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Development and application in Aspen Plus of a process simulation model for the anaerobic digestion of vinasses in UASB reactors: Hydrodynamics and biochemical reactions

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ABSTRACT

UASB reactors are accepted as a suitable technology for biogas production from the anaerobic digestion of vinasse. To describe correctly the behavior of this type of reactors the hydrodynamics as well as the biochemical processes inside the reactor should be considered simultaneously. This represents a complex task during experiments or in full-scale operation. Yet, the better understanding and description of UASB reactors operation would be greatly improved thanks to process simulation tools, saving time and money. In this regard, the aim of this study was to develop a novel simulation model in Aspen Plus® for UASB reactors treating vinasses. The model integrated ADM1– Flow pattern – Biofilms characteristics and the sulfate reduction process. Simulation results from laboratory, pilot and industrial scales showed differences lower than ± 15% respect to the real data. Based on the sulfate reduction process an increment in biogas production of 14% for a SO_4^{2-}/COD ratio of 0.05 was obtained. In agreement with experimental data, the model predicted a reduction of 5% in methane yield and the reactor failure for SO_4^{2-}/COD ratio from 0.07 to 0.1 and higher than 0.1 respectively. Sensitivity analysis based on granule size showed an increment of 16% in biogas generation when the granule diameter was reduced from 4 mm to 1 mm. The hydrodynamic parameters (i.e. Peclet number, dispersion coefficient) evaluated by the model, demonstrated the existence of a non-ideal flow in the reactor.

1. Introduction

Nowadays, the growing development in science and technology has driven a faster advance in the process industries. In this context, the increase in raw materials and energy consumption as well as pollutants generation is a challenge that must be faced not only by researchers but also by policy makers. One way to mitigate this situation is the exploitation of energy sources that are environmentally friendly like renewables (e.g., biogas production from organic wastes) [1]. Anaerobic digestion (AD) is one of the main renewable technologies which is based on the biological treatment of organic wastes in the absence of oxygen [2]. AD is a well– established process for treatment and recycling of biodegradable residues [3] at the time that an energy-rich gas (biogas) is produced. This biogas can be used for several purposes such as cooking, heating, vehicle fuel (if upgraded) and electricity production. In Cuba, only 4% of the total electricity generated is based on renewable sources [4], mainly from the sugar – ethanol industry (~3.35%) due to bagasse combustion, remaining several other wastes streams and technologies still unexploited. The Cuban government has the commitment to promote policies that allow increasing the contribution of the sugar – ethanol industry in the energy matrix through the expansion of renewable energy sources [5].

One of the waste streams still unexploited in Cuba is vinasse. Vinasse, is an acid liquid waste (pH between 3–5) resulting from the distillation of ethanol whether from sugarcane juice or molasses. It is characterized by its high organic matter concentration (30–95 kg_{COD}/

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Nomenclature

Abbreviations

ADM1	Anaerobic Digestion Model No. 1
COD	Chemical oxygen demand
UASB	Up-flow anaerobic sludge blanket
AD	Anaerobic digestion
HRT	Hydraulic retention time
PSM	Process simulation model
SRB	Sulfate reduction bacteria
MPB	Methane production bacteria
VSS	Volatile suspended solids

Variables

Pe	Peclet number (dimensionless)
d	Dispersion number (dimensionless)
u	Up-flow velocity (m/h)
H	Reactor height (m)
R	Granule radius (m)
z	Axial coordinate (m)
D_m	Dispersion coefficient (m^2/h)
I_{NH3}	Ammonia inhibition function (dimensionless)
I_{pH}	pH inhibition function (dimensionless)
I_{H2}	Hydrogen inhibition function (dimensionless)
pH_{LL}	Lower pH limit for pH inhibition (dimensionless)
pH_{UL}	Upper pH limits for pH inhibition (dimensionless)
Kg	Reaction rate in the granule (1/d)
km	Mass transfer coefficient of substrate (m/h)
Da	Diffusivity coefficient in the granules (m^2/h)
k	Reaction rate in the bulk liquid (1/d)
Y	Yield of biomass on the substrate (kg_{VSS} / kg_{COD_Si})
Ks	Half saturation value (10^{-3} kg_{COD}/m^3)
K_{SO4}	Half saturation value for sulfates (10^{-3} kmol/m^3)
K_I	Inhibition coefficient by undissociated H_2S (10^{-3} kmol/m^3)

Greek letters

ϕ_p	Volume fraction occupied by the granules in the reactor (%)
ρ_p	Density of the granules (kg/m^3)
μ_{max}	Maximum specific growth rate of microorganisms (1/d)

m^3) [6,7] and sulfate content (1.5–3.46 $kgSO_4^{2-}/m^3$) [7,8]. In Cuba, more than 60% of the produced vinasse is directly applied on the sugarcane fields [9], which in long term has proved to have a negative impacts for the soil due to salinization [10,11]. The high organic content of vinasses makes it a suitable substrate for AD. During the AD of vinasses a significant fraction of the influent COD is converted into biogas, while the recovered digestate can be used as fertilizer for mineral replacing in the sugarcane fields. Hence, AD has been widely accepted as a promising and feasible treatment for vinasses [2,12].

A typical Cuban distillery can produce 50 $m^3_{ethanol}$ daily and generates up to 15 $m^3_{vinasse}$/ $m^3_{ethanol}$ [9]. Assuming a biogas yield of 10 $m^3_{biogas}/m^3_{vinasse}$ [13] with a low heating value (based on 60%–65% of methane) of ~22 MJ/Nm^3_{biogas} [14] it is possible to produce ~16 GW h per year in one distillery. Currently, there are 16 distilleries operating in Cuba, which makes a theoretical estimation of 256 GW h per year. This value represents 37% of the energy produced in 2016 in the sugar – ethanol sector by bagasse combustion.

The production of biogas by anaerobic degradation is a very complex microbiological process that involves several types of biochemical reactions and depends on several operational factors, such as temperature, organic loading rate, feeding procedure, mixing, retention time, type of substrates, pH, reactor configuration, etc. Laboratory experiments are important references for validation, yet they incur long time delays in the design phase and for decision makers to push towards the final large scale application [15]. However, these issues can be improved by the benefits of using process simulation. In fact, the development of process analysis tools can help to carry out predictions and optimization in less time and less cost than in laboratory or full scale [16,17].

For the study of AD, Anaerobic Digestion Model No. 1 (ADM1) is widely applied and it is considered the most comprehensive model for AD description [18]. The model includes a reaction system, which is divided into: (*i*) biochemical reactions and (*ii*) physico – chemical reactions (i.e., equilibrium and gas – liquid transfer) and takes into account different types of inhibitions. Regarding the reactor configuration, the model was first applied to a continuous stirred tank reactor (CSTR) in steady – state, which is the simplest flow pattern for reactors modeling [14,18].

