ADM1 approach to the performance optimisation and biogas H_2S prediction of a large-scale anaerobic reactor fed on sugarcane vinasse

Jorge Vinicius da Silva Neto, Marcelo Leite Conde Elaiuy and Edson Aparecido Abdul Nour

ABSTRACT

In this paper, we present extensions to the Anaerobic Digestion Model No. 1 (ADM1) to simulate hydrogen sulphide in biogas and solids retention efficiency. The extended model was calibrated and validated against data from a large-scale covered in-ground anaerobic reactor (CIGAR), processing sugarcane vinasse. Comparative scenarios and set-ups of a CIGAR with and without a settling tank unit (settler) were simulated to investigate the reactor's performance. Biogas flow, methane content, and yield with settler were 15,983 Nm^3/d, 57%, and 0.198 $Nm^3CH_4/kgCOD$, respectively, which were 9.4%, 1.8%, and 11.64%, higher than without the settler. Improvements are combination of influent flow rate 116% higher and increased solids retention time by using a settler. The optimised modelled reactor, the volume of which was reduced by 50%, was able to produce 83% more methane per volume of reactor with half the retention time. After model calibration and validation, we assessed the quality of predictions and its utility. The overall quality of predictions was assessed as high accuracy quantitative for CH_4 and medium for H_2S and biogas flow. A practical demonstration of ADM1 to industrial application is presented here to identify the potential optimisation and behaviour of a large-scale anaerobic reactor, reducing, consequently, expenditure, risk, and time.

Key words | ADM1, biogas, H_2S, solid retention, sugarcane vinasse, sulfate reduction

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INTRODUCTION

Vinasse is a wastewater with high chemical oxygen demand (COD) and high sulfate, produced in large volumes during sugarcane ethanol distillation. Anaerobic digestion (AD) is a sustainable bioprocess to unlock the value of sugarcane vinasse (SV) as an energy feedstock through biogas recovery, from which additional bioenergy can be produced, generating electricity in gas engines, steam in boilers or even replacing diesel in sugarcane agricultural operations. There is lack of retrofitted technology from pilot to large-scale (Fuess & Zaiat 2018) and current stage of research on AD of SV is still scarce in Brazil (Moraes *et al.* 2015).

The breakthroughs on AD technologies to new applications are largely guided by mathematical models and to date The Anaerobic Digestion Model No. 1 (ADM1) (Batstone *et al.* 2002a) is the state of the art model. However, since its publication substantial extensions have been proposed to ADM1 (Batstone *et al.* 2006). Two examples of extensions are sulfate reduction (Fedorovich *et al.* 2003; Batstone 2006; Barrera *et al.* 2013, 2015) and decoupling solids retention time (SRT) from hydraulic retention time (HRT) to simulate high rate AD systems (Fedorovich *et al.* 2003; Zaher *et al.* 2003; Feldman *et al.* 2018).

The sulfate extension suggested in Batstone *et al.* (2006) under-predicted H_2S and over-predicted volatile fatty acids, while in Fedorovich *et al.* (2003) it was not calibrated to predict hydrogen sulfide in biogas. These limitations were overcome in Barrera *et al.* (2015) where the extension was validated for sulfate-rich vinasse. It included biochemical routes for depleted hydrogen once sulfate reducing bacteria (SRB) use volatile fatty acids as source of electrons. This extension may be applied to model AD of Brazilian SV, which average SO_4^{-2}:COD ratio of 0.055, shows evidence of a sulfate-rich liquid substrate (Elia Neto *et al.* 2009). Ascertaining sulfate reduction dynamics in AD by modelling

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extension to ADM1 is a useful tool to predict undesirable H_2S in biogas and costs with its removal. Unlike model validation in Barrera *et al.* (2015) for sulfate-rich vinasse using data from laboratory-scale experiments, we show the applicability of their study on sulfate extension to validate a model against data from industry.

Since 1950, the importance of SRT in AD is recognised as a tool to reduce anaerobic reactors size (McCarty 2001). High rate anaerobic reactors are based on decoupling SRT from HRT by promoting biomass retention within reactors (Van Lier *et al.* 2008). Biomass retention can be achieved by settling, attachment or granulation (Dereli *et al.* 2012), although the formation of granular anaerobic biomass, the core of most efficient anaerobic reactors, is occasionally impossible or unstable. In this case, drawing anaerobic biomass out of the effluent in a settling tank and recycling it back to the reactor, increases SRT irrespective of HRT (McCarty 2001; Tauseef *et al.* 2013). This hydraulic configuration is called anaerobic contact process (ACP) and is suitable to disperse or flocculent anaerobic biomass. The retention of biomass allows higher microorganism concentration and lower food to microorganism ratios (F/M), resulting in lower biomass and higher methane production (Low & Chase 1999; Turovskiy & Mathai 2006; Appels *et al.* 2008; Ruiz *et al.* 2011).

In the original ADM1, which is based on a continuous stirred tank reactor (CSTR), the SRT is equivalent to HRT (Batstone *et al.* 2002b) and is limited to biomass growth rate (Abbasi *et al.* 2011). To model a high rate process in ADM1, Batstone *et al.* (2002b) suggest the introduction of a variable to the mass outflow term of the mass balance equation of ADM1 to represent the SRT above HRT in a CSTR (Batstone *et al.* 2002b). Feldman *et al.* (2018) considered an ideal solids separation unit to model the operation of an anaerobic granular Internal Circulation reactor (Feldman *et al.* 2018). Zaher *et al.* (2003) suggest in their model a factor (fxout = SRT/HRT) multiplying the outflow term of mass balance equation which adds proportionality to the model (at constant fxout, decreasing HRT will affect SRT proportionally), efficiency adjustments (different values for different solids retention efficiencies) and shock events simulations. (Zaher *et al.* 2003). Kleerebezem & Loosdrecht (2006) consider that a constant SRT value for AD modelling, as suggested by Batstone *et al.* (2002a), may lead to unrealistic high solids concentrations and, instead, a maximum solids concentration in the reactors should be considered. Reichert (1994) presents an activated sludge model including a settler and sludge recycle, which is suitable to model solids retention in an ACP. In Reichert (1994) model, since the settler is nonideal (i.e. not all solids are retained in the settler), excessively high solids concentration on the reactor, as described by Kleerebezem & Loosdrecht (2006), is avoided.

