled with mathematical models can support optimisation of a biological system and the prediction of reactor behaviour/efficiency under different conditions (Donoso-Bravo et al. 2011). Nevertheless, the industrial application of models is not widespread given the diversity and specific nature of most industrial processes (Batstone & Keller 2003). In addition, the complexity and non-linearity of the AD process and the considerable demand of experimental data for modelling purposes are barriers to modelling at industrial scale.

To date, the Anaerobic Digestion Model No. 1 (ADM1) (Batstone et al. 2002) is commonly regarded as the most realistic and generic model to describe the main biochemical and physico-chemical processes, and gas-liquid mass transfer in anaerobic digestion (Poggio et al. 2016). According to Batstone et al. (2006), ADM1 was originally developed: 1) for full-scale application in plant design, operation, and optimisation, 2) as a working platform for model improvement based on validation studies, and 3) to fulfil the industry needs as a technology transfer tool,

developing operational strategies and evaluating the performance of controllers (Batstone & Steyer 2007). Although the ADM1 Scientific Technical Report (STR) states that the model was developed for application in industry (Batstone et al. 2006), its industrial use to describe a large-scale covered in-ground anaerobic reactor (Cigar) to process wastewater from sugarcane biorefinery has not been reported in the literature. In addition, the practical application of ADM1 under real operating conditions is a difficult task, and the modelling framework presented here addresses some of the issues generating substantial information assessing the viability of model application using real plant data.

The research reported in this paper applies ADM1 in a clear procedure to model the first large-scale Cigar in Brazil, which processes SV to produce biogas and generate bioelectricity for supply to the local grid. The Cigar is one of the components integrating a full biogas plant.

Good modelling practice requires both direct and cross validation and to this end a reasonable volume of data must be available and divided into two subsets. Direct validation consists in evaluating the ability of the model to reproduce the experimental data used for estimating the parameters. It is a necessary condition but not enough to accept the ability of the model to reproduce the behaviour of the system under study. In fact, even fitting well the data used for parameter estimation, the model may not be generalized to represent the behaviour of the system under study by using another subset. Therefore, in this work two subsets of data, based on the sugarcane harvest season for bioethanol and sugar production in 2012 and 2014, were used to direct and cross validate the model, respectively.

METHODS

Cigar set-up and operation

The modelled large-scale anaerobic methanogenic reactor for digestion of SV, Cigar, is located in the area of Ester Mill in the city of Cosmópolis, South East, Brazil. It was designed based on historical qualitative and quantitative data for SV produced by Ester mill, and its design characteristics are shown in Table 1. In the study periods presented here of 2012 (from May 2012 to

December 2012) and 2014 (from August 2014 to November 2014), the Ester Mill sugar production was 110,400 and 100,200 tonnes, respectively. Within the same periods, the hydrous bioethanol production was 69 million and 62 million litres, respectively.

Table 1. Cigar design parameters and main operational data.

Parameter	Value	Units
Flow rate of SV	39.5	$m^3\ h^{-1}$
Concentration of organic matter	30	kg COD m^{-3}
Organic Loading Rate (OLR)	1.99	kg COD m^{-3} day^{-1}
Reactor volume	15,000	m^3
Headspace volume	4,800	m^3
Hydraulic Retention Time	15	days
Conversion rate	0.228	$m^3\ CH_4$ kg COD^{-1}
Biogas rate production	491	$Nm^3\ h^{-1}$
Methane rate production (55%)	270	N $m^3\ h^{-1}\ CH_4$

The reactor is operated under mesophilic conditions at approximately 37º C. The average hydraulic retention time (HRT) was 15 days and Cigar was inoculated with sludge from industrial and domestic sewage treatment plants for the first time in 2010. The blanket of microorganisms in the reactor reached maturity after one and a half years (i.e., steady-state).

Figure 1 presents a simplified schematic flow diagram for Cigar and the other components (mix tank, hydrogen sulphide scrubber, and gas engine) of the biogas plant. Cigar is a 3-chamber reactor where chamber 1 and 2, represent 60% and 20% of total reactor volume, respectively. The remaining 20% volume of chamber 3 is responsible for settling most of the biological activated sludge. The SV from the biorefinery is mixed with liquor from chamber 1 to recirculate the alkalinity, with effect of an overall rise in the influent pH. This mixture enters Cigar from the bottom and flows upwards, as in a typical upflow anaerobic sludge blanket (UASB) reactor, without the phase separator at the top, providing favourable physical and chemical conditions for sludge flocculation. An automated pumping station adjusts flow rates in Cigar, which was measured online using an electromagnetic flow meter model OPTIFLUX KC1000F/6 (Krohne) with a signal converter IFC 100. The flow rate was adjusted based on the organic loading in the SV. Over the study periods, in 2012 and 2014, there were significant variations in the COD concentration and flow rate as can be observed in Figure 2.

The biogas produced is drawn from the reactor headspace and transferred to an aerobic biological scrubbing system for removal hydrogen sulphide. The biogas is then burned in a gas engine connected to a 1 MWe containerized power generation set to produce bioelectricity feeding the local energy grid.