Nevertheless, the AD of vinasses is usually carried out in up-flow anaerobic sludge blanket (UASB) reactors [12], where the flow pattern does not follow a perfect mixing [19–21]. In UASB reactors (biofilm reactors) substrate conversion depends on the mass of biofilm and its growth as well as the substrate concentration in the bulk liquid [22]. In high-strength sulfate-rich wastewaters, like Cuban vinasses, sulfate reducing bacteria can growth and produce considerable amounts of H_2S [2]. The presence of H_2S in the biogas can cause operational problems (e.g. corrosion, SO_x pollution) when it is used as fuel. In this regard, the application of AD models to UASB reactors treating vinasse must include sulfate reduction process in order to estimate H_2S formation [2]. In this way, it is possible to determine whether- or not- biogas meets the quality standards for further technological applications. Previous works have extended the ADM1 model by considering sulfate reduction during the AD of Cuban vinasses in UASB reactors [2,23].

The condition of biomass granules in suspension into the liquid phase depends on the flow pattern inside the reactor. Thus, the task of modeling UASB reactors should be decoupled in two parts: the flow model and the reactions model [19,24,25]. The hydrodynamics behavior of UASB reactors has been widely studied in the literature [20,24,26,27]. Some papers refer to describe the flow pattern as a disperse model [21,28,29] while others refer to a combination of multiple CSTRs [27]. However, very little attention has been dedicated to consider, simultaneously, the behavior of UASB reactor using an ADM1 – based dispersed model and the biofilm development [19,29,30].

Based on the generalized approach of ADM1 it is possible to extend some of its features to biofilms reactors with non-ideal flow pattern. For this, the physico – chemical processes as well as ADM1 kinetic rates should be integrated in the biofilm reaction model including transport and mass transfer. In a study performed by Chen et al. [19] an integrated ADM1 – based dispersed model was developed for UASB reactor considering the flow pattern and the bio – kinetics by mathematical consideration using MATLAB. Odriozola et al. [30] developed a more general model for a UASB reactor which simultaneously considered the reactor performance and the biofilm growth. The model coupled the ADM1 model and the hydrodynamic pattern inside the reactor.

Aspen Engineering® is one of the most powerful frameworks for process simulation, design, optimization, sensitivity and economic analyses that allows great flexibility compared with other process simulator. Despite these advantages, the development of process simulation models for the AD in Aspen environment is still little studied [16,17,31]. For example, Rajendran et al. [16] and Al-Rubaye et al.

[17] developed a process simulation model using Aspen Plus by considering the model in two-stage. The hydrolysis stage was first simulated considering a stoichiometric reactor in which conversion was assumed according to each substrate while the other phases (i.e., acidogenesis, acetogenesis and methanogenesis) were conducted in CSTR model for kinetic rate calculations. Based on Buswell equation Nguyen et al. [32] developed a simple model for the AD stage by using a stoichiometric reactor. The resulting biogas stream was introduced in a power cycle to estimate the energy potential. In none of the previous models sulfate reduction reactions for sulfate-rich liquid wastewater were considered.

In this regard, the present study aims to develop a process simulation model using Aspen Plus for the AD of vinasses in UASB reactor by integrating ADM1– Flow pattern – Biofilms characteristics with the inclusion of sulfate reduction reactions. At the best of our knowledge, the integration of ADM1 – Flow pattern- Biofilms features for the simulation of the AD of vinasses using Aspen Plus has not yet been reported. This will be a useful tool for the correct design and optimization of AD in the context of the sugarcane industry. This paper first introduces in more detail the most common methods for modeling and simulation of AD. Later the methodology followed to obtain an integrated UASB simulation model for vinasse treatment is presented and finally, the obtained results are discussed.

2. Model description

2.1. UASB flow model

As was mentioned above, all the process simulation models developed so far in Aspen Plus for AD have considered completely mixed flow pattern (CSTR) [16,17,33]. However, vinasse is usually treated in UASB reactors instead of CSTR [7], being necessary to include the hydraulic features of these reactors in the model. In this section, the implementation of the flow model in Aspen Plus® v9.0 for an UASB reactor is presented.

There are different approaches to consider flow pattern in UASB reactors. A general approach is considering ideal flow pattern (i.e., plug flow, CSTR) for each reactor zone [25]. On the other hand, the hydraulic performance of UASB reactors could be considered as intermediate between these two ideal patterns [20]. When the degree of mixing is between the ideal patterns of plug flow and perfect mixed, a dispersed flow is obtained in the reactor. Most of the reactors operate at dispersed flow conditions [34]. Moreover, several authors have applied dispersion models to describe UASB hydraulic performance [19,21,31].

In the present process simulation model, only the sludge bed and the blanket are considered, being the model composed by two compartments in series. The first one (i.e., sludge bed) is assumed as a CSTR [35] meanwhile in the second compartment (i.e., blanket) an axial dispersion model is considered for soluble components [19]. The implementation of the axial dispersion in Aspen Plus was carried out via a FORTRAN subroutine. For this, the Peclet number was the parameter took into account for the evaluation of the hydrodynamic behavior in the blanket zone. The Peclet number was calculated according to Eq. (1):

$$Pe = \frac{u * H}{D_m} \quad (1)$$

where Pe is the Peclet number (dimensionless), u is the up-flow velocity (m/h), H the reactor height (m) and D_m is the dispersion coefficient (m^2/h).

The value of D_m is determined from Eq. (2) as a function of the axial coordinate to height ratio as well as the up-flow velocity (u) [26].

$$D_m = 1.03u^{1.11} * 0.009^{\frac{z}{H}} \quad (2)$$

where z is the axial coordinate (m), the rest of the variables are the same as in Eq. (1).

2.2. UASB biochemical reaction model

As mentioned in Section 2.1, the reaction model considers two well-defined zones: the sludge bed and the blanket. Sludge bed in the UASB reactor is composed of anaerobic granules while the blanket consists only of soluble compounds. For the blanket zone only the methanogenic step was considered. Reactions in this case were assumed as those previously proposed by Rajendran et al. [16] in their process simulation model (PSM). For the sludge bed, like in the PSM, the hydrolysis step was set as a system of 13 stoichiometric reactions based on conversion rates. The kinetic constants of the reactions in the next steps of the AD (i.e., acidogenesis, acetogenesis and methanogenesis) were obtained from previous studies [3,18]. The reaction kinetics were calculated in different calculator blocks using FORTRAN subroutines for each step. The stoichiometric reactions in each step could be consulted in [16].