Two ADM1 key-objectives are optimisation of plant design and operational analysis of AD systems to fulfil industry needs. (Batstone 2006; Ozkan-Yucel & Gökçay 2010; Kazadi Mbamba *et al.* 2016). Nevertheless, the literature on the application of ADM1 to industrial case studies is scarce (Dereli 2019) with a few extended benefit-cost analysis.

Modelling sulfate reduction and hydraulic variation in an AD system would address operational analysis and critical issues on design, showing what benefits and limitations are available from industrial application of ADM1.

A recent case study on ADM1 to cover the gaps of its industrial application was published in Elaiuy *et al.* (2018). In this work, the authors calibrated and validated the model of a large-scale covered in-ground anaerobic reactor (CIGAR) in Brazil, which processes SV to produce biogas and generate bioelectricity for supply to the local grid. However, neither model extension nor optimisation alternatives were explored in their model.

Thus, the novelty of this paper is to present a further step to the work of Elaiuy *et al.* (2018) towards the neglected sulfate extension and investigate possible design optimisation by evaluating: (i) sulfate reduction processes in AD of SV and predictions of H_2S in biogas; (ii) extension to ADM1 to incorporate a settler and sludge recycle for the improvement of biomass retention efficiency in the CIGAR reflecting on biogas production and methane yields; (iii) potential CAPEX and OPEX savings.

METHODS

CIGAR configuration and operation

The modelled CIGAR is one of the components of a biogas plant. It is an anaerobic reactor built in 2010 on a sugarcane mill in Brazil. Soil excavation was carried out to fit in-ground the 15,000 m^3 CIGAR, which was lined and covered with high density polyethylene (HDPE) to store biogas underneath a headspace of 4,800 m^3. Inside the CIGAR, vertical HDPE baffles divided the reactor into three communicating chambers. Chamber 1 (C1 – 60% of total reactor volume) was fed with a mixture of raw vinasse and effluent from C1 (recycle stream) mixed in an external mix tank. This mixture was pumped upwards through pipes at the bottom

of the reactor, as in a typical upflow anaerobic sludge blanket (UASB) reactor. The remaining volume of the reactor was split into two chambers, chamber 2 (C2) and chamber 3 (C3). C2 was fed only with effluent from C1, and C3 was designed to settle the anaerobic sludge, which may be recycled back to C1.

The CIGAR was designed to operate under mesophilic conditions (37 °C), 39.5 m^3/h flow rate of SV, 1.99 kgCOD/m^3/d organic loading rate (OLR), 15 days HRT, 0.227 Nm^3 CH_4/kgCOD methane yield to produce 491 Nm^3/h of biogas with 55% CH_4.

A schematic layout of the reactor is presented in Figure 1.

Analytical methods

Data were collected from CIGAR operation over the harvest season of 2012 (Season_12) from May to December for 220 days. Eventually, data were not available due to operational problems. Physico-chemical analyses were carried out by plant operators according to the protocols described by *Standard Methods for the Examination of Water and Wastewater* (APHA 2005), in an on-site laboratory and included analysis of influent, recycle, and effluent streams (Table 1). Biochemical characterisation of the substrate as carbohydrates, lipids, and proteins was performed following the analytical methods described in Elaiuy *et al.* (2018).

Influent flow was measured continuously using a magnetic flow meter OPTIFLUX KC1000F/6 (Krohne) with IFC100 signal converter. Biogas flow was continuously measured using a thermal dispersion mass flow meter FT-2 (Clontech). H_2S was measured daily with precision detection tubes (Kitagawa manual pump model AP20, tubes model 120SH – range of 0.1–4% H_2S). CH_4 was measured 6 times a day with a handheld GEM2000 biogas analyser (Landtec).

Soluble COD removal efficiency

Theoretical oxygen demand (ThOD) of 1 kg of microorganisms as volatile suspended solids (VSS) with an estimated composition of $C_5H_7O_2N$ can be calculated as 1.42 kgCOD/kgVSS (Van Lier *et al.* 2008). Subtracting the ThOD of VSS from the total COD results in a *proxy* soluble COD. Thus, the *proxy* of soluble COD can be calculated by the following equation:

$$COD_{proxy\_soluble} = COD_{total} - 1.42\ x\ VSS \quad (1)$$

COD removal efficiency for the *proxy* soluble COD can be calculated as follows:

$$COD\ Removal\ Efficiency_{proxy\_soluble,\ i} = 1 - COD_{proxy\_soluble,i}/COD_{Influent} \quad (2)$$

Similarly, total COD removal can be calculated for effluent as follows:

$$COD\ Removal\ Efficiency_i = 1 - COD_i/COD_{Influent} \quad (3)$$

where '*i*' refers to recycle or effluent stream.

