Modeling of Anaerobic Digestion of Organic Fraction of MSW at industrial scale

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The industrial process complexity of biogas production is often a drawback to optimization. Kinetic models allowed the understanding of current phenomenon in reactors making possible the automation and control. To deepen the knowledge of the process, a bibliographic research of the scientific, technological and monitoring state-of-art of the anaerobic digestion process was made, including performance calculations to find parameters best suited for optimization. A mathematical model that describes the general degradation of organic fraction of municipal solid waste (OFMSW) in full scale reactors was then developed. The current study is based on models developed by several authors, where it was included the microbial growth kinetics, each one with their own parameters, found in the bibliography. The kinetic flux was divided into three processes: hydrolysis, acidogenic/acetogenic and methanogenic. The model simulates the decomposition of low biodegradable matter in high biodegradable matter, acid formation and production of biogas. It also includes pH calculation and physico-chemical equilibrium relationships among ionized/unionized species. As main simplification, it was considered a biphasic, liquid/gas reactor, isothermal at 35ºC with mass transfer between phases, homogenized and stirred perfectly with 5% of total solids and 50% of volatile solids by total solids. The full scale model was applied to Valorlis reactors, optimizing it by objectives, by changing the operational parameters. The model simulates a start-up with the kinetics according to the researched literature. The steady state is achieved after 6 months at which time the variable values are in accordance with the experimental values observed.

Key-words: Anaerobic Digestion, Scale-up, Modeling, Monitoring

1 INTRODUCTION

The industrial process of anaerobic degradation consists on sequential decomposition of organic matter into biogas, which is a mixture of gases composed essentially by 65-70% of CH₄, 30-35% of CO₂, H₂O and H₂S, N₂ and H₂, (Appels et al., 2008) produced by microbial biomass in oxygen deficient environments. Nowadays, the industrial process is compatible in renewable energy market.

Biogas production in Europe achieved 16.7 toe/1000 inhab in 2009. Germany is the biggest producer, with 51.5 toe/1000 inhab of primer energy, obtained from agriculture residues, like crops, and OFMSW. In 2010, Portugal did not go over 2.2 toe/1000 inhab, but had a growth rate production (EUROBSERVER, 2010).

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In the case study of Valorlis and Suldouro, the industrial process of biogas production, illustrated in Figure 1, is operated in mesophilic with low solid content (5%TS) conditions. This process is patented with BTA® technology and is divided in three steps: dry split-up of putrescible matter from unsorted residue, which will be treated after to valorise metals and plastic. Subsequently, light and heavy non-biodegradable, like grit and stones, are separated from the OFMSW in a wet pre-treatment. After, the final suspension is accumulated in an aerated suspension buffer which distributes in a parallel way into two digesters. The monitoring process follows the standard methodology (e.g. Spangers e Lier, 2006). The main measurements are the biogas rate and quality, pH, temperature, alkalinity, total fatty acids, \( \text{N-NH}_4^+ \), input and output of ST and SV.

The main goal of this Master Thesis was to develop a mechanistic mathematical model of an anaerobic degradation process of OFMSW in an industrial reactor. The model instates a simple flow with the highest biological kinetic that occurs in digesters and the most relevant phys-chemical phenomenon, in order to predict the reactor behaviour, through the operational variables and kinetic constants obtain from bibliography.

2 ANAEROBIC DEGRADATION PROCESS

The anaerobic degradation process is complex and its kinetic reaction rate depends on the subtract used in the operational conditions and the type of bacteria in the inoculum. The organic matter can be generally divided into low and high biodegradable groups. The low biodegradable is composed by heavy weight amine molecules, lipids and carbohydrates, which are hydrolysed or solubilized into high biodegradable matter or monomers like aminoacids, long chain fatty acids and sugars. Then, in the acidogenesis degradation step, the hydrolysed composts are transformed by acid-former bacteria, in absent oxygen environments,
into low weight acids (C1-C5), like valeric, caprionic, propionic, butyric and acetic acid. These composts are then degraded into lower weight molecules, mainly acetate (70%) and hydrogen and carbon dioxide (30%), in the so called acetogenesis, to be used to produce biogas in the methanogenesis step (Di-Berardino, 2006).

