Evaluation of alkalinity spatial distribution in an up-flow fixed bed anaerobic digester
Maha Hmissi, Jérôme Harmand, Victor Alcaraz-Gonzalez and Hedi Shayeb

ABSTRACT
In this paper, an experimental study upon alkalinity and hydrodynamic behavior in an anaerobic up-flow fixed bed reactor for the treatment of tequila vinasses is presented. Measurements of volatile fatty acids, pH, alkalinity and bicarbonate were obtained at three sampling points in the reactor in the axial axis. Then, the spatial distribution of alkalinity is studied and discussed. Moreover, for further control process purposes, a hydrodynamic model based on the use of two interconnected two-steps reduced AM2 type models is proposed and its parameters are identified using experimental data.

Key words | alkalinity, AM2 model, anaerobic up-flow fixed bed reactor, hydrodynamic

INTRODUCTION
The importance of considering hydrodynamics and mixing regime during anaerobic reactor design and performance evaluation has been highlighted in the literature in recent years. For instance, a large number of research studies have been carried out in the last few decades to improve an understanding of the hydrodynamics and the biological degradation of anaerobic biofilter reactors. The interest in this concern lies with the development of hydrodynamic models, which may be useful to better describe dynamics inside the reactor and to study its influence on the bioreactor performance.

In most studies involving fluidized or fixed bed bioreactors, the hydrodynamic behavior is simplified as well-mixed (i.e. CSTR type) and, thus, the concentration gradients are neglected. Nevertheless, it is well known that the distribution of substrates and degradation of intermediates along the reactor height is far from uniform (Bonnet et al. 1997; Giojelli et al. 2001; Béteau et al. 2005). Actually, some research works have proposed simple models for different purposes. For instance, Escudié et al. (2005) modeled the fixed bed reactor considering two interconnected regions: a completely mixed one representing the mixed liquid and a dead zone representing the biofilm. Also, Smith et al. (1996) proposed a different configuration, composed by an ideal continuous stirred tank reactor (CSTR) with a dead zone, followed by a plug flow reactor, and including a bypass. Young & Young (1988) also proposed a model as a combination of ideal systems, composed by: a first CSTR, representing the inlet zone; an ideal plug-flow reactor with a dead zone representing the central part of the anaerobic biofilter reactor and a second CSTR representing the outlet zone.

In the case of fixed bed reactors, only a few works are reported; Aguilar-Garnica et al. (2009) for example, presented a model of two fixed-bed reactors assuming that a biomass concentration gradient existed. On the other hand, concerning hydrodynamics, it has been described with numerous mathematical models, and their calibration relies also on detailed experimental tracer studies. Nevertheless, many of these tracer studies only deal with short-term impulse loadings of a soluble tracer under steady-state conditions and, thus, neglect the dynamics of other components (e.g. distribution of substrates and microorganisms) (Harmand et al. 2002). Other models based on dispersed plug flow and diffusion of the tracer within the biofilm (known as biodiffusion models) have been proposed (Riemer et al. 1980; Bill et al. 1989). Moreover, the estimation of mass transfer fluxes and substrate concentrations inside
anaerobic bioparticles is also a current research field in fixed-bed reactors (Zaiat et al. 2000).

However, even when these models deal with the hydrodynamic inside the reactor, most of the above studies do not take into account the physicochemical phenomena concerning alkalinity. Actually, it is generally accepted that alkalinity is one of the most important variables to assess the anaerobic digestion (AD) stability. In fact, it is well known that the main alkalinity components in an AD process are bicarbonate and volatile fatty acids (VFA) concentrations. Thus, in the case of wastewaters with high buffering capacity, pH measurements may be rather not enough to indicate process changes and therefore pH only is not adapted for process supervision and control (Hawkes et al. 1993). Hence, in order to guarantee operational stability in AD processes, monitoring and control of alkalinity becomes even more important than only pH or VFA (Ripley et al. 1986; Steyer et al. 2002; Alcaraz-González et al. 2015). This fact may take a major importance in fixed bed reactors, because, as it is well known, liquid phase concentrations are spatially distributed and a substrate gradient takes place in this kind of reactor configuration. Moreover, hydrodynamic studies consider only theoretical diffusion and transport phenomena but not physicochemical phenomena concerning alkalinity. In the literature, in the knowledge of authors, the hydrodynamic behavior of species involved on alkalinitities in up-flow fixed bed reactor for AD of granular sludge has not be treated. On the other hand, concerning anaerobic fixed bed reactors, many researchers have widely used a reduced-order model AM2 which was developed and validated by Bernard et al. (2001) for designing several monitoring and control approaches (Alcaraz-González et al. 2002; Lopez-Banuelos et al. 2008).