During Season_12, high values of VSS in effluent and recycle, from chambers 3 and 1, respectively, denoted anaerobic biomass being washed out from both chambers, which was confirmed by Imhoff cone settleable solids tests. The comparison of *proxy* soluble COD removal efficiency between effluent and recycle, based on operational

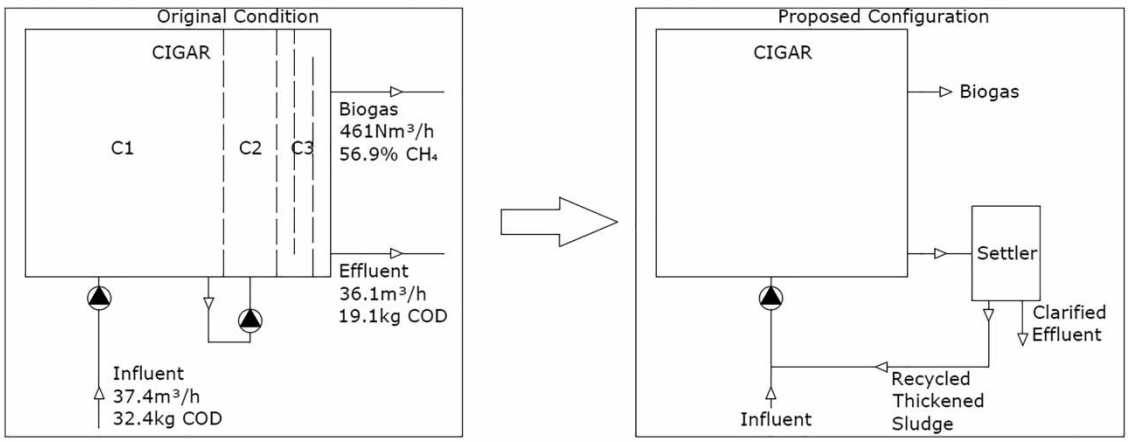

Figure 1 | CIGAR – original and proposed configurations.

Table 1 | Physico-chemical analyses, method, and frequency

Parameter	Method	Frequency
Temperature	APHA 2550	Continuously (online)
pH	APHA 4500	Continuously (online) for mixed influent, daily for other streams
COD concentration	APHA 5,220	Daily
Total solids (TS)	APHA 2,540B	Weekly
Total volatile solids (TVS)	APHA 2,540E	Weekly
Total suspended solids (TSS)	APHA 2,540D	Weekly
Volatile suspended solids (VSS)	APHA 2,540E	Daily
Volatile fatty acids (VFA)	APHA 5,560	Daily
Partial alkalinity	APHA 2,320	Daily
Total Kjeldahl nitrogen (TKN)	APHA 4,500	Biweekly
Total ammonia nitrogen (TAN)	APHA 4,500	Biweekly
Sulfate (SO_4^{-2})	Turbidimetric (APHA 9,038)	Randomly

data from Season_12, will be presented and discussed further on to justify possible optimisation of plant design.

Settler – preliminary test

In 2012, a small settler was connected to the CIGAR to evaluate effluent solids reduction. Its overall performance was an average retention of 53% volatile solids (VS) loaded and 54% COD loaded in a concentrated stream of thickened sludge, corresponding to 20% of settler inflow. Average VS of thickened sludge was 13,792 mg/L, 2.6 times higher than the VS of settler inflow (i.e., CIGAR effluent). Similarly, average COD of thickened sludge was equal to 39,430 mg/L, 2.7 times higher than the settler inflow COD.

Based on this preliminary test, using a settler to clarify the effluent from the CIGAR and return the thickened sludge back to the reactor, would increase the SRT and biomass concentration in the CIGAR. By doing so, it is expected higher methane yield, lower biomass production, and better effluent quality. Besides, we assume that a settler would be more efficient than C3, which was designed for the same purpose, simplifying reactor design, construction, and operation. This assumption is investigated in this paper by the inclusion of a settler and sludge recycle to ADM1 and will be discussed later. Figure 1 presents a schematic flow diagram for the original condition and proposed configuration, along with a simplified mass balance.

Modelling framework

The model under study, implemented in Aquasim 2.1G, combines two updates to the previous model described in Elaiuy *et al.* (2018): the sulfur chain reactions and the sludge retention and recycle. The first update evaluates the H_2S in biogas to better assess its concentration for suitable biogas cleaning process, where Season_12 data were used to calibrate and validate the model. The second update simulates the overall performance of the CIGAR with improved solids retention and possible design modifications, aiming at cost reduction and improved performance, where typical vinasse COD values were used for simulations with the previously validated model.

Sulfur chain extension in ADM1

Original ADM1 does not include the sulfur chain processes (Batstone *et al.* 2002b). To account to this chain of reactions, three species of sulfur reducing bacteria (SRB) were added to the model, propionate sulfate reducing bacteria (pSRB), acetate sulfate reducing bacteria (aSRB), and hydrogenotrophic sulfate reducing bacteria (hSRB), including their respective substrates uptake and decay processes.

A simplified extension including only hSRB would not consider volatile fatty acids (VFA) consumption by SRB, limiting the assessment of their impact on methane production (Batstone *et al.* 2006). On the other hand, included in the model extension, butyrate and valerate seemed unnecessary due to their low concentration in the AD of SV under study, adding unnecessary complexity to the model (Barrera *et al.* 2015).

Also, three acid/base dissociation process (H_2SO_4, HSO_4^- and H_2S) and H_2S gas transfer from liquid to gas phase process were added to the original ADM1.

SRBs considered consume, each one, all together with sulfate, hydrogen, propionate and acetate.

Reaction rates were considered as dual Monod kinetics, where rates are simultaneously dependent on two substrates concentration: hydrogen, propionate, and acetate for each one of the species considered and sulfate concentration for all SRB.