The inhibition effect (i.e., ammonia inhibition (I_{NH3}), pH inhibition (I_{pH}) and hydrogen inhibition (I_{H2})) was considered in each calculator block where the inhibitions constants were taken from Angelidaki et al. [3]. Low pH inhibition (pH_{LL}) was considered for the acidogenic and acetogenic phases meanwhile low and high pH inhibition (pH_{UL}) was considered for the methanogenic step. Values for pH_{LL} and pH_{UL} were set to 6 and 8.5 respectively [3].

The stoichiometry for sulfate reduction bacteria (SRB) reactions included in the model are shown in Eqs. (3–5). Values for kinetic rates calculations as well as inhibition effects were taken from Barrera et al. [2].The reaction rates for Eqs. (3–5) were determined by a FORTRAN subroutine in a calculator block. Table 1 shows the kinetic parameters considered in the sulfate reduction calculator.

- Propionate SRB (p-SRB)

$$C_2H_5COOH + 0.75\ H_2SO_4 \rightarrow CH_3COOH + CO_2 + H_2O + 0.75\ H_2S \quad (3)$$

- Acetate SRB (a-SRB)

$$CH_3COOH + H_2SO_4 \rightarrow 2CO_2 + 2H_2O + H_2S \quad (4)$$

- Hydrogenotrophic SRB (h-SRB)

$$4H_2 + H_2SO_4 \rightarrow H_2S + 4H_2O \quad (5)$$

In the sludge bed several assumptions and simplifications were made for the proposed model: (*i*) granules are perfect spherical shells with a constant radius (R); (*ii*) degradation of substrate was described by Monod kinetics; (*iii*) the granule bed was described as a CSTR (substrate concentration in the liquid volume of the bed is constant); (*iv*) the UASB reactor was operated at steady state conditions [22,24,25].

The reaction rates in the granules are different (lower) from those calculated from the PSM, in which granules were not considered. In the

Table 1
Kinetic parameters considered in the sulfate reduction calculators.

Kinetic parameters	Sulfate reduction reactions [a]		
	p-SRB	a-SRB	h-SRB
μ_{max} [1/d]	0.290	0.243	0.977
km [kg_{COD_Si} / kg_{VSS} / d]	9.60	4.19	26.7
Ks [10^{-3} kg_{COD} /m^3]	15.0	25.0	0.100
K_{SO4} [10^{-3} kmol / m^3]	0.190	0.20	0.104
Y [kg_{VSS} / kg_{COD_Si}]	0.0300	0.0360	0.0366
K_I [10^{-3} kmol / m^3]	6.80	18.8	7.80

SRB: sulfate reduction bacteria.
p-SRB: propionate SRB.
a-SRB: acetate SRB.
h-SRB: hydrogenotrophic SRB.
[a] Barrera et al. [2].

present model the reaction rates in the granules are calculated for acidogenic, acetogenic, methanogenic and sulfate reduction steps according to Eq. (6) [36]:

$$Kg = f(k_m,\ \varphi_p,\ D_a,\ R,\ k,\ \rho_p) \tag{6}$$

where Kg is the reaction rate in the granules (1/d), k_m is the mass transfer coefficient of substrate (m/h), φ_p is the volume fraction occupied by the granules (%), D_a is the diffusivity coefficient in the granule (m^2/h), R is the radius of the granules (m), k is the reaction rate in the bulk liquid (1/d), ρ_p is the density of the granules (kg/m^3).

2.3. Integration of UASB flow and reaction models

The integration of the proposed models presented in sections 2.1 and 2.2 allows evaluating the effect of the hydrodynamic behavior on the reaction performance. In this study, the solution proposed by Danckwerts [37] (Eqs. (7)–(9)) in terms of the non-dimensional concentration (F) as a function of the axial coordinate to height ratio (ξ) was applied. Finally, the conversion (X) can be calculated from the evaluation of (1-F) or directly from Eq. (10). All the terms in Eqs. (7–10) are the same defined in sections 2.1 and 2.2.

$$\xi = {}^{z}/_{H} \tag{7}$$

$$\beta = \left(1 + \frac{4 * k * H}{u * P_e}\right)^{1/2} \tag{8}$$

$$F(\xi) = exp^{\left(\frac{P_e}{2}*\xi\right)} * \left\{ \frac{2(1+\beta)* exp^{\left[\frac{P_e*\beta}{2}*(1-\xi)\right]} - 2(1-\beta)* exp^{\left[\frac{P_e*\beta}{2}*(\xi-1)\right]}}{(1+\beta)^{2}* exp^{\left(\frac{P_e}{2}\beta\right)} - (1-\beta)^{2}* exp^{\left(\frac{-P_e}{2}\beta\right)}} \right\} \tag{9}$$

$$X(1) = 1 - \frac{4\beta}{(1+\beta)^{2}* exp^{\left[-\frac{P_e}{2}*(1-\beta)\right]} - (1-\beta)^{2}* exp^{\left[-\frac{P_e}{2}*(1+\beta)\right]}} \tag{10}$$

2.4. Model implementation

The first step for the model implementation in Aspen Plus® v9.0 is the definition of the components and the determination of the physical properties. As presented by Rajendra et al., cellulose, hemicellulose and dextrose were added as carbohydrates. Proteins were classified as soluble and insoluble. Lipids comprised of tripalmate, triolein, and palmito-olein can be entered in the model [16]. Missing properties for complex compounds were obtained from Wooley and Putsche [38].

The COD of the vinasse stream was obtained by using Aspen Property Sets (i.e., CODMX). In all cases, the composition of the carbohydrates, proteins and lipids was adjusted to fit the values of COD and density of the reactor feed. The thermodynamic property method chosen was the Non-Random Two-Liquid (NRTL) as the most recommended method for system in liquid phase. This allows the calculations in gas – liquid systems, like biogas production based on activity coefficients and mole fractions [33,39].