In this study, we propose a new hydrodynamic and biokinetic model giving a better understanding of the physicochemical phenomena that take place in a fixed bed AD bioreactor as well as the axial distribution of chemical species involved in alkalinity, and the alkalinity itself. In this work, we use also the so-called AD model AM2 as a basis for the development of the hydrodynamic proposed model. The main idea is to integrate two interconnected reactors, each one following the AM2 model, but considering a recirculation flux for taking into account hydrodynamic features suited for further process control purposes.

By way of validation, a pilot-scale fixed bed up-flow AD process containing a high biomass concentration treating tequila vinasses was studied: an experimental study of the hydrodynamic behavior of chemical species and how it influences alkalinity is presented. Measurements of VFA, pH, alkalinity and bicarbonate were obtained at three sampling points in the bioreactor. Then we used the reduced model of Bernard et al. (2001) (AM2) as a basis for the development of a hydrodynamic model. This model fails in the prediction of the spatial distribution of alkalinity; for this reason, a modification taking into account the influence of nitrogen in alkalinity is also proposed.

### MATERIALS AND METHODS

#### The reactor and operating conditions

The treated wastewater was raw tequila vinasses obtained from a tequila factory located at Guadalajara-Jalisco, Mexico. Characteristics of this effluent are given in Table 1.

It is important to remark the relatively high value of VFA concentration. As it is well known, VFA are the main substrates used by syntrophic bacteria and methanogenic archaea to produce methane (Steyer et al. 2002). However, even when it may be only a small fraction in terms of the total chemical oxygen demand (COD), it can be enough for causing inhibition by substrate and operational instability in the methanogenic phase (Méndez-Acosta et al. 2010).

The experiments were carried out in an anaerobic up-flow continuous fixed bed reactor of 1.65 m height and 0.6 m diameter with a 445 L total useful volume (Garcia-Sandoval et al. 2016). Inside the digester there is a vertical layout of Cloisonyle® tubes, where each tube has in its interior a honeycomb arrangement that is used as support for microorganisms growing. The reactor was inoculated with granular anaerobic sludge. Used tequila vinasses were diluted (70% H2O–30% vinasses) for giving a COD influent concentration around 10 g/L. The feeding flow

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate (mg/L)</td>
<td>11.1</td>
</tr>
<tr>
<td>Sulfate (mg/L)</td>
<td>679</td>
</tr>
<tr>
<td>Nitrogen (mg/L)</td>
<td>15–40</td>
</tr>
<tr>
<td>Phosphorus (mg/L)</td>
<td>3.90</td>
</tr>
<tr>
<td>COD (g/L)</td>
<td>25–60</td>
</tr>
<tr>
<td>pH</td>
<td>3–4</td>
</tr>
<tr>
<td>VFA (mg/L)</td>
<td>2,500–3,000</td>
</tr>
</tbody>
</table>
Q_{in} at the start up was 7 L/h and then it was decreased to 5 L/h once the composition in CH₄ of the biogas was greater than 60%. The pH of the diluted vinasses were previously adjusted to 6.5–7.0 before feeding by adding a 0.1 M NaOH solution and mixed with a recirculation coming from the outlet (see Figure 1). The recirculation flow was Q_{r} = 150 L/h.

The hydraulic retention time (HRT) was fixed at around 3.71 days with an organic loading rate (OLR) 2.7 gCOD L⁻¹ day⁻¹. pH, VFA, bicarbonate and alkalinities were measured once a day. The digester was operated under mesophilic conditions; the reactor temperature was regulated at 37 °C by using an immersion circulator and water as heat transfer liquid which was conducted through the reactor jacket. The pressure was the atmospheric at Guadalajara (635 hPa). The AD process was operated during 35 days. However, it is important to remark that the starting period, when the reactor is still in the colonization stage should not be taken into account for the interpretation of results. Indeed, during this period, there occur other biological, chemical and physical phenomena that do not correspond to the normal operation of a bioreactor. In fact, only the last 25 days were taken into account in the discussion once those acceptable conditions were achieved.