SRB kinetic and stoichiometric parameters were adopted from Barrera *et al.* (2015) and Solon (2015), respectively. The following reactions were added, as shown below.

$$C_2H_5COOH + 0.75H_2SO_4 \rightarrow CH_3COOH + CO_2 + H_2O + 0.75H_2S \quad (4)$$

$$CH_3COOH + H_2SO_4 \rightarrow 2CO_2 + 2H_2O + H_2S \quad (5)$$

$$4H_2 + H_2SO_4 \rightarrow H_2S + 4H_2O \quad (6)$$

Sulfide produced by sulfate reduction is found in the gas and liquid stream. In the liquid stream, it may be undissociated (H_2S) or dissociated (HS^-) in proportions defined by dissociation constant, Henry's Law constant and environmental conditions, including reactor pressure, temperature and pH. Acid-base equilibrium for both H_2S and H_2SO_4 were implemented as algebraic equations, with the two dissociations of H_2SO_4 included, as suggested by Knobel & Lewis (2002).

Sulfur was introduced to the model as an input variable, read according to available data for sulfate. The statistical mode was used when data for sulfate were rather sparse. By doing so, misled SO_4^{-2} values interpolated by Aquasim were avoided. H_2S transfer to gas phase was implemented similarly to other gases (CH_4, CO_2 and H_2), with gas constants from Sander (1999).

Inhibition by free H_2S was considered for hydrogen, acetate, butyrate, propionate, and valerate degrading organisms, as well as for all SRB. The formulation used was presented in Fedorovich *et al.* (2003) as a first order inhibition kinetics. For ease of calculation, only one constant for all bacterial groups affected by H_2S inhibition was used.

The model including sulfur consists of 25 biochemical process, 11 of them subject to one or more inhibition process, 9 the acid-base equilibrium process, and 4 the liquid-gas transfer physical process, implemented as differential and algebraical equations system in a completely stirred tank reactor composed of a liquid phase and a headspace.

Parameter estimation and model validation procedure. The model incorporating the sulfur chain processes includes the maximum substrate uptake rate (MSUR) and half saturation constant (HSC) of the three SRB groups considered.

Before parameter estimation, the model was tested with the same set of parameters that describes the SRB groups in Barrera *et al.* (2015) against dataset from Season_12. After visual inspection of results, as suggested by Donoso-Bravo *et al.* (2011), simulations for biogas and methane agreed well with measured data. However, deviations were noted between simulated and measured values for H_2S during the first 70 days and good correlation for the remaining days (data not shown). For this reason, from 220 days of operational data of Season_12, the first 70 days were discarded.

The remaining 150 days of Season_12 were split into two subsets, one for parameter estimation and the other one for cross validation.

The first subset of data, used for parameter estimation, ranged from day 70 to day 150. The initial 10 days (70–80) were used as a ramp and did not account to model error calculations. The second subset of data, used for cross validation, ranged from day 140 to day 220 and again, the first 10 days (140–150) used as a ramp were discarded for error calculations.

SRB constants (MSUR and HSC for acetate hydrogen, propionate, and sulfate) were estimated by Aquasim built-in function for parameter estimation. The function target was to minimise the difference between simulated and measured H_2S concentration in biogas.

With respect to model accuracy, the relative absolute error (rAE) was used to evaluate deviations between measured and simulated values.

rAE is calculated following the equation below:

$$\mathrm{rAE} = \frac{\sum_{i=1}^{n}\left(\frac{|y_{m,i} - y_i(p)|}{y_{m,i}}\right)}{n} \quad (7)$$

where $y_{m,i}$ is the i^{th} measured value, $y_i(p)$ is the model prediction at the time corresponding to data point i, which by its turn is a function of the set of parameters p to be estimated, and n is the number of observations.

For rAE results, we adopted the following classification from Batstone *et al.* (2002a), thereby qualifying the model quantitative predictions as high accuracy (rAE ± 10%) and medium accuracy (rAE 10–30%).

Sludge retention

Model inputs and description. Influent COD was set constant to 31.5 $kgCOD/m^3$, adopted from Elia Neto *et al.*

(2009) who have reported an average characterisation of vinasse from 20 ethanol mills across Brazil. The main idea behind setting this value from another author was to assume an average COD for Brazilian SV, in order to avoid specific mill-type influent and project a potential national biogas production.

Disintegration of particulate matter (originated from influent and decayed bacterial biomass) was considered as first order kinetics reaction, resulting in carbohydrates, proteins, lipids and inerts (soluble and particulate). Substrate was biochemically fractionated as 44% carbohydrates (f_{ch}), 30% proteins (f_{pr}), and 26% lipids (f_{li}), according to Elaiuy *et al.* (2018). Although particulate composites vary in time, fractions of carbohydrates, proteins, and lipids were assumed constant in the simulations. Besides, their hydrolysis constant was kept the same, $0.66\ d^{-1}$ for all three components.

The degradation extent (f_d) describing the degradable ThOD fraction of substrate converted to methane was set to 50% as estimated in Elaiuy *et al.* (2018). The kinetic parameters to model sulfate reduction process in the AD of SV were initially kept the same as in Barrera *et al.* (2015). Apart from these, stoichiometric and kinetic parameters were based on the work of Rosen & Jeppsson (2006). The charge balance of the influent was determined from measured values of influent pH, VFA concentration, inorganic nitrogen (calculated as TAN), and inorganic carbon (calculated through partial alkalinity measurements) (Elaiuy *et al.* 2018).

Settler and sludge recycle modelling. To simulate the inflow of sludge recycle from the settler back to the CIGAR an advective link with a bifurcation was implemented in Aquasim, as suggested in Reichert (1994). To model the settler, a variable (*recircX*) defining the solids retention efficiency was implemented in Aquasim and set constant to 43% (10% lower than the real capacity of the tested settler) to allow some uncertainty of model predictions. This variable multiplies each solids concentration in the CIGAR's effluent, calculating the solids mass flow rate driven to recycle stream. To simplify the implementation the advective link was set only to transport solids. With this modelling structure, there is no need to calculate actual SRT, which is difficult in in-ground anaerobic reactors, where sampling the sludge bed is not practical or accurate.

Proposed CIGAR set-ups. The 40% volume of the CIGAR occupied by C2 and C3 were responsible for only 21% of total biogas over Season_12. These percentages were calculated comparing COD removal between recycle and effluent streams.