Due to the high mesh of different kinetic processes in anaerobic digestion, it often occurs undesired instabilities, which can induce an accumulation of toxic intermediate composts or deficient bacteria substrates leading to lower biogas production (Boe, 2000). The resolution of these problems is often a difficult obstacle to the industrial operator to overtake due to lack in scientific knowledge of the biochemical process. A good solution to this and other problems is the development of mathematical models that characterize the phenomenon with more relevance, making possible a better monitor and operation control. On the other hand, models can be useful to industry because they allow the optimization of retention time, biogas rate with a better methane quality, assess parameters performance to different inflow scenarios without damaging the real process (Appels et al., 2008).

3 MODEL DESCRIPTION

The development of the mechanistic mathematical model in this master thesis assembles different models developed by various authors (Moletta et al., 1986; Kiely et al., 1996; Markel & Krauth, 1999; Keshkar et al., 2001; Liu et al., 2007).

Due to the difficult interpretation of all transient physic-biochemical reactions, a simplification of the process was made to describe the overall industrial production. Therefore, it was considered that the global system is divided in three interdependent subsystems as describe by Markel & Krauth (1999).

This interdependence involves (1) biological conversion, (2) physic-chemical equilibrium and (3) mass transfer between liquid/gas phases. It was also considered that the reactor is biphasic, liquid/gas, isothermal at 35°C, without solid accumulation in the bottom; both phases are perfect stirred. This hypothesis can be considered valid because the suspension of the industrial reactor is highly recirculated and the temperature in the reactor is maintained constant through an external heat exchanger. The chemical and biochemical reactions occur only in the liquid phase, as it is considered that these reactions in the gas phase are negligible. The liquid phase essentially contains a mixture of complex particulate matter in suspension, hydrolysed matter, organic acids and biomass. Inert and other organic non-biodegradable materials were not considered in the mass balance because they do not interfere in the kinetic reactions.

In order to describe globally the kinetics reactions in the liquid phase volume, the degradation steps were reduced to three biomass groups (hydrolysis, acidogenesis/acetogenesis, methanoogenesis), with different kinetics constants, used to compute the decomposition flow of each substrate and intermediate consumed and produced.

The regulation function of hydrogen in the most favourable thermodynamic reactions such as the degradation of propionic and butyric acid to produce acetic acid wasn’t considered because it was assumed that production and consumed hydrogen occur instantaneously (Kiely et al., 1996)
and hydrogen partial pressure is negligible in good steady state conditions (Di-Berardino, 2006).

3.1 Model Structure

Substrates and intermediates were grouped in global state variables, according to the type of industrial experimental data provided by EFACER Ambiente during the year 2011: low biodegradable organic matter, such carbohydrates, proteins and lipids, were grouped in a variable called particular matter, \(S_p\); hydrolysed matter, such sugars, aminoacids and long chain fatty acids are presented as global hydrolysed solids variable, \(S_h\); each short acid were summarized in a total volatile acid variable, AOV. The anaerobic degradation flow is illustrated in Figure 2.

3.1.1 Liquid phase equations

Traditionally, hydrolysis has been considered as a first order reaction, for instance in ADM1 model (Batstone, 2002). Yet, this simplification doesn’t appear to comprise all the processes that occur in hydrolysis. It is observed that there are some dependencies to the hydrolytic biomass or an enzymatic activity of the particulate matter degradation rate (Vavilin et al., 2008). So, it was considered a Monod kinetic (equation 1), developed in 1940 (Gerber e Span, 2008), with an affinity to a particular limiting substrate. Cell death was also included in the model as a first order, as shown in equation 2.

As indicated in different kinetic models (Gerber e Span, 2008), inhibition effects, such acids and ammonia toxicity, are included as Andrews (1968) kinetic growth rate (equation 3), as described by Kiely et al. 1996).

The basis of all mathematical models is a mass balance for a specific state variable. This describes accumulation and reaction within a system in relation to flow across the system boundaries (see equation 4).