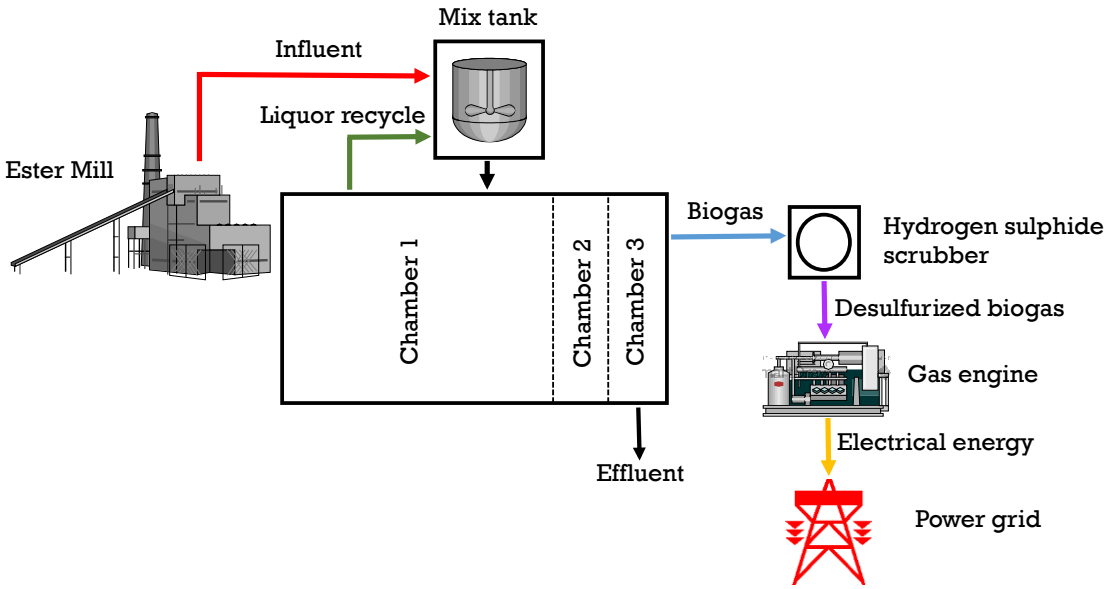

Figure 1. Simplified biogas plant-wide layout under study.

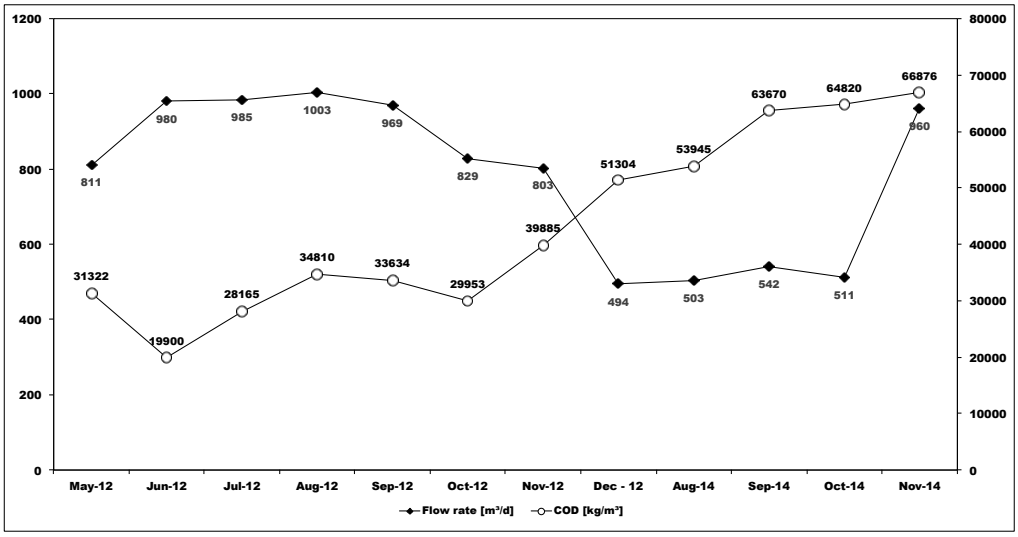

Figure 2. Averages of COD concentrations and flow rate in 2012 and 2014.

Cigar monitoring

Influent and effluent

The mixed influent from the mix tank and the effluent from chamber 3 were sampled, analysed, and recorded based on the biogas plant operating routine, containing the most relevant information at the lowest cost of monitoring. Since the reactor was located in a remote area, the biogas plant

counted on a laboratory scale to carry out same day analyses to avoid either sample storage or transport. Recorded data from online and offline analyses provided by the plant operators were used in the model simulations. The sample collection and physico-chemical analyses of the mixed influent in the mix tank and the effluent in chamber 3, were done frequently by plant operators according to the protocols described by the Standard Methods for the Examination of Water and Wastewater (APHA 2012) – Table 2.

Table 2. Physico-chemical parameters analysed, method and frequency.

Parameter	(APHA, 2012)	Frequency
Temperature	2550	constant (online)
pH	4500	constant (online)
COD concentration	5220	daily (offline)
Total solids (TS)	2540B	weekly (offline)
Total volatile solids (TVS)	2540E	weekly(offline)
Total suspended solids (TSS)	2540D	weekly (offline)
Volatile suspended solids (VSS)	2540E	daily (offline)
Volatile fatty acids (VFA)	5560	daily (offline)
Partial alkalinity	2320	daily (offline)
Total Kjeldahl nitrogen (TKN)	4500	fortnightly (offline)
Total ammonia nitrogen (TAN)	4500	fortnightly (offline)

The biochemical composition of the substrate was divided amongst, carbohydrates, lipids and proteins, and analyzed according to the following analytical methods: carbohydrates by the Lane & Eynon (1923) method and lipids by the Bligh & Dyer (1959) method. The total protein content was estimated by multiplying the total Kjeldahl nitrogen by factor 6.25, based on the food industry standard for protein determination (Mariotti et al. 2008). The inert fraction in the influent was calculated as ash content (i.e., the difference between the average of TS and VS).

Biogas

The biogas flow was measured online using a Vortex M84 flow meter (Foxboro®) and its content (%CH_4) was measured using a Landtec GEM^{TM} 2000. Equipment calibrations were undertaken constantly to ensure accuracy in the measurements.

Modelling methods

Cigar implementation and inputs

Cigar was implemented as a single stage model in Aquasim 2.1 d (Reichert 1998) and modelled as a mixed liquid reactor with constant volume, and gas diffusion to a mixed gas headspace. For model simplicity and simulation efficiency the three chambers in the Cigar were lumped together and modelled as a CSTR reactor. In fact, samples at different points (chamber 1, recycle point, and chamber 3) were analysed for COD, TSS, and VSS (results not shown); the results were comparable in their values and showed a certain degree of sludge dispersion in the reaction zone. For this main reason we believe that our reactor should be modelled as a CSTR. Reactors such as UASBs can behave as CSTR, given their hydrodynamics influenced by the fluid flow characteristics, particles sizes, multiphase interactions, chaotic advection, and substrate dispersion (Heertjes & Kuijenhoven 1982, Peña et al. 2006).

The original ADM1 as described in the IWA STR (Batstone et al. 2002) was used in this paper. Different researchers have developed and proposed a series of extensions to functionally upgrade the ADM1 to allow for plant-wide phosphorus (P) simulation (Flores-Alsina et al. 2016, Solon 2017) and the influence of ionic strength (as activity corrections) and ion pairing (Solon et al. 2015). However, those updates were not implemented in this study, given the lack of P measurements in the available experimental data and the relative low ionic strength of the SV. Regarding the latter, Solon et al. (2015) recommends to implement the correction for ADM1 in case of high ionic strength (e.g. $I > 0.2$ mol L^{-1}) such as in manure and high-solids digestion.