Fig. 1 shows the flowsheet for the process simulation model of UASB reactor treating vinasse. For building the simulation flowsheet the reactor models from the Model Palette in Aspen are selected. The stoichiometric reactor model (HYDROLYS) was used for the hydrolysis

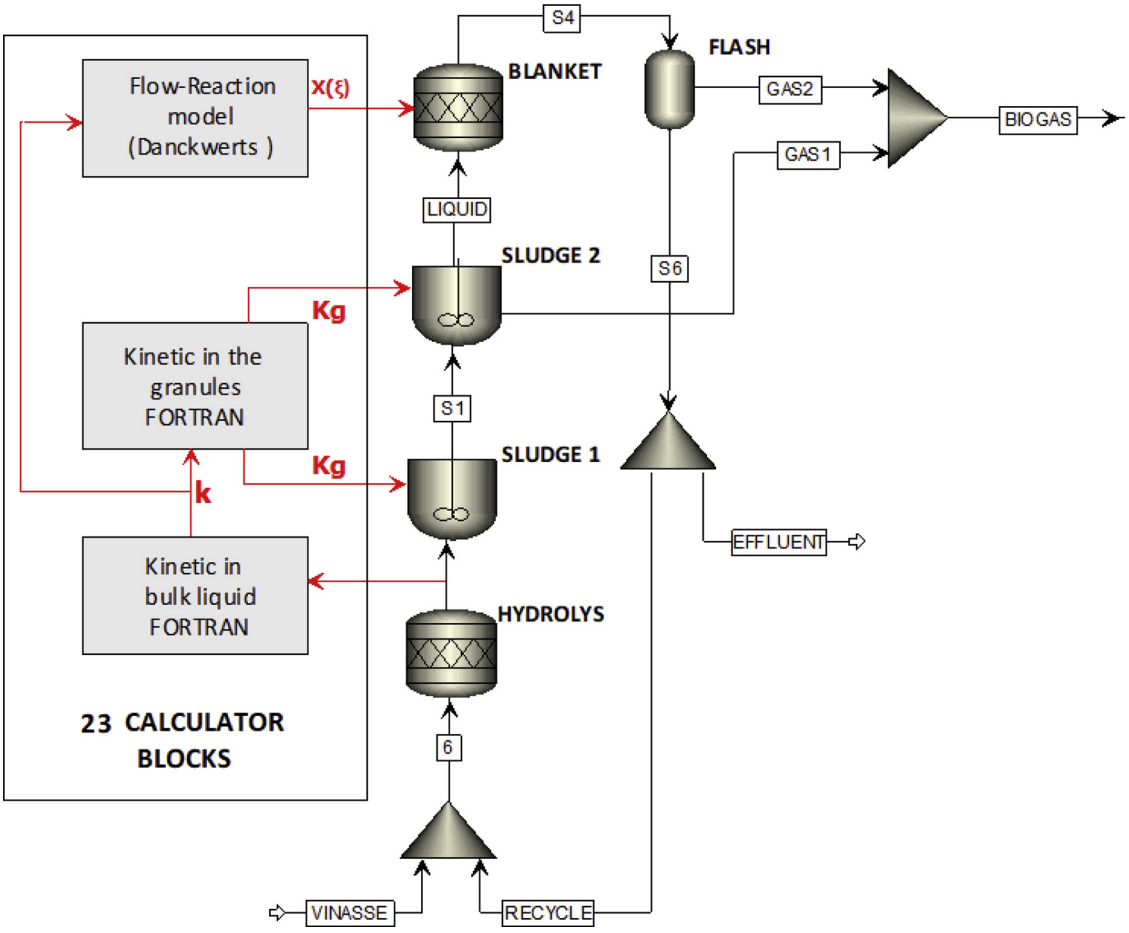

Fig. 1. Flowsheet of the UASB simulation model.

stage [16] and the methanogenic reactions in the blanket (BLANKET). On the other hand, the continuous stirred tank reactor (CSTR) was employed for the sludge bed simulation (SLUDGE 1 and 2). A FLASH model for the gas – liquid separation followed by a Splitter to obtain the dry biogas were used. Operational conditions such as temperature, stream compositions, pressure, residence time, up-flow velocity, and granules radius were fixed depending on the case under study (see Table 2).

In Fig. 1, from the products released in the hydrolysis stage, different calculator blocks are activated depending on the monomers present in the system. For each calculator block the reaction rates in bulk liquid (k) are recalculated and exported to each set of reactions (amino acid degradation, acidogenesis, acetogenesis and methanogenesis) [16]. Additionally, a reaction set for sulfate reduction is included as well. The k values are used for the next group of calculator blocks to estimate the kinetic rate in the granules (K_g). Once the kinetic parameters are updated for each set of reactions, this information is used in both CSTR reactors to calculate the biogas production in the sludge bed. To improve the convergence of the model, due to the inclusion of sulfate reduction in the SLUDGE 1 reactor only amino acid degradation was considered. The rest of the reaction sets take place in the SLUDGE 2 reactor.

The liquid output from the SLUDGE 2 reactor passes through the BLANKET reactor where only the reactions of the methanogenesis phase are considered. In this model, the conversion rate is calculated in a calculator block Eqs. (7–10). A recycle stream (i.e., 20 % w/w of the liquid effluent) was added to increase the methane yield.

2.5. Model validation

Three case studies were used to validate the model at different scales: Case 1 at laboratory scale, Case 2 at pilot scale and, Case 3 at industrial scale (Table 2). In Case 1, vinasse from a Cuban distillery was used as substrate with an inlet flow rate of 0.72 L/d. All the operational conditions as well as the inlet composition of vinasse were taken from Barrera et al. [23,40]. In Case 2, a UASB reactor with an influent flow rate of 46 L/d was considered. The process conditions and the vinasse characterization were adopted from Del Nery et al. [41]. For Case 3, data from a large-scale reactor treating sugarcane vinasse were used. The feed composition was based on Elaiuy et al. [42]. Table 2 shows the characterization of the influent stream for each study case and the operational conditions adopted during the model implementation.

2.6. Statistical analysis

As a first step, the accuracy of the model was tested based on the mean absolute relative error between the simulation results and the data from the above cases. Besides, the analysis of the variance (One factor ANOVA) was used to test for significant differences between the study cases (i.e., Case 1, Case 2 and Case 3) and the simulation results in terms of biogas composition, methane yield and, COD removal efficiency using a 95.0% Least Significant Difference (LSD) method [43]. The assessment of the data was made by using the software package STATPHRAFICS Centurion XV. II.