![Figure 2. Scheme of proposed model.](image-url)

\[
\frac{r_{S_j}}{X_j} = \frac{\mu_{max}}{K_{S_j} + S_j} \tag{1}
\]

where:
- \(\frac{r_{S_j}}{X_j}\) - biomass growth rate \(X_j\) limited to by a substrate, \(S_j\) (kg.kg\(^{-1}\).d\(^{-1}\))
- \(\mu_{max}\) - biomass maximum specific growth rate (d\(^{-1}\))
- \(K_{S_j}\) - saturation constant of limiting substrate \(S_j\) (kg. m\(^{-3}\))

\[
r_{d_j} = k_d X_j \tag{2}
\]

where:
- \(r_{d_j}\) - biomass death rate (kg.kg\(^{-1}\).d\(^{-1}\))
- \(k_d\) - death constant (d\(^{-1}\))
- \(X_j\) - biomass concentration (kg. m\(^{-3}\))

\[
r_{S_j}/X_j = \frac{\mu_{max}}{1 + \frac{K_{S_j} + S_j}{K_i + K_{S_j}} + S_j} \tag{3}
\]

Where:
- \(K_i\) – inhibitor concentration which reduces the microorganism growth at 50% (kg m\(^{-3}\))
\[
\frac{dS_i}{dt} = \frac{Q_V(s_{i,in} - s_{i,at})}{V_L} + \sum \frac{r_{s_j/X_j}}{Y_{X_j/S_j}} \tag{4}
\]

Where:
- \( Q_V \) - volumetric flow of liquid phase (m\(^3\) d\(^{-1}\))
- \( V_L \) - liquid phase volume (m\(^3\))
- \( Y_{X_j/S_j} \) - yield, as a ratio between biomass growth and substrate conversion velocity [kg(X)/kg(S)]

### 3.1.2 Gas phase equation

In the gas phase, it was considered only the methane and carbon dioxide produced in the liquid phase. With a relatively low solubility at 35°C, it was considered that methane is insoluble so the partial pressure in the gas phase is equal to the partial pressure in the liquid phase. The same argument can't be applied to CO\(_2\) because this gas is soluble and the gas/liquid phases are at equilibrium and can be computed using equation 5.

The mass transfer between phases can't be considered constant, because CO\(_2\) and CH\(_4\) production are dependent of biomass concentration. To interpret the partial pressure of each component equation 6 was considered. This equation represents the partial pressure balance described as the difference between pressure gases in both phases (Kiely et al., 1996).

\[
\frac{d(p_{G_{bi}})}{dt} = \frac{R \cdot T}{V_G} \cdot \rho_{C_{bi}} \cdot V_L - p_{C_{bi}} \cdot \frac{Q_G \cdot V_L}{V_G} \tag{6}
\]

Where:
- \( V_G \) - gas volume reactor (m\(^3\))
- \( R \) - perfect gas universal constant, (bar K\(^{-1}\) kmol\(^{-1}\))
- \( T \) - reactor temperature (K)
- \( Q_G \) - biogas rate (m\(^3\) d\(^{-1}\))

### 3.1.3 pH and Alkalinity calculation

pH has a large impact on acid-base equilibrium equations, such as undissociated fatty acids (HA/A\(^-\)) or ammonia (NH\(_3\)/NH\(_4\)\(^+\)), which have a big influence in their toxicity and of course ionic carbon (Cl\(^-\)) dissociation fraction, such as carbon dioxide, bicarbonate and carbonate (CO\(_2\)/HCO\(_3\)\(^-\)/CO\(_3\)\(^2-\)). A charge balance of the main intervenient ionic species (in terms of total concentration, as described by Smith & Chen (2006) to compute mass balance and pH) was used (equation 7) using an iterative method (Figure 3) in each time step until reach a predefined tolerance value, knowing that equilibrium kinetic are much more faster than biological processes (Batstone, 2002).