Likewise, different inhibition parameters and functions, compared to the original ADM1 implementation have been recommended, for instance, for ammonia (Wett et al. 2014, Wilson et al. 2012) and VFA (Pratt et al. 2012). Especially regarding ammonia, there are experimental evidences that free ammonia inhibition coefficients are higher than previously believed (Batstone et al. 2010). However, given the lack of consensus in the scientific community, the original implementation was maintained in our study.

Stoichiometric and kinetic parameters were based on the work of Rosén & Jeppsson (2006). The ADM1 composite material X_c, which describes the substrate, was discarded as suggested in Poggio

et al. (2016), avoiding a two-step solubilisation processes; instead the substrate was described directly in terms of its carbohydrates, proteins, lipids and inerts fraction. The ash fraction was included in the loadings to predict the accumulation of the non-biodegradable fraction of the substrate in the Cigar. TS, VS measurements and the calculated ash fraction were read into Aquasim as real list variables.

Initial conditions were established by running a whole year steady-state simulation of the same system, and considering a constant loading rate equal to the average of the measured loading rates of 2012 and a constant substrate composition equal to the average of the measured compositions of 2012 - the outputs of that simulation were used as initial conditions for the simulations here presented and kept the same in the two data sets.

The temperature was set to 310 K (37° C) based on average historical mesophilic conditions measured for Cigar. Real list variables were read into Aquasim for daily COD measurements and daily feed flow rates, which were highly variable over the Cigar operation.

Substrate fractionation

The fractionation of the substrate into three biochemical compound groups: carbohydrates, proteins, and lipids is a critical step for appropriate ADM1 implementation (Ramirez et al. 2009a). ADM1 is COD-based to describe the organic matter transformations. Therefore, the elemental formula of each biochemical compound, which allocates the calculated theoretical oxygen demand (ThOD), was used to obtain concentrations in kgCOD m^{-3}. The proportions of individual organic fractions (i.e., carbohydrates, proteins, and lipids in kg m^{-3}) were multiplied by the ThOD of each compound.

Charge balance

The charge balance was included for the description of the substrate loadings. The following dynamic state variables in ADM1, S_{ac}, S_{pro}, S_{bu}, S_{va}, S_{in}, and S_{ic} have a charge, whilst all other variables are electro-neutral (Nopens et al. 2009). One of the approaches for modelling acid-base equations is the charge balance, described by Eq. (1) for anaerobic digestion. The unknown variables are S_{CAT}, S_{AN}, and pH, with two degrees of freedom. In our case, the pH values of the

influent stream were used (setting α-values, OH^-, and H^+) to remove a degree of freedom. The other degree of freedom was removed when S_{CAT} exceeded S_{AN}, then S_{AN} was set to zero and vice versa to close the charge balance (Poggio et al. 2016).

$$S_{\mathrm{CAT}} - S_{\mathrm{AN}} = S_{ac}\alpha_{ac} + S_{pro}\alpha_{pro} + S_{bu}\alpha_{bu} + S_{va}\alpha_{va} + S_{IN}\alpha_{IN} + S_{IC}\alpha_{IC} + OH^- + H^+ \quad (1)$$

Only total VFA was routinely analysed by plant operators and most VFA in SV was assumed to be mostly acetate, as shown in Leite et al. (2015). Inorganic carbon S_{IC}, calculated through partial alkalinity measurements (real alkalinity for anaerobic reactors 5.75<pH initial<8) was set to zero, as the pH of the influent was always below 5. The TAN measured in the substrate was entered as S_{IN} (inorganic nitrogen fraction). The specific charge coefficient α_i was calculated as described in Nopens et al. (2009). The hydrogen and hydroxide ions were determined as $H^+ = 10^{-pH}$ and $OH^- = 10^{(-pKw+pH)}$ (pK_w=14).

The dynamic state variables changed according to feed streams, thereby S_{CAT} and S_{AN} were calculated at given dates taking into account pH, VFA, inorganic nitrogen, inorganic carbon, and accurate temperature measurement in the laboratory. Inputs for S_{CAT} and S_{AN} were read into Aquasim as real list variables.

Kinetic fractionation

The COD input of SV, as in any anaerobic digestion system of organic residues, was divided into biodegradable and non-biodegradable fractions (Angelidaki & Sanders 2004). The degradation extent (f_d) was introduced to describe the degradable ThOD fraction of substrate that is converted to methane (Jensen et al. 2011). This degradable fraction is made up of soluble fraction f_s and a particulate fraction (1-f_s). The non-degradable fraction (1-f_d) is composed essentially of an inert fraction X_I. The literature shows that hydrolysis and disintegration rates originally suggested in ADM1 are too high and are more likely to describe activated sludge substrate (Vavilin et al. 2008, Köch et al. 2010). The disintegration step was omitted assuming direct hydrolysis of proteins (X_{pr}), carbohydrates (X_{ch}), and lipids (X_{li}) (Jensen et al. 2011). The particulate components of the substrate (i.e., carbohydrates, proteins, and lipids) have different hydrolysis rates (Mata-Alvarez et al. 2011).

However, without experimental measurements of the products of hydrolysis (sugar, aminoacids, LCFA) the calibration of the three hydrolysis parameters would result in a higher uncertainty in the obtained values of the parameters. Therefore, to increase the parameters identifiability, only one "lumped" first order hydrolysis rate parameter is considered and calibrated. A similar approach is also followed by Lübken et al. (2007), Arnell et al. (2016), Batstone et al. (2009). In addition, the hydrolysis of particulate substrate, which is described as rate-limiting step in anaerobic digestion (Vavilin et al. 2008), was implemented by a first order hydrolysis kinetics.