3. Results and discussion

3.1. Model validation and statistical analysis

Data for the comparison between the model outputs and the operating parameters in UASB reactors were taken under different conditions (i.e., organic loading rates, sulfate concentration, residence time, up-flow velocity) and scales. Table 3 shows the biogas composition obtained after the simulation of UASB reactors at different scales based on CH_4 and CO_2 content. The highest values of the mean relative error (MrE) for CH_4 and CO_2 compositions were obtained in Case 2 (Table 3). According to these results, the accuracy for biogas composition predictions are high (MrE ≤ 10%) and medium (10%–30%) respectively [44]. The ANOVA analysis showed that there were no significant differences regarding CH_4 (p-value = 0.832; pooled standard deviation = 6.33) and CO_2 content (p-value = 0.691; pooled standard deviation = 6.10) between the experimental data (study cases) and the simulated data

Concerning H_2S composition, only Case 1 was considered because of the data availability for validation. A medium accuracy (14.2%) was achieved in this case. However, without the inclusion of the sulfate reduction reaction set, the accuracy of the model for H_2S prediction would be even lower (> 35.0%). The non-consideration of H_2S formation during the design of a biogas plant based on vinasses as a substrate can lead to operational problems (e.g., corrosion), increasing the maintenance costs of the equipment fed by the gas. On the other hand, the costs of biogas cleaning could be underestimated, since this is a capital-intensive multistage operation, which can also carry out high maintenance costs due to media replacements (depending on the technology) and/or power costs [8].

Regarding to methane yields, the accuracy of the results was high in Case 1 and 3 (MrE ≤ 10%). For Case 2 a medium accuracy was obtained, however the value is closer to the lowest limit of the interval for the medium accuracy (10%–30%). No significant differences (p-value = 0.967; pooled standard deviation = 57.7) were found after the ANOVA analysis for the methane yield between the experimental data and the simulated results. The COD removal efficiency showed a mean relative error less than 5% in all cases with no significant differences observed respect the experimental data (p-value = 0.944; pooled standard deviation = 13.1). From the above analyses (i.e., mean relative error and ANOVA) it is concluded the good agreement between the simulations results and data from UASB reactors. Moreover, the simulation model could predict biogas production from vinasses at different scales accurately.

3.2. Sulfate reduction process analysis

Under a substrate-limiting condition, methane production bacteria (MPB) and sulfate reduction bacteria (SRB) compete for acetate and hydrogen, determining the amount of methane that could be produced

Table 2
Influent characterization and operational conditions for the model implementation.

Parameters	Case 1[a]	Case 2[b]	Case 3[c]
Vinasse composition			
COD [kg/m^3]	65.2	21.6	61.0
Total volatile solids [kg/m^3]	47.1	9.34	32.21
Volatile acids [kg/m^3]	1.36	2.21	2.36
SO_4^{2-} [kg/m^3]	3.96	1.19	n.a[d]
Carbohydrates [%] [e]	86.0	67.0	14.0
Proteins [%][e]	13.0	16.0	8.00
Lipids [%][e]	0.500	2.00	3.00
pH	4.83	4.20	4.04
Operational conditions			
Temperature [^{o}C]	35.0	35.0	35.0
Pressure [kPa]	101.3	101.3	101.3
Reactor volume [m^3]	4.50×10^{-3}	0.120	15,000
Hydraulic retention time [d]	4.86	2.40	15.0
Organic loading rate [kg/m^3/d]	9.89	10.0	1.99
Up-flow velocity [m/h]	0.100	6.94×10^{-2}	1.00
Granule diameter [10^{-3}m]	4.00	4.00	4.00
Fraction of volume occupied by granule [%]	40.0	50.0	80.0

[a] Barrera et al. [23].
[b] Del Nery et al. [41].
[c] Elaiuy et al. [42].
[d] No data available.
[e] % of total volatile solids.

Table 3
Results from the simulation model of UASB reactors treating vinasses.

Case study	Experimental cases			Simulation cases		
	Biogas composition[d] [%v/v]	Methane yield[e] [$NmlCH_4/gCOD_{removed}$]	COD removal[f] [%]	Biogas composition[d,g] [%v/v]	Methane yield[e,g] [$NmlCH_4/gCOD_{removed}$]	COD removal[f,g] [%]
Case 1[a]	52.5 $\%CH_4$ 45.9 $\%CO_2$	336	65.5	53.6 $\%CH_4$ **(2.03)** 43.1 $\%CO_2$ **(6.45)**	310 **(7.83)**	63.4 **(3.21)**
Case 2[b]	65.0 $\%CH_4$ 35.0 $\%CO_2$	316	90.5	67.7 $\%CH_4$ **(4.12)** 30.4 $\%CO_2$ **(13.1)**	351 **(11.1)**	93.0 **(2.76)**
Case 3[c]	55.0 $\%CH_4$ 45.0 $\%CO_2$	228	70.5	57.3 $\%CH_4$ **(4.18)** 39.8 $\%CO_2$ **(11.6)**	213 **(6.58)**	67.4 **(4.40)**

[a]Barrera et al. [23,40].
[b]Del Nery et al. [41].
[c]Elaiuy et al. [42].
[d,e,f]p-Value > 0.05 (95.0% CI) denote no significant difference between the experimental cases and the simulated cases for biogas composition (CH_4, CO_2), methane yield and COD removal for each case study.
[g]Values in parenthesis refer to mean relative error between the experimental and the simulated cases in %.

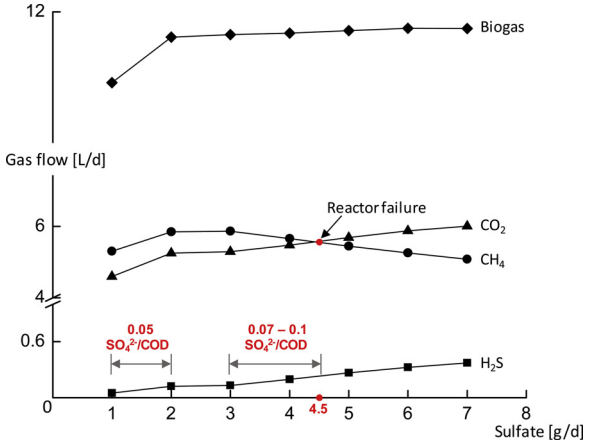

Fig. 2. Variation of gas phase under different sulfate loads.