**Online measurements**

The digester was fully instrumented and automated, allowing the on-line monitoring of pH, temperature, pressure, biogas and wastewater flow rates. A National Instruments cRIO9004- device was used for data acquisition, treatment and storage. A graphical interface with National Instruments LabView program was created to see in real time and to modify control variables, to set parameters, and for obtaining data.

Measurements of VFA and bicarbonates were performed by using an online AnaSense® (Applitek) titrimetric analyzer, pH, partial alkalinity (PA), total alkalinity (TA) and intermediate alkalinity (IA = TA-PA), as well as alkalinity factor \( \alpha = \frac{IA}{TA} \), were also measured with the online AnaSense. CO₂/CH₄ gas percentage was measured using an Ultramat 23 sensor (Siemens®).

To follow axial distribution in the reactor, sampling devices were installed at three locations within the reactor (see Figure 1). The three sampling devices were installed at heights of 25, 50.0, and 75.0 cm from the base of the reactor corresponding to the bottom, middle and top. The effluent exit corresponded to a distance of 165 cm from the reactor base.

**THE PROPOSED MODEL**

**Hydrodynamics**

The objective in this section is to show the main structure and hydrodynamics features of the up-flow fixed-bed reactor. To model the behavior of liquid phase, a series of connected ideal continuous-stirred tank reactor (CSTR) compartment is proposed. At a first instance, three CSTRs were tested such that each sampling point represents a CSTR. However, as it will be seen in the following sections, the difference...
between the top and the bottom for both; experimental and theoretical, was not extremely significant. Therefore, in order to reduce the complexity of the system, a model with only two CSTRs perfectly mixed with recirculation was been developed (see Figure 2). This model assumes that the whole volume can be divided into two equal volumes: \( V_1 = 222.5 \, L \) and \( V_2 = 222.5 \, L \), the sum of these two volumes corresponds about to the total reactor volume. The input flow was \( Q_{in} = 5 \, L/h \). The mass balances at each compartment is described as follows:

**Mass balance in CSTR1:**

\[
\frac{dC_{1j}}{dt} = Q_{in} \times C_{1in,j} + Q_r \times C_{2j} - (Q_{in} + Q_r) \times C_{1j} \pm R(C_{1j})
\]

**Mass balance in CSTR2:**

\[
\frac{dC_{2j}}{dt} = (Q_{in} + Q_r) \times C_{1j} - (Q_{in} + Q_r) \times C_{2j} \pm R(C_{2j})
\]

where the \( j \) index represents the different components involved in the mass balance, and the term \( R(C_j) \) represents the biological reaction of the component \( j \) at each tank.

**Biokinetics**

The model proposed in this work is based on the reduced-order model for AD processes proposed and experimentally validated by Bernard et al. (2001). This model is based on a two-step mass balance approach: acidogenesis and methanogenesis. The bacterial population is assumed to be divided into two main groups. The model also incorporates electrochemical equilibria in order to calculate the quantity of inorganic carbon (C) and the strong ions concentration Z. These compounds are then taken into account to estimate the gas outflow (\( CO_2, CH_4 \)). Then, for each compartment, the biokinetic behavior may be depicted as follows (Bernard et al. 2001):

\[
\frac{dX_1}{dt} = (\mu_1(S_1) - aD)X_1
\]

\[
\frac{dS_1}{dt} = D(S_{1in} - S_1) - k_1\mu_1(S_1)X_1
\]

\[
\frac{dX_2}{dt} = (\mu_2(S_2) - aD)X_2
\]

\[
\frac{dS_2}{dt} = D(S_{2in} - S_2) + k_2\mu_1(S_1)X_1 - k_3\mu_2(S_2)X_2
\]

\[
\frac{dZ}{dt} = D(Z_{in} - Z)
\]

\[
\frac{dC}{dt} = D(C_{in} - C) - q_c(\xi) + k_4\mu_1(S_1)X_1 + k_5\mu_2(S_2)X_2
\]

\[
\mu_1 = \mu_{1max} \frac{S_1}{(S_1 + K_{s1})}
\]

\[
\mu_2 = \mu_{2max} \frac{S_1}{(S_2 + K_{s2} + (S_2^2/K_{I2}))}
\]

\[
q_c = KLa(C + S_2 - Z - K_H P_c)
\]

\[
q_M = k_6\mu_2(S_2)X_2
\]

\[
P_c = \frac{\phi - \sqrt{\phi^2 - 4K_H P_T(C + S_2 - Z)}}{2K_H}
\]

\[
\phi = \frac{Z + S_2 - Z + K_H P_T + k_6\mu_2X_2}{KLa}
\]

\[
BIC = Z - S_2
\]