Parameter estimation

Preliminarily, the state at the end of the first period (2012) was assumed as the initial condition for parameter estimation. Further, we estimated two key parameters used to indicate the degradable COD: the degradation extent (f_d) and the first order hydrolysis rate coefficient (k_{hyd}), in attention to reactor dynamic inputs (Batstone et al. 2009). Also, the choice of hydrolysis was initially based on the evidence that kinetic parameters used to describe hydrolysis of carbohydrates, proteins, and lipids are assumed as unrealistic values in the original ADM1 (Kazadi Mbamba et al. 2016). Both parameters were estimated and validated against biogas flow rate. They were estimated by a function implemented in Aquasim to minimize the sum of the squares of weighted deviations between measurements and calculated model outcomes (Reichert, 1998).

$$X^2 = \sum_{i=1}^{n} \left(\frac{y_{m,i} - y_i(p)}{\sigma_{m,i}} \right)^2 \qquad (2)$$

where $y_{m,i}$ is the ith measured value of the target measurement, assumed to be a normally distributed random variable; $y_i(p)$ is the model prediction at the time corresponding to data point i, which could be considered a function of the set of parameters p to be estimated; $\sigma_{m,i}$ is the standard error of the measurement $y_{m,i}$ and weights each term of the sum.

The secant algorithm in Aquasim was selected for numerical minimization of Eq. (2) due to possible nonlinearity of the model equations and numerical integration procedure (Lübken et al. 2007). The standard error of the estimated parameters are calculated by Aquasim as an output of the

secant algorithm, and then divided by the estimated values to determine the uncertainty in the parameters. We therefore present a more reliable evidence of representing model uncertainty than providing only model goodness of fit values (Jensen et al. 2011).

Model validation

To assess the accuracy of predictions for direct and cross validation using two subsets of data based on the sugarcane harvest season in 2012 and 2014, the relative absolute error (rAE) between measured and simulated values was determined as per Eq. (3), where $y_{m,i}$ is the ith measured value, assumed to be a normally distributed random variable; $y_i(p)$ is the model prediction at the time corresponding to data point *i*, which could be considered a function of the set of parameters *p* to be estimated and *n* is the number of observations. This allow us to classify the quality of predictions according two classes (Batstone & Keller 2003): high (±10%) or medium (10% - 30%) accurate quantitative prediction.

$$rAE = \frac{\sum_{i=1}^{n}\left(\frac{\left|y_{m,i} - y_i(p)\right|}{y_{m,i}}\right)}{n} \quad (3)$$

RESULTS

SV characterization and biochemical fractionation

The SV feed stream for Cigar in both periods of study was characterized based on samples analysed in the laboratory scale biogas plant. The average results from 2012 and 2014 are shown in Table 3. Average COD and total solids in 2014 were both twice those in 2012. This can be explained because the biorefinery produced more sugar than bioethanol in 2014/2015, leaving higher concentrations in the SV. Also high concentration of organic matter in SV is generally followed by an increase in organic acids levels, which explains about twofold of VFA in 2014 compared to 2012.

Table 3. Average substrate characterization ± standard deviation in 2012 and 2014.

Parameter	2012	2014	Units
pH	4.03±0.4	4.04±0.2	n/a
COD concentration	30.55±11.2	61.04±7.6	g L^{-1}
Total solids (TS)	24.06±7.8	42.22±6.3	g L^{-1}
Total volatile solids (TVS)	17.15±7.5	32.21±4.2	g L^{-1}
Total suspended solids (TSS)	11.4±8.4	10.18±5.2	g L^{-1}
Volatile suspended solids (VSS)	8.22±6.3	5.54±2.1	g L^{-1}
Volatile fatty acids (VFA)	2.36±0.8	4.02±1.4	g L^{-1}
Partial alkalinity	0	0	$gCaCO_3$ L^{-1}
Total *Kjeldahl* nitrogen (TKN)	0.41±0.09	0.45±0.16	g L^{-1}
Total ammonia nitrogen (TAN)	0.15±0.11	0.19±0.08	$gN\text{-}NH_4$ L^{-1}

Table 4 shows the results of the substrate biochemical fractionation in carbohydrates (f_{ch}), proteins (f_{pr}), and lipids (f_{li}) on a COD basis. The carbohydrates concentration is higher than lipids and proteins as found in Barrera et al. (2015). However, it is noteworthy that protein content of the SV analysed in this study was relatively high when compared to other studies (Leite et al. 2015, Barrera et al. 2015). In the bioethanol distillery the yeast *Saccharomyces cerevisiae* resulting from alcohol fermentation is composed by 26.95% of crude protein, which may be lost during the process to the SV. Another assumption for the high protein content is possibly the estimation using a constant factor of 6.25 as reported in Mariotti et al. (2008).

Table 4. Fractionation of substrate into biochemical compounds.

Biochemical compost	Concentration (g/L)	Elemental* formula	ThOD (gCOD/gVS)	Concentration (gCOD/L)	(% COD_{th})
Carbohydrates (f_{ch})	4.4	$C_6H_{10}O_5$	1.184	5.21	44%
Proteins (f_{pr})	2.6	$C_5H_7O_2N$	1.415	3.68	30%
Lipids (f_{li})	1.1	$C_{57}H_{104}O_6$	2.874	3.16	26%

*Angelidaki & Sanders (2004)

The charge balance influences directly the reactor pH and its results are shown in Table 5, indicated as state variables in ADM1. Despite the fact plant operators claimed to analyse the influent frequently, necessary data to calculate S_{CAT} and S_{AN} was only found at given dates shown in Table 5. This in turn would possibly affect the results of pH, which is an interaction of all charge bearing species in the system, and will be discussed later.

Table 5. Substrate description based on charge balance.

Date	pH	VFA - S_{ac} (gCOD L^{-1})	ADM1 state variables			
			S_{IC} (kmol m^{-3})	S_{IN} (kmol m^{-3})	S_{CAT} (kmol m^{-3})	S_{AN} (kmol m^{-3})
2012						
05/09	4.15	2.793	0	0.0117	0	0.0054
02/10	3.87	2.029	0	0.0117	0	0.0083
09/10	3.85	2.806	0	0.0122	0	0.0076
16/10	3.53	2.305	0	0.0196	0	0.0180
23/10	3.85	2.241	0	0.0086	0	0.0050
30/10	4.74	1.631	0	0.0089	0.003	0
06/11	4.09	3.525	0	0.01071	0	0.0011
14/11	4.00	2.664	0	0.0143	0	0.0083
20/11	4.17	3.563	0	0.0085	0.003	0
23/11	3.99	3.191	0	0.0173	0	0.0025
27/11	4.24	3.274	0	0.0275	0.001	0
2014						
01/08	4.12	3.807	0	0.025	0	1.67E-10
06/08	4.21	7.942	0	0.0214	0.005	2.05E-10
13/08	4.28	5.059	0	0.0277	0	2.41E-10
15/08	4.47	5.059	0	0.0286	0	3.74E-10
27/08	3.8	4.353	0	0.0338	0	7.99E-11
29/08	4.2	4.301	0	0.0344	0	2.01E-10
03/09	4.18	4.680	0	0.0339	0	1.92E-10
05/09	4.15	4.699	0	0.329	0	1.79E-10
10/09	4.03	4.179	0	0.0274	0	1.36E-10
17/09	4.21	5.322	0	0.0236	0	2.05E-10
19/09	3.84	4.051	0	0.0189	0	8.76E-11
26/09	4.19	2.343	0	0.0216	0	1.96E-10
01/10	4.21	4.693	0	0.257	0	2.05E-10
03/10	3.9	3.428	0	0.0264	0	1.01E-10
08/10	3.45	3.351	0	0.0238	0	3.57E-11