This low performance may be due to inefficient biomass retention and to address this problem the following operational set-ups (Setup1, Setup2, Setup3) for the CIGAR were modelled considering the applicability in full-scale system. The optimisation study is based on Setup3.

Setup1. Chambers are lumped together as a single reactor;

Setup2. Chambers are lumped together as a single reactor and connected to an external settler;

Setup3. Volume of the single reactor is reduced by 50% and connected to an external settler.

Modelled scenarios. Setup1 and Setup2 were subject to six different scenarios (SC1 to SC6), each one at higher flow rate (Table 2). By doing so, we could verify the collapse of the reactor due to biomass washout by increasing the flow rate and assess the performance of Setup1 and Setup2. In each scenario, an initial flow rate ramp of 10 days was undertaken to gradually increase the biomass concentration as the flow increases in a dynamic equilibrium. Therefore, as soon as the flow rate becomes constant, the system will have reached a steady state condition. If the ramp is too steep, chances are the reactor will collapse because biomass growth rate does not follow the increased flow rate.

After the 10-day-ramp, each scenario had a constant flow over 210 days, resulting in a total of 220 days of CIGAR operation for each scenario (average operation period of sugarcane mills in Brazil).

Steady state simulations for methane yield, biogas flow and CH_4 were performed in all set-ups and scenarios. Therefore, variations in biogas production and its composition could be attributed to biomass retention effects and not to other variables.

Table 2 | Characteristics of modelled scenarios

Scenarios	Influent flow rate (after 10 days ramp) [m^3/d]	HRT [d]	Increase in influent flow rate compared to nominal value
SC1	948	15.2	0%
SC2	1,090	13.2	15%
SC3	1,232	11.7	30%
SC4	1,417	10.2	50%
SC5	1,514	9.5	60%
SC6	2,050	7.0	116%

RESULTS

CIGAR monitoring

Characteristics of influent, effluent, recycle streams, and biogas composition covering 220 days are shown in Table 3. The average of each dataset was calculated ± one standard deviation. The varying characteristics can be noted by the dispersion of datasets relative to their average, indicating dynamic behaviour of loading conditions. It is noteworthy that SV characteristics vary over Season_12, depending on production schedules of ethanol and sugar by the sugarcane mill.

Soluble and total COD values for recycle (C2) and effluent (C3), in Table 3, indicate that effluent total COD is 21% lower than recycle total COD, and effluent soluble COD is 11% lower than recycle soluble COD.

Total COD removal efficiency for recycle and effluent streams were 32% and 46%, respectively. Soluble COD removal efficiency for recycle and effluent streams were 65% and 69%, respectively, indicating high soluble COD removal efficiency for both streams.

Assuming that the difference between total and soluble COD is due to anaerobic biomass washout, we presume that increased solid retention using a settler could improve the CIGAR overall performance. A settler could replace C2 and C3 in a more efficient way, reducing by 40% the volume of the CIGAR, whilst improving its overall performance. Furthermore, both chambers add constructive complexity that affects CAPEX and OPEX due to extra pumps, valves, pipes and HDPE baffles.

Table 3 | Characteristics of influent, effluent, recycle streams, and biogas composition during entire season_12

	Minimum	Average	Standard deviation	Maximum
Influent total COD (kg/m^3)	4.30	30.05	10.64	71.61
Effluent total COD (kg/m^3)	2.51	16.17	9.87	52.46
Effluent VSS (kg/m^3)	0.40	4.58	3.52	16.70
Effluent soluble COD (kg/m^3)	0.84	9.36	7.54	33.61
Recycle total COD (kg/m^3)	2.39	20.55	10.04	52.88
Recycle VSS (kg/m^3)	0.40	6.44	4.53	20.90
Recycle soluble COD (kg/m^3)	0.56	10.55	7.00	28.02
Influent (g SO_4^{-2} /m^3)	250	1,357	579	2,750
Influent SO_4^{-2}: COD	0.01	0.05	0.03	0.18
H_2S (ppm)	7,500	14,856	3,889	30,000
CH_4 (%)	31.5	57.2	6.5	77.5

Sulfur chain modelling

Direct and cross validation

The kinetic parameters to model sulfate reduction process in the AD of SV (Table 4) were estimated against the first aforementioned dataset. The results of estimated parameters are mostly similar to Barrera *et al.* (2015), except for Km_aSRB, Ks_aSRB, Km_pSRB, and Ks_pSRB. A primary driver for these differences is the SO_4^{-2}:COD ratio. Whilst this ratio averaged 0.0502 in this work, a higher ratio was found in Barrera *et al.* (2015). There was competition for acetate between SRB and methanogens as long as inhibition related to COD:SO_4 ratio was not severe (COD:SO_4 < 0.1) (Barrera *et al.* 2013). The uptake of acetate and neglected propionate by methanogens reflected in lower Km_aSRB and higher Ks_aSRB. Nonetheless, Ks_SO_4_aSRB, Ks_SO_4_hSRB, and Ks_SO_4_pSRB, which are needed to predict S_{SO4}, are similar to parameters from Barrera *et al.* (2015).

Since other parameters used in the present model were calibrated in previous work for AD of SV, only MSUR and HSC of SRB were selected for calibration.

The simulations shown in Figure 2(a) are split into direct and cross validation of the model for H_2S and there is a good fit between simulated and measured values on both sides. The quality of prediction was sensitive to a few kinetic parameters: Km_aSRB, Ks_aSRB, Km_pSRB, and Ks_pSRB. Notwithstanding, direct validation shows higher quality of prediction (rAE 13.3%) than cross validation (rAE 17.4%), both are in the range of medium (10–30%) accurate quantitative prediction. The same quality of prediction for H_2S was found in Barrera *et al.* (2015). Furthermore, given the scale and the uncontrolled environment of this work, rAE for both direct and cross validations can be considered satisfactory when compared to other studies, which reported similar rAE under laboratory conditions.