Figure 2 | Compartments structure of the proposed model.
\[ CO_2 = C - Z + S_2 \]  

(16)

\[ pH = -\log_{10} \left( K_b \frac{C - Z + S_2}{Z + S_2} \right) \]  

(17)

In this model, \( S_1 (\text{g/L}), S_2 (\text{mg/L}), X_1 (\text{g/L}), X_2 (\text{g/L}) \), are the concentrations of organic substrate (as COD), VFA, acidogenic and methanogenic bacteria, respectively. \( \mu_1 \) and \( \mu_2 \) (1/d), \( Z \) (mEq/L), and \( C \) (mmol/L), \( P_c \) (kPa), \( P_T \) (atm), \( q_c \) (L/h), \( q_M \) (L/h), \( K_b \), \( D \) (1/d), \( \alpha \) are, respectively, the specific growth rates of acidogenesis and methanization, the total strong ions concentration and the total inorganic carbon concentration, the carbon dioxide and the total pressures, respectively, the carbon dioxide and methane flow rates, an affinity constant, the dilution rate and the fraction of bacteria in the liquid phase, respectively, while \( k_1, k_2, k_3, k_4, k_5 \) and \( k_6 \) are yield coefficients. \( \mu_{1\text{max}}, \mu_{2\text{max}}, K_{s1}, K_{s2} \) and \( K_{12} \) are biokinetic parameters, \( KLa \) (1/d) represents the liquid-gas transfer coefficient and \( K_{ij} \) (mmol/L/atm) is the Henry’s constant.

It is important to notice that the strong ions concentration \( Z \) is linked to the total alkalinity (TA) by the relation \( Z = TA + 5 \text{ mmol/L} \) but only to pHs close to 7 (Mendez-Acosta et al. 2010). As it is the normal operating point in AD process, \( Z \) is often confused with alkalinity. However, the absence of biological reactions in the dynamic of \( Z \) makes it an inactive species. Thus, for the original AM2, the spatial distribution of \( Z \) does not take place. For this reason, the modification of the dynamic of \( Z \) must be taken in consideration to show the distribution of alkalinity along the reactor, as it will be shown after.

Actually, as will be shown afterwards in the Results and Discussion section, model (see Equation (7)) fails in the prediction of \( Z \). Thus, modifications proposed by Hassam et al. (2015) on the dynamics of \( Z \) by considering other possible biological reactions have been taken into account, as well. The modified model is justified in the present real case and allows improving the predictions of the alkalinity. Nevertheless, for a better understanding, these modifications will be introduced after.

**Model identification: sensitivity analysis**

In this section, a sensitivity analysis of the proposed model is developed in order to identify the dominant parameters. Different approaches are available to determine the functions of sensitivity \( \frac{\partial y_i}{\partial p_i} \). For instance, a deviation \( \Delta p_i \) for the parameter \( p_i \), where \( y_i \) is the simulated value, can be taken into account for estimating the sensitivity of a state with respect to the considered parameter. Thus, the following sensitivity index proposed by Dochain & Vanrolleghem (2001) has been considered:

\[ \delta_{ij} = \frac{p_i}{y_i(p_i)} \frac{y_i(p_i + \Delta p_i) - y_i(p_i)}{\Delta p_i} \cdot 100 \]  

(18)

The perturbation factor \( \Delta p_i \) was set to 20% for all the calculations of sensitivity.