Performance of the CIGAR

Figure 3 shows a good correlation between the average organic loading and the biogas flow rate, as should be expected in a non-inhibited system. However, the biogas production tends to decline relatively to the OLR in 2014.

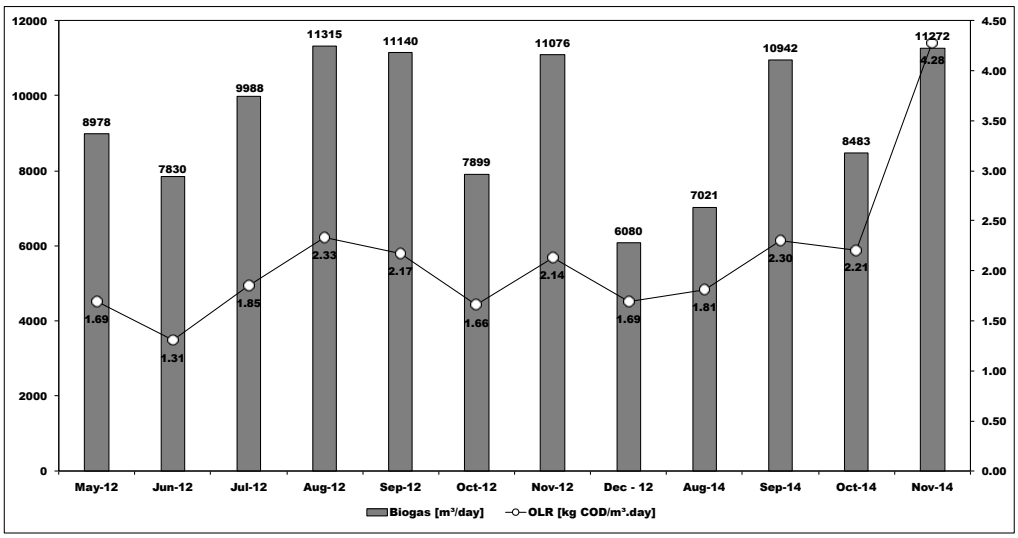

Figure 3. Averages of biogas and organic loading rate in 2012 and 2014

Ammonia inhibition is a key phenomenon affecting the dynamic of anaerobic digestion, especially the acetoclastic methanogenesis. A wide range of inhibiting ammonia concentrations has been reported in the literature, with the inhibitory TAN concentration that caused a 50% reduction in methane production rate ranging from 1.7 to 14 g/L (Chen et al. 2008). The inhibitory effect is due to free ammonia rather than ion ammonium: in the original ADM1 implementation, the 50% inhibitory concentration for the free ammonia is recommended at 0.0018 M, (i.e., 25 mg/L N-NH_3). In this study, the TAN concentration in the vinasse was, on average, 0.15 and 0.19 g/L in 2012 and 2014, respectively, which at an experimental average pH of 7.5 and at 37° C, corresponds to a free ammonia concentration of 5.7 and 7.3 mg/L N-NH_3. Considering these values, it can be concluded that ammonia inhibition plays a minor role in the dynamics of the system. Furthermore, we show in Figure 3 a good correlation between the average organic loading and the biogas flow rate, as should be expected in a non-inhibited system.

Initial simulations, kinetic fractionation and parameter estimation

Initial dynamic simulations were performed to evaluate deviations between simulated and measured biogas, which are graphically evident in Figure 4. The default value for k_{hyd} and the assumed value for f_d are presented in Table 6. Both values were reduced after parameter estimation based on biogas yield showing great sensitivity. This study confirms that default ADM1 values of 10 d^{-1} for hydrolysis constants are high as suggested in (Lübken et al. 2007, Vavilin et al. 2008).The

degradability f_d of 50% estimated is consistent with the characteristics of SV, which is composed by easily degradable organic material, mostly in the form of acetate and reducing sugars. In addition, as shown in Poggio et al. (2016) k_{hyd} and f_d are correlated parameters, which leads to increased uncertainty as observed in k_{hyd}. However, their correlation can offset possible adjustments between both parameters (Jensen et al. 2011).