\[
\rho_{Gl_i} = k_{i,a} \cdot \left( C_{Gl_i}(I) - \frac{p_{Gl_i}}{H_{Gl_i}} \right) \tag{5}
\]

where:
- \( \rho_{Gl_i} \) - molar transference flow between liquid/gas phases (kmol m\(^3\) d\(^{-1}\))
- \( k_{i,a} \) - volumetric mass transfer coefficient (d\(^{-1}\))
- \( C_{Gl_i}(I) \) - dissolve gas in liquid (kmol m\(^3\))
- \( p_{Gl_i} \) - partial pressure of gas i (bar)
- \( H_{Gl_i} \) - Henry constant (bar kmol\(^{-1}\) m\(^3\))

![Figure 31. Iterative method to compute pH and equilibrium ionic species](image)

It was also considered that other positive or negative ionic species (Z\(_0\)\(^+\) - Z\(_0\)\(^-\)) like Na\(^+\), K\(^+\), Cl\(^-\) or SO\(_4\)\(^2-\), are cancelled.
\[ H^+ + NH_4^+ + Z_0^- = OH^- + A^- + HCO_3^- + CO_3^{2-} + Z_0^- \]  
\(7\)

Alkalinity was also calculated (equation 8) in order to interpret pH sensibility to volatile fatty acids accumulation. Alkalinity units were described in terms of CaCO\(_3\). The buffer capacity produced, at a normal pH values between 6 and 7.7, is exclusively given by carbonic acid dissociation, neglecting ammonia effect and volatile fatty acids (Di-Berardino, 2006).

\[ ALC = OH^- + HCO_3^- + 2CO_3^{2-} - H^+ \]  
\(8\)

4 IMPLEMENTATION OF MECHANISTIC MODEL

Based on the kinetic equation, it was created a global reaction mechanism of all biochemical process and established the pH influence of intermediate produced species, named hydrolysed solids and total fatty acids based on kinetic parameters referred in bibliography.

The differential equations were integrated using 4\(^{th}\) order Runge-Kutta method in MatLab Software. The resolution in time, was extended to a sufficient long period close to a stationary situation. The initial conditions correspond to a start-up simulation in a situation where solid concentration is approximately zero, with a non-null biomass concentration, as indicated in Table 1. In a situation where the industrial production was fed in a stationary condition, a cross calibration was made in order to minimize the difference between the model and industrial parameters. The chosen period that corresponds to stationary conditions was the 20-37 weeks of 2011, where \(Q_v\) is constant and equal to 50 m\(^3\)/day and \(V_L\) equal to 2000 m\(^3\) in both reactors. It was considered, as a simplification, that \(SV^{input}\) is the \(S_p^{input}\) e \(S_h^{input}\) sum and equal to 49g/l and 1g/l, respectively. It was considered that both digesters had the same design characteristics and gas volumes, equal to 100 m\(^3\) each, with a biogas rate of \(0.81 \pm 0.14\) m\(^3\)/m\(^3\)react/d, with a methane quality equal to 58\(\pm\)6%.

To compute \(CO_2\) mass transfer rate, a \(k_{i,a}\) of 100 d\(^{-1}\) (Graef e Andrews, 1973) and a Henry constant of 28,43 bar/(mol/l) (Markel e Krauth,1999) were considered as both liquid and gas phases are in equilibrium. The ammonia mass production rate is a result of protein decomposition during the hydrolysis (Di-Berardino, 2006), with a yield

**Table 1. Initial and start-up conditions.**

<table>
<thead>
<tr>
<th>(S_p)</th>
<th>(S_h)</th>
<th>VFA(_i)</th>
<th>(NH_3)</th>
<th>(X_h)</th>
<th>(X_a)</th>
<th>(X_m)</th>
<th>(CH_4)</th>
<th>(Cl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condições iniciais</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0,05</td>
<td>0,05</td>
<td>0,01</td>
<td>0</td>
</tr>
<tr>
<td>Condições de entrada</td>
<td>49</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
The differential equations of each species were solved numerically by using the fourth order Runge–Kutta method simultaneously with iterative pH calculation, in a transient state, taking into account gas mass transfer in order to interpret as much as possible the physical and chemical phenomena in the industrial reactors. Simulated operational parameters were optimized by objectives, cross-calibrated with experimental parameters, such as biogas rate, in terms of methane and CO₂ production, organic acids, ammonia, pH, alkalinity in the reactor.