**RESULTS AND DISCUSSION**

**General**

After the start-up stage, the functioning conditions allowed the good interaction between the microbiological system and the continuous conditions. This phenomenon can be interpreted as a direct result of the sludge adaptation for the assimilation of the different nutrients contained in tequila vinasses. For instance, in Figure 3 it can be seen that the methane percentage was found to be higher than 65%, while it was, most of the time, in a range of 70–75%. The percentage of CO2 remained around 25–30%. Moreover, the corresponding methane yield was 0.32–0.54 m3 CH4/kgCOD removed. Furthermore, the alkalinity factor \( \alpha \) remained close to 0.3. This value, \( \alpha = 0.3 \), together with \( TA > 60 \) are the most common reference values concerning alkalinites suggested in the literature in order to guarantee operational stability (Ripley et al. 1986; Alcaraz-González et al. 2015).

In our case, the evolution of experiments indicated that the substrate was quickly hydrolyzed and the hydrolyzed organic matter transformed to VFA, suggesting the start of the stabilization phase. The average of VFA concentration at the bottom was 510 mg/L, which was mainly composed by acetate while it was 330 mg/L in the effluent.

During the last week of experiments, the differences between concentrations at the bed bottom and in the effluent decreased and the production of VFA also decreased highlighting the fact that, as expected, microbial populations were also able to consume acids.

VFA and bicarbonate measurements are important to assess a digester’s stability. Besides, as it was established before, alkalinity is a better alternative than the pH to indicate the accumulation of VFA, because the increase in VFA will directly affect alkalinity before an important change of pH. However, it is well known that the total alkalinity...
(TA) is not very sensitive at pH around 7 (Méndez-Acosta et al. 2013; Alcaraz-González et al. 2013). Furthermore, at this pH, the partial alkalinity and bicarbonate measurements are very close (Zaher et al. 2002), but the difference may become very important at pH < 6.5.

Moreover, notice that the alkalinity factor $\alpha$ was kept around 0.3, preventing the accumulation of VFA and as a consequence, guaranteeing the operational stability of the process (Ripley et al. 1986). As, at pH close to 7, alkalinity is often mainly due to the bicarbonate buffer, it has been proposed since the early 1960s that its measurement can be used in control strategies for anaerobic digesters (McCarty 1964). Actually, it is important to notice that in most papers of anaerobic digestion literature dealing with operational stability, pH control alone, or VFA control alone are not enough to guarantee stability and, as a consequence, alkalinity control is needed (Ripley et al. 1986; Steyer et al. 2002; Alcaraz-González et al. 2013).

Notice also that even when Figure 3(a)–3(d) represent the influent and effluent dynamical behavior for VFA, bicarbonate, PA and alkalinity factor $\alpha$, there exists already an important difference between these two positions, which strongly suggest effectively that it exists an internal spatial distribution into the bioreactor, as will be seen hereafter.

Figure 3 | Global dynamical behavior of the bioreactor: (a) VFAs (mg/L) influent–effluent profile, (b) bicarbonate (mEq/L) influent–effluent profile, (c) PA (mEq/L) influent–effluent profile, (d) alkalinity factor (dimensionless), (e) biogas composition (%), (f) methane yield (m3 CH4/kg COD removed).

Sensitivity analysis

The parameters’ influence on the proposed model is presented in Figure 4. This sensitivity analysis is presented in % for the model parameters. As can be seen in this figure, the parameters influencing $S_2$ are: $\mu_{1\text{max}}, \mu_{2\text{max}}, K_{s_2}, k_1, k_2$ and $k_3$. Besides, the initial concentration of methanogenic bacteria ($X_{o2}$) had an important impact on $S_2$. On the other hand, it was determined that the parameters $\mu_{1\text{max}}, K_{s_1}$ and $k_1$ influence $S_1$ (results are not shown), while the parameters $k_5$ and $k_6$ had very little influence on $S_2$. Moreover, the parameters influencing $S_2$ are those influencing bicarbonate more the initial concentration of the alkalinity $Z$.

Identification of parameters values from experimental results

The parameters identification consists in finding the set of parameters that minimize a global criterion based on the error between simulated values and measurements. The identification algorithm provides a unique value, and the corresponding parameter is then identifiable (Dochain & Winkin 1995). Then, in order to compare the hydrodynamic predictions to the experimental results, the model was recalibrated.
In this section, the simulation results are also presented, together with experimental points in Figure 5(a)–5(d). The proposed model parameters were estimated by minimizing the difference between the measurements and model outputs. Table 2 summarizes the obtained estimated kinetic parameters and yield coefficients ratio values of the proposed model.