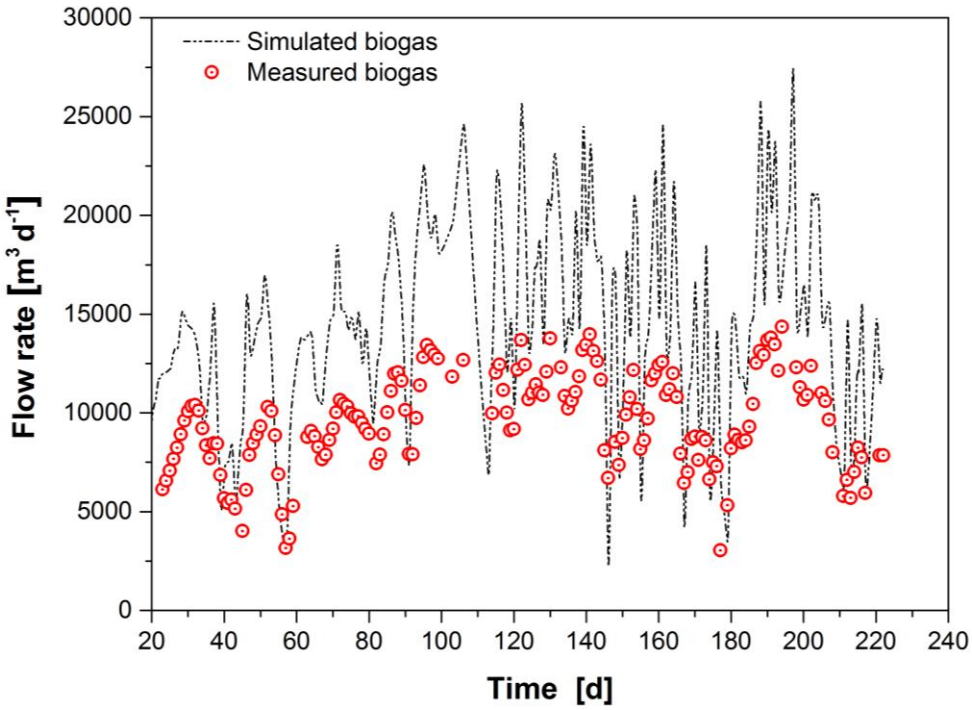

Figure 4. Initial dynamic simulations and results for measured biogas (markers) and simulated biogas (line).

Table 6. Results of model parameter estimation including intial values and standard erros.

Parameters	Initial values	Estimated	Standard errors (%)
f_d	0.70 *	0.50	2.7
k_{hyd}	10 [a]	0.66	18.4

[a] ADM1 STR *assumed value

Direct validation

The simulations in Figure 5 indicate that, after parameter estimation of f_d and k_{hyd}, there is a good fit between simulated and measured biogas. The biogas prediction was assessed as medium, regarding 18.2% of rAE. However, possible discrepancies between measurements and simulation results may be attributed to the ADM1 gas/liquid transfer coefficients for all gases, which in fact differ from reality (Ramirez et al. 2009b).

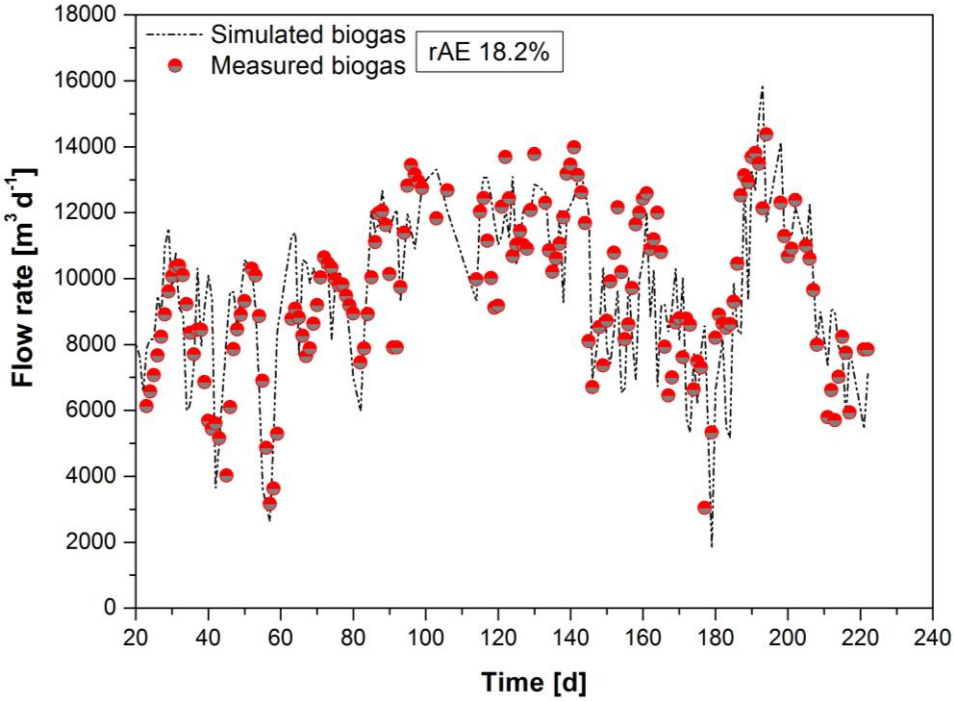

Figure 5. rAE for simulated results (line) and measured data (markers) for biogas production in 2012 – direct validation.

The deviations between simulated and measured outputs of methane and carbon dioxide levels after the parameter estimation of f_d and k_{hyd} were also evaluated. The results are shown in Figure 6 (A) and 6 (B), respectively. A good fit was achieved both for methane and carbon dioxide, which is an indicator for a realistic substrate characterization (Lübken et al. 2007). These predictions were assessed as high accuracy quantitative for methane with 6.8% of rAE and medium for carbon dioxide with 11.4 % of rAE.

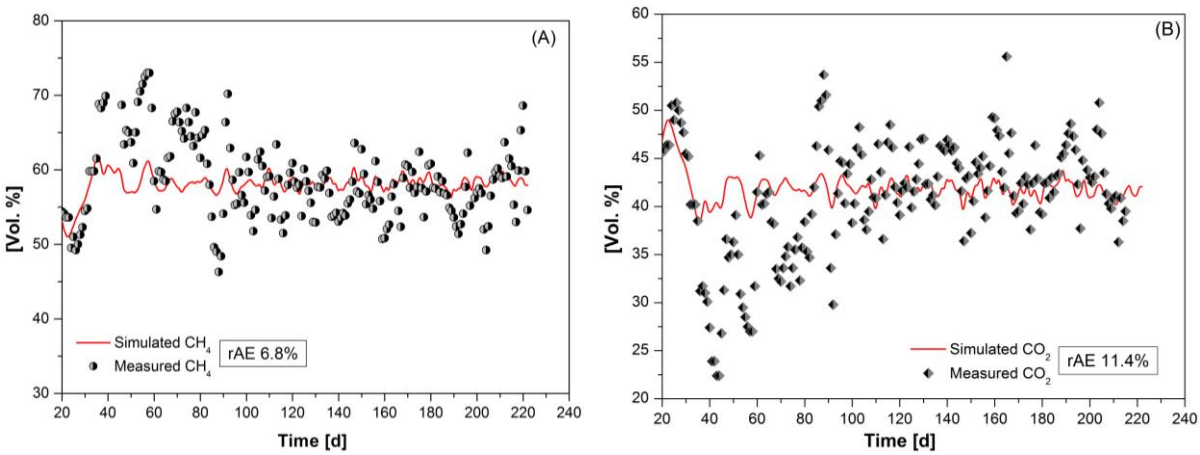

Figure 6. rAE for simulated results (line) and measured data (markers) for methane (A) and carbon dioxide (B) – direct validation.