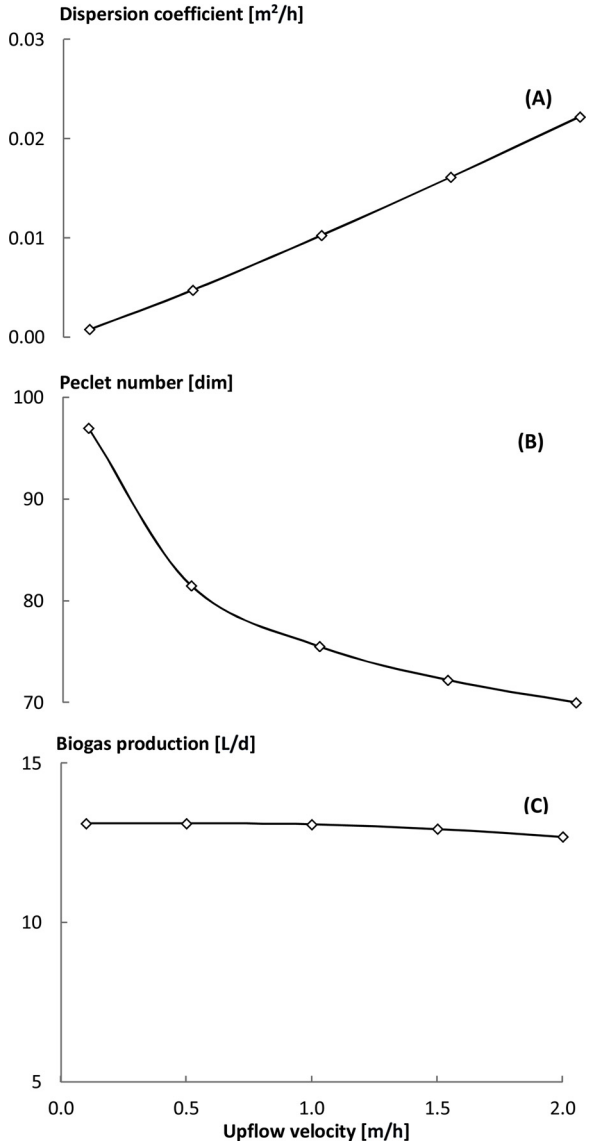

Fig. 3. Effect of the up-flow velocity on the hydrodynamic parameters and the biogas production.

in the process [14]. The pH is one of the factors that affect the result of the competition between MPB and SRB, ranging between 6.5 and 8.0 in the liquid phase of anaerobic reactors [14,23]. According to Khanal [8], variations of pH in the range of 6.0–8.0 could have an important impact on H_2S concentration and consequently in the biogas quality. Simulation results for Case 1 showed that a reduction of pH from 8.0 to 6.5 yielded an increment of H_2S production from 368 to 391 mg of H2S per day (~6.25%), affecting the gas quality. Similar behavior was found by Omil et al. [45] for a pH reduction from 8.0 to 7.0 in an UASB reactor.

Another factor that affects the gas quality due to the formation of H_2S is the SO_4^{2-}/COD ratio. Fig. 2 shows the results from a sensitivity analysis based on changes in H_2SO_4 loads (taken as SO_4^{2-}) in the influent stream. During the simulation, the COD values was kept constant, being the SO_4^{2-}/COD ratio gradually increased while the rest of the conditions were the same as in Case 1. According to Fig. 2 the biogas production was slightly increased (~14%) when the SO_4^{2-} load reached ~2 g/d. This behavior was the same observed by Barrera et al. [40] for an equal value of SO_4^{2-}/COD ratio. The same authors obtained, for a further increase in SO_4^{2-} load, an increment of H_2S in the gas phase (Fig. 2). From Fig. 2 it is also observed that the methane yield is gradually reduced (~5%) for a H_2SO_4 raising from 3 g/d to 4.5 g/d, meanwhile biogas production is slightly increased. For a SO_4^{2-}/COD ratio of 0.1 Barrera et al. [40] determined a reduction of the methane yield of 8% indicating the inhibition of methanogens. According to Fig. 2, the model predicts the failure of the reactor for H_2SO_4 loads higher than 4.5 g/d. Under these conditions, even though there is no reduction in the biogas generation, the quality of the gas phase is drastically degraded because of the low methane yield. However, it

could be possible a successful operation under high sulfate concentration if the SO_4^{2-}/COD ratio is lower than 0.1 due to high COD values [46].

3.3. Effect of granule size on biogas production

The performance of UASB reactors is sensitive to the granule size in the sludge bed as it depends of two main factors: the settling velocity and the mass-transfer limitations of the granules. Settling velocity is especially important when dealing with up-flow velocities higher than 1.75 m/h under peak flow conditions avoiding washout [47]. The granule size may rise the resistance to substrate diffusion inside the granule becoming the rate-limiting step and reducing the biochemical activity [24,48,49]. The estimation of the biogas production in the implemented model is a function of the granule size. Granule sizes in the range of 4 mm to 1 mm of diameter were considered for Case 1. The results showed that the lower the granule size the greater the biogas production. The best condition was obtained for 1 mm of diameter, which yielded ~14.5 L_{biogas}/d. According to Eq. (6), a decrease in granule size raises the reaction rate inside the granules (*Kg*), promoting the substrate conversion as well as the biogas production. From a physical point of view, an increment in granule size leads to a reduction in the surface-to-volume ratio, becoming the inlet and outlet of substrate and products respectively the limiting step for the substrate removal [50]. On the other hand, if the granule bed volume remains unchanged, it is possible to increase the surface-to-volume ratio for smaller granules. The result is an increment of the substrate flux into the granules as well as in the substrate uptake, yielding an increase of the biogas production. Particularly for Case 1, the reduction of granule size from 4 mm to 1 mm yielded an increment in biogas production equal to 16% compared with the base conditions. Comparison between the sensitivity analysis and the experimental results showed the accuracy of the integrated model, being in agreement with the experimental behavior reported for the sludge bed by several authors [24,32,48,51].

It should be mentioned that controversies about the effect of granule size on the biogas production were found in the literature. According to Wu et al. [49], there is a positive relationship between the granule size and the biogas production, determined by the internal structure of the granules (i.e. pore size, porosity factor). On the other hand, Bhunia and Ghangrekar [47] found out a direct proportional relationship between the specific methanogenic activity and the granule size. This study covered a diameter range from 0.270 mm to 3.03 mm. However, the authors declared a possible inhibition beyond 3.03 mm because of diffusional resistance inside the granules, as predicted by the proposed process simulation model.

3.4. Hydrodynamic behavior

The hydrodynamic performance in the model was evaluated through Eqs. (1–2). Fig. 3a–b shows the results for Case 1 regarding the influence of the up-flow velocity on the dispersion coefficient and the Peclet number respectively. Values for D_m in the range of 0.008 m^2/h – 0.012 m^2/h have been obtained during the hydrodynamic modeling of UASB reactor under similar conditions from those of Case 1 [19]. These values correspond to those predicted for the implemented process simulation model in the range of 0.5–1.5 m/h for the up-flow velocity. Regarding the Peclet number, an increment in the up-flow velocity by a factor of 5 respect to Case 1 leads to a reduction of *Pe* of about 15% (Fig. 3b). The reduction in *Pe*increases the dispersion number *d* ($d = Pe^{-1}$). For the range of *Pe* the corresponding *d* values are between 0.010 and 0.014 (Fig. 3b). According to Plascencia-Jatomea et al. [52], for $0 < d < 1$ the mixing pattern in the reactor corresponds to non-ideal (dispersed flow). The small values of the dispersion number obtained by the process simulation model are in agreement with the lab-scale, where very small diameter/height ratio are found [53].