Simulated H_2S concentration in biogas ranged from 0.94% to 2.01% and is close to ranges found in the literature using SV. For example, 1.5–3.0%, was reported in Cortes Pires *et al.* (2015); Leme & Seabra (2017); Nandy *et al.* (2002); Yasar *et al.* (2015) and 1.25–1.75% in Barrera *et al.* (2015).

Despite the variability in the influent composition over Season_12, the simulation is consistent after parameter estimation (Figure 2(a)). However, the quality of prediction was less accurate in the cross validation but yet classified as medium accuracy.

Most of H_2S was overestimated by the model. 55% and 62% of simulated values were higher than measured values for direct and cross validation, respectively.

Table 4 | Comparison of kinetic parameters reported in Barrera *et al.* (2015) and estimated in this work

Parameter	Description	Barrera *et al.* (2015)	Estimated in this work
Km_aSRB	MSUR[a] for acetate SRB	18.5	4.47
Km_hSRB	MSUR[a] for hydrogen SRB	63	65.0
Km_pSRB	MSUR[a] for propionate SRB	23	30.0
Ks_aSRB	Acetate HSC[b] for acetate SRB	0.120	0.0201
Ks_hSRB	Hydrogen HSC[b] for hydrogen SRB	6E-06	5.41E-06
Ks_pSRB	Propionate HSC[b] for propionate SRB	0.110	0.0160
Ks_SO_4_aSRB	Sulfate HSC[b] for acetate SRB	0.001	0.00100
Ks_SO_4_hSRB	Sulfate HSC[b] for hydrogen SRB	0.00105	0.00105
Ks_SO_4_pSRB	Sulfate HSC[b] for propionate SRB	0.002	0.00200

[a]Maximum substrate uptake rate.
[b]Half saturation constant.

Also, 57% and 46% of simulated values had errors within +/−10% for direct and cross validation, respectively. However, if we consider the season average H_2S content in biogas the difference between measured and simulated values was 3.08% for the first subset and 8.91% for the second subset.

The rAE for biogas flow in the direct validation of this work was 12.7% (Figure 2(b)), smaller than in Elaiuy *et al.* (2018), possibly because of free H_2S inhibition to microorganisms, which was the highest among all inhibitions (data not shown).

Similar quality of predictions for biogas flow were presented in Dereli (2019), simulating a full-scale anaerobic reactor.

The same rAE of 6.1% for CH_4 was found in the direct and cross validation, which can be visually confirmed by small deviation between simulated and measured outputs of CH_4 in both sides of Figure 2(c). Nevertheless, this rAE is higher than the rAE found in Elaiuy *et al.* (2018), possibly because of the use of methane precursors in the H_2S production instead of CH_4 production.

Additionally, compared calculated averages for days 80–220 of simulated and measured biogas flow and CH_4 show differences of −4.9% and −2.3%, respectively.

Sludge recycle – modelled scenarios

Simulation results of Setup1 and Setup2 for biogas flow, methane content, and methane yield are illustrated in Table 5. Comparing results, it was found that Setup2 had better performance than Setup1 in all simulated scenarios.

Maximum influent flow rate for SC5 and SC6 were respectively 60% and 116% higher than the nominal reactor design flow rate, meaning above that, imminent biomass washout and reactor collapse. The maximum influent flow rate for Setup2 was higher than for Setup1 before reactor collapse. This is attributed to better biomass retention in Setup2, since it is 52% higher than in Setup1 regarding SC1 (data not shown). We assume that the influent flow rate could be even higher as long as the settler has an improved performance.

It is important to highlight that for Setup1 and Setup2 the stepwise increasing flow rate in each SC, results in a reduction in HRT followed by lower methane yield (Figure 3(a)) and methane content (Figure 3(b)). Nevertheless, these reductions were smaller for Setup2 than for Setup1.

Simulated methane yield of 0.193 Nm^3CH_4/kgCOD for Setup1 was similar to 0.196 Nm^3CH_4/kgCOD measured in 2012. These figures are smaller than CIGAR projected methane yield of 0.227 Nm^3CH_4/kgCOD. However, the amount of methane recovered per kilogram of COD removed is more realistic in the simulations since we adopted 50% of COD removal compared to nominal CIGAR design of 65%.

Average methane yield of 0.225 Nm^3CH_4/kgCOD for large-scale projects has been reported in Silva Neto *et al.* (2019). Another possible explanation to this discrepancy may be attributed to either higher degradation of substrates or superior SRT. To verify the latter, we simulated a settler with 80% solids retention efficiency and CIGAR influent flow rate of 948 m^3/d, resulting in a methane yield of 0.221 Nm^3CH_4/kgCOD. This result is 6% higher than simulations where the settler was set to 43% of solids retention efficiency and only 4% lower than average methane yield reported in the literature.