The difference between the concentrations of anions and cations calculated in the feeds predicts the pH in the system (Ramirez et al. 2009b). The simulations of pH variable, shown in Figure 7 (A) and 6 (B), tend to underestimate the pH in both periods. This lack of fit could be explained by possible inaccuracies in the description of the charge balance of the substrate, with cations and anions loading, being calculated only during the dates presented in Table 5; apart from these dates yearly average values were used. Only between day 20 and 30 for the period of 2012 the model was able to improve the fit.

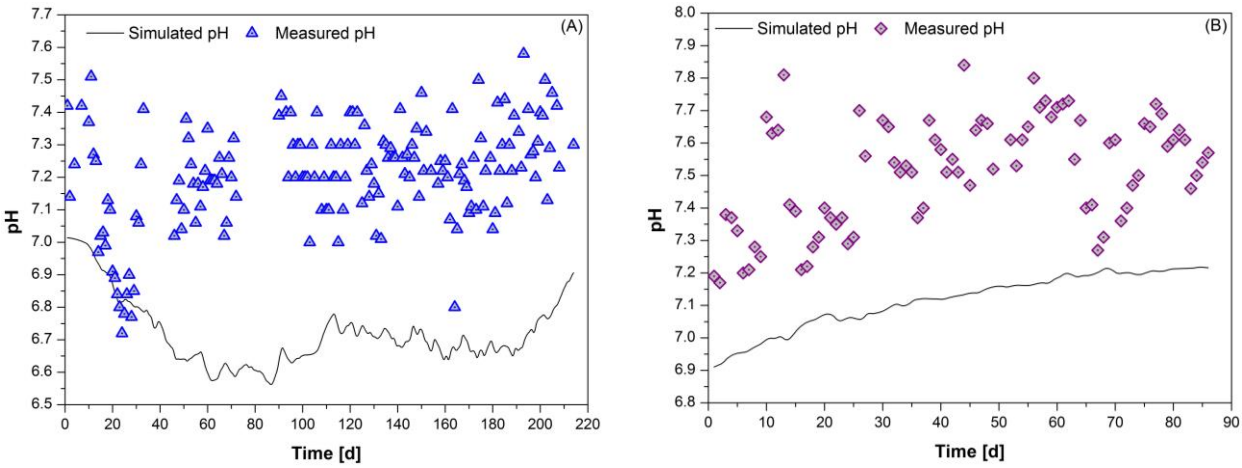

Figure 7. Simulated results (line) and measured data (markers) for pH in both periods under study: 2012 (A) and 2014 (B).

The model tends to over predict the COD concentrations (Figure 8), although, the trend is qualitatively followed by an increase in the COD concentrations.

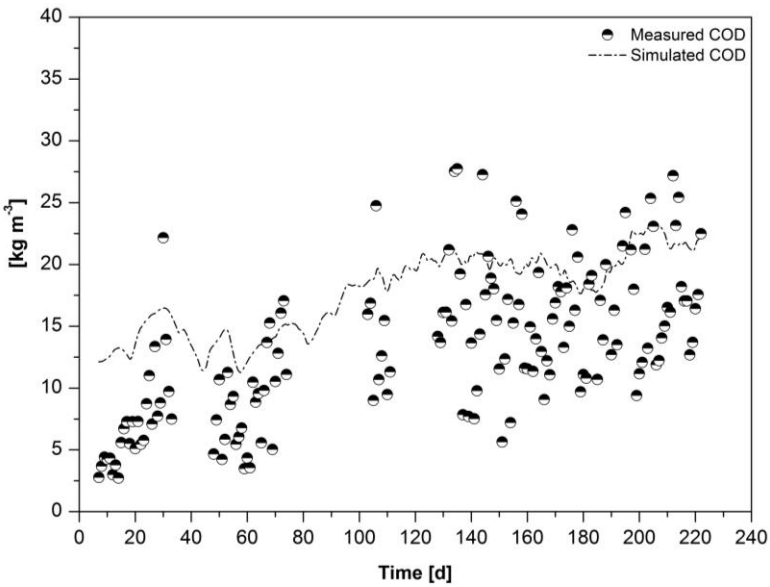

Figure 8. Simulated results (line) and measured data (markers) for COD concentrations in 2012.

Cross validation

The cross validation procedure was implemented to check whether the model gives a reliable picture of the quality of the prediction on a second dataset after parameter estimation. To this end, the same values for the estimated parameters were kept in the cross validation. The Cigar operation summed up 96 days in 2014 under the same setup previously described in 2012.

As presented in Figure 9, samples of biogas in 2014 are fewer than in 2012 but do so clearly and visibly a good fit between measured and simulated biogas. At the same time, the quality of biogas prediction was classified as medium accuracy showing a higher error (rAE 20%) resulting in a lower quality of prediction. This suggests that an increased solids concentration in the vinasse in 2014, as observed in Table 3, compared to 2012 may be affecting the estimated hydrolysis constants of 0.66 d^{-1}, which are sensitive to solids concentration (Köch et al. 2010).