**Axial distribution**

Figure 5(a)–5(d) show experimentally the spatial distribution of alkalinity, bicarbonate, pH and total VFA along the reactor height. The samples were taken in three spatial locations: bottom (valve 1), middle (valve 2) and the top of the reactor (valve 3) but to demonstrate the spatial distribution we took only the profiles for valves 1 and 3 because of the small separation between each one (25 cm). Then we chose two valves (1 and 3) separated by 50 cm. Thus, as it can be stated before, only the bottom and the top experimental results are shown here because they are enough to show the different variables axial distribution. In the same context, we recall that for the same reasons, in order to reduce the complexity of the system, and without loss of generality, only a two-compartment CSTRs model, instead of three, was taken as representative of the overall system. In general, model outputs followed the experimental results with reasonable accuracy.

Figure 5(a) shows that the distribution of total VFA along the reactor height was experimentally observed, the gradient of VFA decreased from the bottom to the top. The concentrations at position 1 and at position 3 differed significantly, indicating that most of the bacterial activity...
was located in the higher part of the reactor. The production of VFA was followed by the methanization process, which was more intensive in the upper part of the reactor. The behavior of the VFA is related to the VFA degradation rate distributions which were different at each reactor cross section. This trend agrees with the model results in Yang et al. (2015) in an EGSB reactor: they explained numerically that the distribution of reaction rates indicated that, due to the well influent distribution, a plug flow was well created in the reactor, which was beneficial for VFA degradation.

A comparison of measured and predicted VFA concentrations at the bottom and the top of the reactor, shows qualitatively similar trends. VFA were predicted with good accuracy and the proposed model reproduced the measurements adequately.

The production of VFA was less stable, then it decreased and the gradient of VFA was clearly observed. It should be

![Figure 5](image-url)  
Comparison of measured and predicted concentrations and spatial distribution of: (a) VFA (mg/L), (b) pH (dimensionless), (c) bicarbonate (mEq/L), (d) alkalinity (mEq/L).

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Estimates of the kinetic parameters and of the yield coefficients</th>
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<tbody>
<tr>
<td>Parameter</td>
<td>Meaning</td>
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<tr>
<td>$k_1$</td>
<td>Yield coefficient for COD degradation</td>
</tr>
<tr>
<td>$k_2$</td>
<td>Yield coefficient for VFA production</td>
</tr>
<tr>
<td>$k_3$</td>
<td>Yield coefficient for VFA consumption</td>
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<tr>
<td>$k_4$</td>
<td>Yield coefficient for CO$_2$ production due to X1</td>
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<td>$k_5$</td>
<td>Yield coefficient for CO$_2$ production due to X2</td>
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<td>$k_6$</td>
<td>Yield coefficient for CH$_4$ production</td>
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<tr>
<td>$\mu_{1max}$</td>
<td>Maximum acidogenic biomass growth rate</td>
</tr>
<tr>
<td>$\mu_{2max}$</td>
<td>Maximum methanogenic biomass growth rate</td>
</tr>
<tr>
<td>$K_{1}$</td>
<td>Half-saturated constant associated with S1</td>
</tr>
<tr>
<td>$K_{2}$</td>
<td>Half-saturated constant associated with S2</td>
</tr>
<tr>
<td>$K_{12}$</td>
<td>Inhibition constant associated with S2</td>
</tr>
<tr>
<td>$K_{h}$</td>
<td>Hydrolysis constant</td>
</tr>
</tbody>
</table>
noted that some measurements of VFA exhibited variability because of the variation of recirculation.

Figure 5(b) shows also the distribution of pH along the reactor height. Inside the fixed bed, pH values were observed in the interval of 7.2–7.55. This pH interval allows the conclusion that an appropriate performance of the methanogenic phase was achieved. The gradient of pH increased from the bottom to the top and the gradient was clearly observed. A comparison of measured and predicted pH also shows a reasonable fitting, but predictions revealed some deviations in the first day and pH was underestimated, which may be caused by a problem of initialization or a not modeled phenomenon like inhibitions.

On the other hand, hydrodynamics of physicochemical phenomena has been studied, the alkalinity TA can be expressed using pH exclusively, functions that acts as factors of true state variables like VFA and total inorganic carbon, or even Z (Alcaraz-González et al. 2013). The fluctuations of the profile of pH caused observable changes in TA, the gradients of TA and bicarbonate also increase along the reactor height from the bottom to the top (see Figure 5(c)).