Changes in the hydrodynamic behavior could have a direct impact on the biogas production. According to Fig. 3c, a slightly decrease in the biogas production was obtained when up-flow velocity was increased. This is consistent with the experimental performance of UASB reactors, in which at higher velocities there is an approach to the washout point, consequently, there is a loss of biomass and a drop in biogas generation [54].

The up-flow velocity is directly related to the HRT and plays an important role in entrapping suspended solids. A decrease of this parameter promotes an increase in the HRT, yielding a higher concentration of biomass in the system and improving the removal efficiency of the system. However, it should be mentioned that the process simulation model implemented in the present work is not very sensitivity to variations in the up-flow velocity. For Case 1, the reduction in biogas production was only of ~3.5% when the up-flow velocity was increased up to 2 m/h, which can be considered as negligible. According to Gonzalez-Gil et al. [48], the up-flow velocity does not have a strong influence on the substrate conversion rate of the anaerobic granules for values higher than 1 m/h. This is supported by experimental studies where the external mass-transport resistance is normally not rate-limiting for granular sludge [48].

The effect of the up-flow velocity – HRT are linked to other parameters such as reactor design, operating conditions and range of HRT, making necessary a careful evaluation of each specific case [55].

4. Conclusions

An integrated process simulation model for UASB reactors was implemented in Aspen Plus®. A mean relative error lower than ± 15% with no significant differences between the experimental data and the simulation results (i.e., biogas composition, methane yield and COD removal) was obtained. The model predicted the failure of the reactor at lab-scale for a SO_4^{2}/COD higher than 0.1 in agreement with the experimental results. Granule size appeared to have an important influence on biogas production in the UASB reactor. Simulation results showed an increase of 16% of biogas production when granule diameter was reduced from 4.00 mm to 1.00 mm at Case 1 conditions. The hydrodynamic study showed a negligible effect of the up-flow velocity on the substrate conversion. The integrated process simulation model could be used for predicting UASB performance during vinasses treatment.

Declaration of Competing Interest

None.

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References

[1] J. Lauwers, et al., Mathematical modelling of anaerobic digestion of biomass and waste: power and limitations, Prog. Energy Combust. Sci. 39 (4) (2013) 383–402.
[2] E.L. Barrera, et al., The sulfur chain in biogas production from sulfate-rich liquid substrates: a review on dynamic modeling with vinasse as model substrate, J. Chem. Technol. Biotechnol. 88 (8) (2013) 1405–1420.
[3] I. Angelidaki, L. Ellegaard, B.K. Ahring, A comprehensive model of anaerobic bioconversion of complex substrates to biogas, Biotechnol. Bioeng. 63 (3) (1999) 363–372.
[4] J. Lorenzo-Llanes, E. Kalogirou, Waste-to-energy conversion in havana: technical and economic analysis, Soc. Sci. 8 (4) (2019) 1–17.
[5] J.A. Suarez, et al., The state and prospects of renewable energy in Cuba, Energy Sources Part B Econ. Plan. Policy 11 (2) (2016) 111–117.
[6] A.R. Prazeres, et al., Treatment of vinasse from sugarcane ethanol industry: H2SO4, NaOH and Ca(OH)2 precipitations, FeCl3 coagulation-flocculation and atmospheric CO2 carbonation, J. Environ. Chem. Eng. (2019) p. 103203.
[7] E. España-Gamboa, et al., Vinasses: characterization and treatments, Waste Manag.