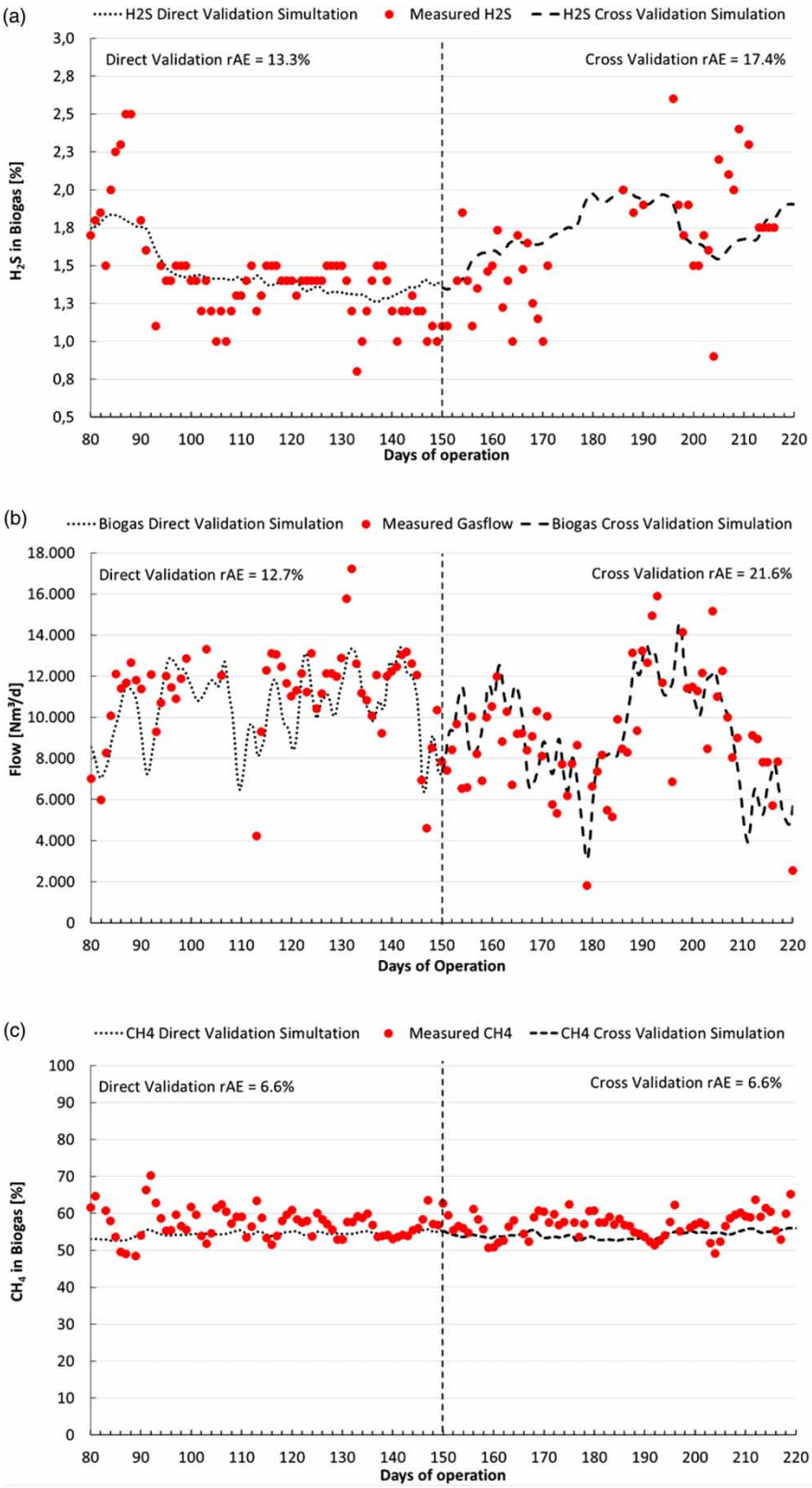

Figure 2 | rAE of measured and simulated (a) H_2S, (b) biogas flow and (c) CH_4 – direct and cross validation.

Table 5 | Results of biogas flow, methane content, and methane yield from different scenarios and set-ups under study

	Setup1 (Without settler)			Setup2 (With settler)			Comparison Setup2 × Setup1		
Scenario	Biogas flow [Nm^3/d]	Methane content [%]	Methane yield [$Nm^3CH_4/kgCOD$]	Biogas flow [Nm^3/d]	Methane content [%]	Methane yield [$Nm^3CH_4/kgCOD$]	Biogas flow	Methane content	Methane yield
SC1	9,858	56.8	0.193	10,593	57.2	0.208	7.5%	0.7%	7.5%
SC2	11,125	56.7	0.190	11,951	57.2	0.205	7.4%	0.8%	8.0%
SC3	12,411	56.6	0.186	13,471	57.1	0.203	8.5%	1.0%	8.8%
SC4	14,047	56.3	0.181	15,287	57.0	0.200	8.8%	1.4%	10.4%
SC5	14,611	56.0	0.178	15,983	57.0	0.198	9.4%	1.8%	11.6%
SC6	Collapse			20,958	56.6	0.189	N/A		