Alkalinity presents an important factor affecting the process. In this work, TA was ≥60 mEq/L until day 21, then it decreased. Notice that on the same day, VFA also decreased.

During the last week, we observed a significant decrease of bicarbonate measurements, which was influenced by the decrease of VFA in the same period. The combined effect of the decrease in these two variables, VFA and bicarbonate, was not only the decrease of TA itself but also a relative loss on the spatial distribution degree. In fact, during the last week, TA was around 40 mEq/L, and its spatial distribution was effectively reduced.

Experimentally, the axial distribution of TA was perfectly observed. However, the proposed model failed in predicting gradient concentration concerning Z. As was discussed before, the reason for this failure has been detected in the absence of biological reaction in the mass balance of the alkalinity Z (see Figure 5(d)). As a consequence, the simulated bicarbonate gradient is not sufficiently pronounced because of the strong link between the bicarbonate and Z. Indeed, the concentration of bicarbonate presents about 70% of Z and 20% of VFA (see Figure 5(c)).

For the bicarbonate, the gradient was observed and was very well predicted with the proposed model, but in the last few days it was overestimated (see Figure 5(c)).

The hydrodynamic behavior of alkalinity inside the reactor suggests that physicochemical interactions and equilibriums may prevail in some cases over simple diffusion and transport phenomena. The proposed model was able to simulate VFA, pH and bicarbonate gradients in the reactor. However, as stated before, we highlighted the absence of axial distribution for Z. In order to correct this failure, we propose a modification of the model by adapting a new version of AM2 which has been developed by Hassam et al. (2015), accounting for the dynamics of the inorganic nitrogen concentration. This modification makes Z a reactive species, whereas it was not in the original AM2. Thus, we used this modification to improve the predictions of the alkalinity as is depicted in the next section.

AM2 modification accounting for the role of nitrogen

In this section, we used the modifications made by Hassam et al. (2015) on the dynamics of Z by adding biological reactions and we tried to improve the predictions of the alkalinity. The first modification was to include the hydrolysis step that describes the degradation into soluble organic substances of the particulate substrate such as lipids, polysaccharides, and proteins possibly coming from suspended biomass (Cedeño 1995).

Then, we introduced to the AM2 model the ammonium released from protein hydrolysis in order to consider its contribution to the alkalinity of the solution. In the AM2, three components contain nitrogen: the degradable substrate $S_1$, whose nitrogen content is $N_{S_1}$, the acidogenic biomass ($X_1$) and the methanogenic biomass ($X_2$) whose nitrogen content is $N_{bac}$.

Arrizon & Gschaedler (2007) affirm that if an adequate source of nitrogen is present, the tequila fermentation length can be reduced by increasing sugar transport (Salmon et al. 1993), causing an accelerated fermentation rate, alcohol and some volatile compounds.

Thus, we add an additional state variable ($X_T$) including particulate substrates related to polysaccharides, to proteins and to lipids, i.e. the differential system previously described was modified by adding one more differential equation describing the $X_T$ mass balance:

$$\frac{dX_T}{dt} = D(T_{ini} - X_T) - k_{hyd}X_T$$  \hspace{1cm} (19)

where $k_{hyd}$ is the hydrolysis constant ($d^{-1}$) by modifying the dynamic of $S_1$ into the following:

$$\frac{dS_1}{dt} = D(S_{ini} - S_1) - k_{1}\mu_1(S_1)X_1 + k_{hyd}X_T$$  \hspace{1cm} (20)
And by adding the dynamic of inorganic nitrogen concentration in the dynamic of \( Z \):

\[
\frac{dZ_{\text{modified}}}{dt} = D(Z_{in} - Z) \\
+ [k_1N_{S1} - N_{bac}\mu_{1\text{max}}\frac{S_1}{S_1 + K_{s1}}X_1] \\
- N_{bac}\mu_{2\text{max}}\frac{S_2}{S_2 + K_{s2} + (S_2/K_{r2})}X_2 \\
+ k_dN_{bac}\mu_{1\text{max}}X_1 + k_dN_{bac}\mu_{2\text{max}}X_2 
\] (21)

where \( k_d \) is a decay constant. It was estimated to be 10\% of the maximum bacterial growth rates, respectively, \( \mu_{1\text{max}} \) and \( \mu_{2\text{max}} \).