Res. 29 (12) (2011) 1235–1250.
[8] S.K. Khanal, Bioenergy recovery from sulfate-rich waste streams and strategies for sulfide removal, in: S.K. Khanal (Ed.), Anaerobic Biotechnology for Bioenergy Production Principles and Applications Anaerobic Biotechnology, John Wiley & Sons, Iowa, USA, 2008, pp. 133–149.
[9] O.P. Ones, Modelling, Simulation and Analysis for Energy Purposes of Hydrated Ethanol Distilleries in Chemical Engineering Departament, Technological University of Havana (Cujae), Havana, Cuba (In Spanish), 2012.
[10] B.G. de Oliveira, et al., Soil greenhouse gas fluxes from vinasse application in Brazilian sugarcane areas, Geoderma 200 (2013) 77–84.
[11] L.T. Fuess, M.L. Garcia, Implications of stillage land disposal: a critical review on the impacts of fertigation, J. Environ. Manage. 145 (2014) 210–229.
[12] W.C. Nadaleti, et al., National potential production of methane and electrical energy from sugarcane vinasse in Brazil: a thermo-economic analysis, J. Environ. Chem. Eng. (2019) p. 103422.
[13] B.S. Moraes, et al., Anaerobic digestion of vinasse from sugarcane biorefineries in Brazil from energy, environmental, and economic perspectives: profit or expense? Appl. Energy 113 (2014) 825–835.
[14] S. Harikishan, Biogas processing and utilization as an energy source, in: S.K. Khanal (Ed.), Anaerobic Biotechnology for Bioenergy Production Principles and Applications Anaerobic Biotechnology, John Wiley & Sons, Iowa, USA, 2008, pp. 267–290.
[15] J. Pagés-Díaz, et al., A comparison of process performance during the anaerobic mono-and co-digestion of slaughterhouse waste through different operational modes, J. Environ. Sci. 64 (2018) 149–156.
[16] K. Rajendran, et al., A novel process simulation model (PSM) for anaerobic digestion using Aspen Plus, Bioresour. Technol. 168 (2014) 7–13.
[17] H. Al-Rubaye, et al., Process simulation of two-stage anaerobic digestion for methane production, Biofuels (2017) 1–11.
[18] D.J. Batstone, et al., The IWA anaerobic digestion model no 1 (ADM1), Water Sci. Technol. 45 (10) (2002) 65–73.
[19] Y. Chen, et al., Mathematical modeling of upflow anaerobic sludge blanket (UASB) reactors: simultaneous accounting for hydrodynamics and bio-dynamics, Chem. Eng. Sci. 137 (2015) 677–684.
[20] D.J. Batstone, J. Hernandez, J.E. Schmidt, Hydraulics of laboratory and full-scale upflow anaerobic sludge blanket (UASB) reactors, Biotechnol. Bioeng. 91 (3) (2005) 387–391.
[21] M. Peña, D. Mara, G. Avella, Dispersion and treatment performance analysis of an UASB reactor under different hydraulic loading rates, Water Res. 40 (3) (2006) 445–452.
[22] B.E. Rittmann, P.L. McCarty, Model of steady-state-biofilm kinetics, Biotechnol. Bioeng. 22 (11) (1980) 2343–2357.
[23] E.L. Barrera, et al., Modeling the anaerobic digestion of cane-molasses vinasse: extension of the Anaerobic Digestion Model No. 1 (ADM1) with sulfate reduction for a very high strength and sulfate rich wastewater, Water Res. 71 (2015) 42–54.
[24] M.M. Wu, R.F. Hickey, Dynamic model for UASB reactor including reactor hydraulics, reaction, and diffusion, J. Environ. Eng. 123 (3) (1997) 244–252.
[25] V. Saravanan, T. Sreekrishnan, Modelling anaerobic biofilm reactors—a review, J. Environ. Manage. 81 (1) (2006) 1–18.
[26] Y. Zeng, et al., Hydraulic modeling and axial dispersion analysis of UASB reactor, Biochem. Eng. J. 25 (2) (2005) 113–123.
[27] R. Rodríguez-Gómez, et al., A model to describe the performance of the UASB reactor, Biodegradation 25 (2) (2014) 239–251.
[28] A. Singhal, et al., Axial dispersion model for upflow anaerobic sludge blanket reactors, Biotechnol. Prog. 14 (4) (1998) 645–648.
[29] S. Mu, et al., Simulation and control of an upflow anaerobic sludge blanket (UASB) reactor using an ADM1-based distributed parameter model, Ind. Eng. Chem. Res. 46 (5) (2007) 1519–1526.
[30] M. Odriozola, I. López, L. Borzacconi, Modeling granule development and reactor performance on anaerobic granular sludge reactors, J. Environ. Chem. Eng. 4 (2) (2016) 1615–1628.
[31] H.H. Nguyen, S. Heaven, C. Banks, Energy potential from the anaerobic digestion of food waste in municipal solid waste stream of urban areas in Vietnam, Int. J. Energy Environ. Eng. 5 (4) (2014) 365–374.
[32] Y. Nalinga, I. Legonda, The effect of particles size on biogas production, Int. J. Innov. Res. Technol. Sci 4 (2) (2016) 9–13.
[33] R.P. Serrano, Biogas Process Simulation Using Aspen Plus, in Chemical Engineering, Syddansk Universitet, Denmark, 2011 p. 39.
[34] J.B. Butt, H. Heinemann (Ed.), Modeling of Real Reactors, in Reaction Kinetics and Reactor Design, CRC Press, Boca Raton, 2000, pp. 331–397.
[35] W. Bolle, et al., An integral dynamic model for the UASB reactor, Biotechnol. Bioeng. 28 (11) (1986) 1621–1636.
[36] R. Rodríguez-Gómez, L. Moreno, L. Liu, A model to predict the behavior of UASB reactors, Int. J. Environ. Res. 7 (3) (2013) 705–714.
[37] P.V. Danckwerts, Continuous flow systems: distribution of residence times, Chem. Eng. Sci. 2 (1) (1953) 1–13.
[38] R.J. Wooley, V. Putsche, Development of an ASPEN PLUS Physical Property Database for Biofuels Components, National Renewable Energy Laboratory, Golden, CO, USA, 1996.
[39] D. Bravo, et al., Aspen Plus process-simulation model: producing biogas from VOC emissions in an anaerobic bioscrubber, J. Environ. Manage. 213 (2018) 530–540.
[40] E.L. Barrera, et al., Characterization of the sulfate reduction process in the anaerobic digestion of a very high strength and sulfate rich vinasse, Chem. Eng. J. 248 (2014) 383–393.
[41] V. Del Nery, et al., Hydraulic and organic rates applied to pilot scale UASB reactor for sugar cane vinasse degradation and biogas generation, Biomass Bioenergy 119 (2018) 411–417.
[42] M.L.C. Elaiuy, et al., ADM1 Modelling of large-scale covered in-ground anaerobic reactor treating sugarcane vinasse, Water Sci. Technol. 77 (5) (2018) 1397–1409.
[43] D.C. Montgomery, G.C. Runger, Applied Statistics and Probability for Engineers, John Wiley & Sons, 2010.
[44] D. Batstone, J. Keller, Industrial applications of the IWA anaerobic digestion model No. 1 (ADM1), Water Sci. Technol. 47 (12) (2003) 199–206.
[45] F. Omil, et al., Effect of upward velocity and sulfide concentration on volatile fatty acid degradation in a sulfidogenic granular sludge reactor, Process. Biochem. 31 (7) (1996) 699–710.
[46] A.C. Wilkie, K.J. Riedesel, J.M. Owens, Stillage characterization and anaerobic treatment of ethanol stillage from conventional and cellulosic feedstocks, Biomass Bioenergy 19 (2) (2000) 63–102.
[47] P. Bhunia, M. Ghangrekar, Required minimum granule size in UASB reactor and characteristics variation with size, Bioresour. Technol. 98 (5) (2007) 994–999.
[48] G. Gonzalez-Gil, et al., Kinetics and mass-transfer phenomena in anaerobic granular sludge, Biotechnol. Bioeng. 73 (2) (2001) 125–134.
[49] J. Wu, et al., Size effect of anaerobic granular sludge on biogas production: a micro scale study, Bioresour. Technol. 202 (2016) 165–171.
[50] S. Pavlostathis, E. Giraldo-Gomez, Kinetics of anaerobic treatment: a critical review, Crit. Rev. Environ. Sci. Technol. 21 (5-6) (1991) 411–490.
[51] M. Sebola, E. Muzenda, H. Tesfagiorgis, Effect of particle size on anaerobic digestion of different feedstocks, South Afr. J. Chem. Eng. 20 (3) (2015) 11–26.
[52] R. Plascencia-Jatomea, et al., Hydrodynamic study of a novel membrane aerated biofilm reactor (MABR): tracer experiments and CFD simulation, Chem. Eng. Sci. 138 (2015) 324–332.
[53] A. Bittante, et al., Residence time and axial dispersion of liquids in Trickle Bed Reactors at laboratory scale, Chem. Eng. J. 250 (2014) 99–111.
[54] S.K. Khanal, Anaerobic reactor configurations for bioenergy production, in: S.K. Khanal (Ed.), Anaerobic Biotechnology for Bioenergy Production Principles and Applications Anaerobic Biotechnology, John Wiley & Sons, Iowa, USA, 2008, pp. 93–112.
[55] S.M.M. Vieira, A.D. García, Sewage treatment by UASB-reactor. Operation results and recommendations for design and utilization, Water Sci. Technol. 25 (7) (1992) 143–157.