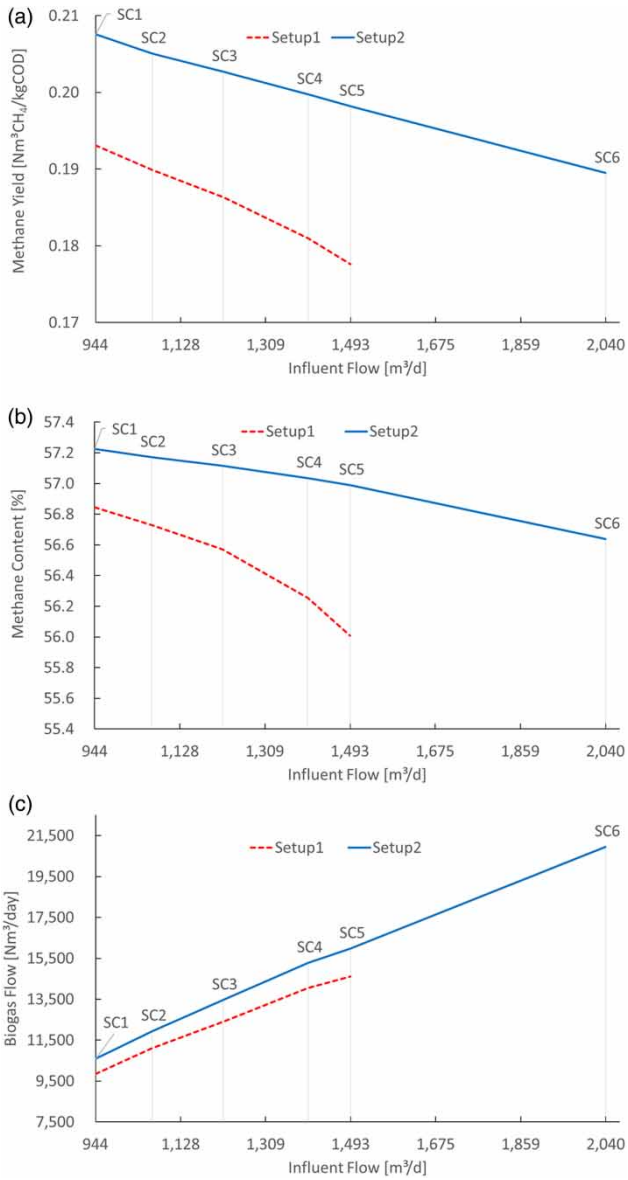

Figure 3 | (a) Methane yield, (b) methane content, (c) biogas flow for modelled scenarios and setups.

The biogas flow was higher for Setup2 than for Setup1 (Figure 3(c)) as a result of increased biomass concentration, thus lower food to microorganism ratio (F/M).

The OLR was 4.5 $kgCOD/m^3/d$ for SC6 and 3.3 $kgCOD/m^3/d$ for SC5, which are close to values found in Wilkie *et al.* (2000), ranging between 4.6 and 5 $kgCOD/m^3/d$ for ACP digesting sugarcane vinasse. Also, OLRs for SC5 and SC6 were higher than the nominal CIGAR design and Season_12 measured values of 1.99 $kgCOD/m^3/d$ and 2.06 $kgO_2/m^3/d$, respectively.

CIGAR economics – Setup3 analysis

A comparative analysis between Setup1 and Setup3 after simulations is presented in Table 6. The reactor for Setup3 is 50% smaller than Setup1, and yet it was able to produce 83% more methane per cubic meter of reactor at half of HRT of Setup1. However, the methane yield and total biogas flow rate dropped by 7.8% and 8.3%, respectively. Notwithstanding, Setup3 has higher biogas production per volume of reactor, it is not possible to achieve the same biogas production as in Setup1. Even though the OLR is higher for Setup 3, the methane yield is smaller.

By reducing the size of the CIGAR and simplifying its design, as shown in Setup 3, it will have an impact on CAPEX planned. Since the majority of capital expenditures occur upfront in the construction stage, costs allocated to land, material, and equipped facilities, for example, will be significantly reduced. OPEX will follow the same trend, including, for example, electricity consumption, staffing, and general overhead. In summary, the optimised CIGAR is a proposed solution that minimises capital and operational expenditures. This involves redesigning not only the reactor but its operation.

Whilst there is certainly scope for potential CAPEX and OPEX savings given the size and complexity reductions, in

Table 6 | Summarised comparison between original (Setup1) and optimised reactor (Setup3)

Parameter	Unit	Original reactor (Setup1)	Optimised reactor (Setup3)	Comparison optimised x original
HRT	[d]	15.2	7.6	−50%
Biogas flow rate	[Nm^3/d]	10,593	9,781	−8.30%
Methane content	[%]	57.2	56.8	−0.70%
Methane yield	[Nm^3CH_4/kgCOD]	0.208	0.191	−7.80%
Methane production	[Nm^3CH_4/m^3reactor]	0.421	0.771	83%
Total volume earthworks	[m^3]	20,304 m^3	10,867 m^3	−46%
HDPE liner/cover area	[m^2]	10,204 m^2	5,109 m^2	−50%
Total pipework	[m]	757 m	345 m	−54%
Pumping system		4 pumps, 2 flow meters, 4 VSD[a]	2 pumps, 1 flow meter, 2 VSDs	−50%

[a]VSD = Variable Speed Driver.

this work we did not take into account expenditures involving the settler.

CONCLUSIONS

Vinasse is a high COD, high sulfate, low pH, seasonally produced wastewater and biogas production from it should be done with special attention in planning, design and operation.

A practical demonstration of ADM1 to industrial application is presented here to identify the potential optimisation and behaviour of a large-scale anaerobic reactor processing SV, reducing, consequently, expenditure, risk, and time.

The modelled higher SRT optimised reactor showed higher biogas production and methane per volume of reactor, followed by a reduced HRT from 15 to 7 days.

By adding an external settler with sludge return substantial savings in materials and services associated with a lagoon-type digestor construction and operation costs can be obtained. Moreover, methane yield, methane concentration and biogas production can be higher when SRT is higher.

The predictions of H_2S levels in biogas by ADM1, based on sulfate and COD content, is a useful tool to assess biogas composition, especially for projects where the gas is not yet under production, but wastewater composition is available.

The quality of predictions of the model allows practitioners and designers of vinasse-to-energy projects to anticipate with reasonable accuracy the H_2S levels in biogas and plan ahead appropriate biogas downstream processing and technology to convert biogas into clean renewable bioenergy. The H_2S model presented small differences between the averages of modelled results and large-scale reactor measured data. The model can be qualified as medium accuracy based on rAE, although the majority of calculated values were within a +/− 10% error range. The model also improves the accuracy in prediction of energetic value of biogas by reducing errors in biogas flow and CH_4 content compared to previous models.

Electricity or fuel (as biomethane) produced from vinasse biogas are not the subject of any premium price or incentives, and treatment of sugarcane vinasse is not compulsory for mills in Brazil. Upon these circumstances, the actual scenario of vinasse-to-biogas projects will only be profitable if special attention is given to mathematical models such as ADM1 for evaluation, optimisation, and design of existing and planned biogas plants.

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