After the introduction of these modifications, we optimize the model again and estimated parameters are presented in Table 2. As it may be expected, after the model modification, some parameters have varied. The change in the values obtained by adjustment reflects only the effect of the modification of the model. These changes may appear important in some cases but these changes are logical and come from the introduction in the model of the new variable \( X_T \). First, the decrease of \( k_1 \) and \( K_{s1} \) mean that only a part of the organic substrate is available for immediate degradation by biomass \( X_1 \) but with a better affinity. Thus, the remaining organic substrate is considered in the COD balance by adding \( X_T \). As a consequence, the production of \( S_2 \) by degradation of \( S_1 \) is lower, which is reflected by the decrease of \( k_2 \) and the increase of \( K_{s2} \). On the other hand, the consumption of \( S_2 \) by biomass \( X_2 \) is faster due the increase of \( k_3 \) and \( \mu_{2\text{max}} \). Concerning VFA and total inorganic carbon \( C \), it is important to recall that they play an important role in the alkalinity. Thus, the new values of \( k_3 \) and \( \mu_{2\text{max}} \) are adopted to better adjust the model to experimental alkalinity data.

The predictions of alkalinity are improved and the gradient from the bottom to the top is clearly observed; it increases from the bottom to the top, the same behavior as the bicarbonate. Moreover the gradient of bicarbonate becomes more pronounced (see Figure 6(a)–6(b)).

Figure 6 | Comparison of measured and predicted concentrations and spatial distribution into the up-flow fixed bed bioreactor: (a) bicarbonate (mEq/L) and (b) alkalinity (mEq/L) after the modification of the model.
The proposed model with the modification accounting for the role of nitrogen in the dynamic of $Z$ improves the hydrodynamic behavior of physicochemical phenomena concerning alkalinity. Alkalinity and bicarbonate are very well predicted with good accuracy.

The calibration of the proposed model using the experimental data acquired on the pilot reactor is a methodological approach to demonstrate the interest of improving the description of hydrodynamics, notably with respect to the axial distribution of the species involved in alkalinity. The model is not directly extrapolable at the industrial scale without prior calibration of the hydrodynamic model (e.g. determination of the axial dispersion rate or Péclet number $Pe$). Nevertheless, it is important to notice that the experimental study carried out in this paper was made in a pilot reactor with a relatively short axial length. In such a case, valves located for the measurement points were made only with a linear distribution and the distances between them were also relatively short. However, the modification proposed in this paper upon the model allowed predicting the axial distribution observed experimentally. At the industrial scale, with longer packed bed reactors, a higher spatial distribution is expected and then additional considerations should be done in order to better appreciate and to study this effect. For instance, a more convenient approach for modeling this kind of systems should be the use of partial differential equations (PDE). Nevertheless, the fact of demonstrating and modeling the axial alkalinity distribution in an anaerobic digester where chemical equilibrium is much faster than biological reactions, show the usefulness of this study even at the pilot scale.

CONCLUSIONS

In this work, an experimental study has been carried out in order to assess the hydrodynamic behavior of species involved in alkalinity in an up-flow fixed bed bioreactor in terms of spatial axial distribution. It has been shown that spatial distribution of alkalinity factors given only by diffusion and transport could be affected by other phenomena, either biological and/or physicochemical. Concerning hydrodynamics, and for further control purposes, a simplified model based on CSTR type reactors connected in series with recirculation has been proposed. Using this configuration, together with the anaerobic digestion AM2 model, it was possible to predict the existence of VFA, $pH$ and bicarbonate gradients along the reactor height with a very good accuracy. However, with respect to strong ions ($Z$), very closely associated with alkalinity, the absence of biological reactions in the AM2 model does not allow prediction of the same behavior. Nevertheless, based on recent literature, a modification proposing to incorporate the dynamics of the inorganic nitrogen concentration to the dynamic of $Z$, allowed improvement of the predictions of $Z$ and therefore of alkalinity. For future work, further studies, including tracers and specific inner located sensors, as well as the effect of scaling-up, are contemplated. Biomass spatial distribution studies are also planned.

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