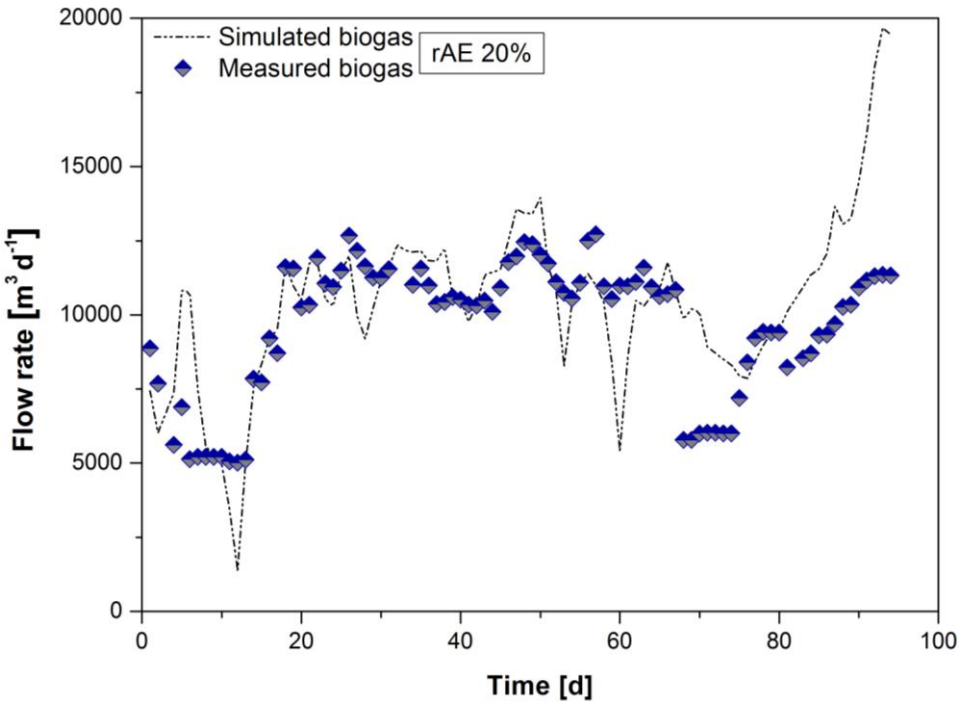

Figure 9. rAE for simulated results (line) and measured data (markers) for biogas production in 2014 – cross validation.

The rAE of 6.6% and 8% for methane and carbon dioxide, respectively, confirm the well fitted visual impression of the plots in Figure 10 (A) and 10 (B). The error for methane in the cross validation (rAE 6.6%) was quite similar to direct validation (rAE 6.8%), and validates the value of the estimate degradation extent (f_d) describing the degradable ThOD fraction of substrate that is converted to methane. Again, followed by a lower error (rAE 8%) for carbon dioxide in the cross

validation (Figure 10 (B)), a good prediction of biogas composition showed an evidence of realistic substrate characterization (Lübken et al. 2007).

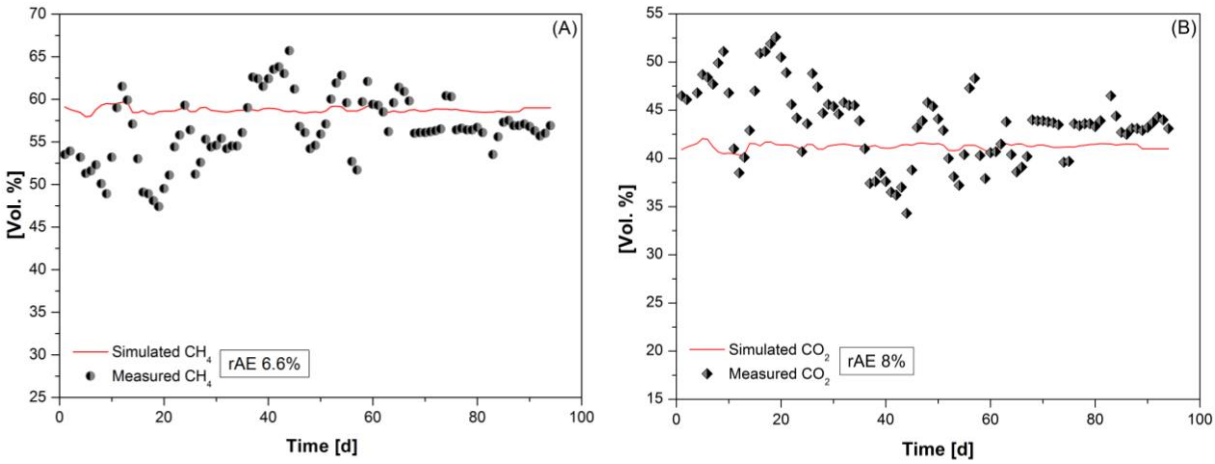

Figure 10. rAE for simulated results (line) and measured data (markers) for (A) methane and (B) carbon dioxide – cross validation.

As noted in Figure 11, there were significant fluctuations in the measured COD concentrations that could not be explained by the model in 2014. This result suggests that possibly, some parameters not calibrated in this study are reflecting an inconsistency between simulated and measured COD concentrations.

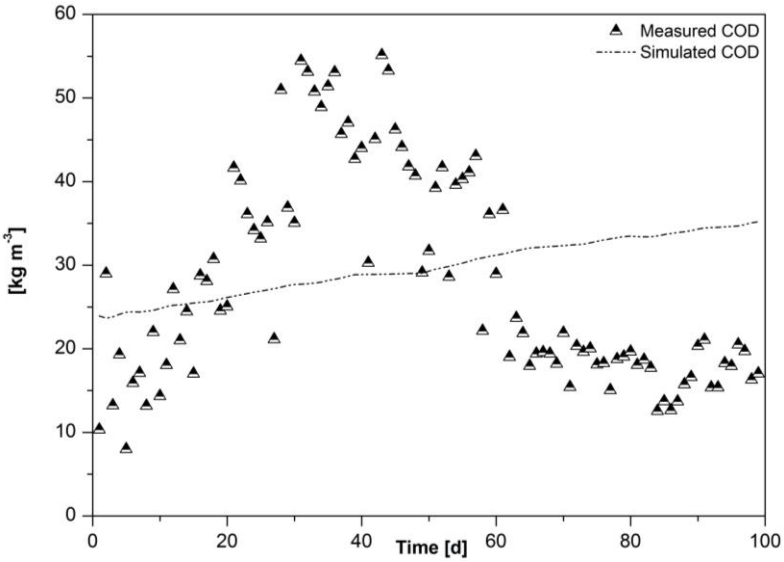

Figure 11. Simulated results (line) and measured data (markers) for COD concentrations in 2014.

CONCLUSIONS

Motivated by practical and industrial application of ADM1, for both different reactors types and substrates, we have demonstrated in a clear procedure the implementation of ADM1 to specific large-scale reactor for anaerobic digestion of sugarcane vinasse. The substrate characterization for ADM1 in terms of its biochemical make-up (i.e., carbohydrates, proteins, and lipids), based on the food industry standards were found to be valid when applied to describe sugarcane vinasse. The quality of the predictions supported by the uncertainty of the estimation of the parameters, as given by their calculated standard errors, provides a trustworthy assessment of the model performance on future data. However, the lack of data to provide ADM1 charge balance inputs to cover all dynamic feed streams resulted in poor pH simulations.

Therefore, taking into account the scale of the reactor presented here and the complexity of ADM1, a practical industrial application to model a large-scale anaerobic digester under dynamic feed streams, is a useful tool to predict the biogas yields and its composition.

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