5 RESULTS AND DISCUSSION

The first simulation results weren’t adequate due to the fact that kinetic parameters referred in bibliography were calibrated in batch systems, leading to a simulation with a large error compared to industrial experimental parameters. In order to optimize the model parameters, a regular calibration methodology was applied and the physical meaning was taken into account in order to interpret the phenomenon occurred in the reactor. The new parameters can be seen in Table 2.

With this calibration, it was possible to simulate and interpret correctly the main industrial biogas process, as it is shown in Figure 4 and 5. The model tends to a steady state condition after 180 days (6 months) of the start-up and achieves the experimental parameters value, with a 10% error, as illustrated in Table 3.

### Table 2. Kinetic parameters, used in the proposed model (adapt from Liu et al. (2007)) and new constants after calibration.

<table>
<thead>
<tr>
<th>Kinetic constant</th>
<th>( \mu_{\text{max}} ) [d⁻¹]</th>
<th>( K_a ) [d⁻¹]</th>
<th>( K_s ) [g(Sᵢ)/l]</th>
<th>( Y_{\text{cons}} )</th>
<th>( Y_{\text{prod}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( X_h )</td>
<td>0.3</td>
<td>0.06</td>
<td>10</td>
<td>0.2</td>
<td>0.22</td>
</tr>
<tr>
<td>( X_a )</td>
<td>(0.18)</td>
<td>0.04</td>
<td>(0.66)</td>
<td>0.188</td>
<td>2.65</td>
</tr>
<tr>
<td>( X_m )</td>
<td>0.6</td>
<td>0.016</td>
<td>0.003</td>
<td>0.08</td>
<td>-</td>
</tr>
<tr>
<td>CO₂</td>
<td>-</td>
<td>-</td>
<td>0.0208</td>
<td>-</td>
<td>0.08</td>
</tr>
<tr>
<td>CH₄</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>32</td>
</tr>
</tbody>
</table>

\( \mu_{\text{max}} \) \( K_a \) \( K_s \) \( Y_{\text{cons}} \) \( Y_{\text{prod}} \) \[g(X_i)/g(S_i)] \[g(S_i)/l]

\( () \)-changed values; *-acids inhibition; **-ammonia inhibition

In Figure 4 it is illustrated the biogas quality rate simulation in a start-up scenario. The simulation shows that in the beginning, the CO₂ rate is bigger than methane because the hydrolysis and acid-formers growth is greater than methane-formers, so when this bacteria group achieves a certain biomass concentration, the methane production increases rapidly, related to the stimulator effect of acetate consumption. It was achieved a maximum yield of 1 m³/m³_react/d with a 50% methane quality, on day 130, stabilizing at 0.85 m³/m³_react/d with a 60% methane quality after 180 days.

Due to the low alkalinity, the buffer capacity was not enough to maintain the pH stable in the beginning of the start-up, but as time passed the buffer capacity increased and the pH responded well to the increase of acid concentration.
Table 3. Comparison between model values at a steady state condition and industrial experimental parameters in a period where the organic load was constant and equal to 1.2 kg VS/m³react/d.

<table>
<thead>
<tr>
<th>Model (St. State)</th>
<th>Valorilis CVO</th>
</tr>
</thead>
<tbody>
<tr>
<td>VS₃out (g/L)</td>
<td>17</td>
</tr>
<tr>
<td>ALK (g CaCO₃/L)</td>
<td>13</td>
</tr>
<tr>
<td>VFAₐ (g CH₃COOH/L)</td>
<td>0.06</td>
</tr>
<tr>
<td>pH</td>
<td>7.6</td>
</tr>
<tr>
<td>N – NH₄⁺ (g/L)</td>
<td>1.5</td>
</tr>
<tr>
<td>Biogas (m³/m³/dia)</td>
<td>0.85</td>
</tr>
<tr>
<td>%Methane</td>
<td>60</td>
</tr>
</tbody>
</table>

6 CONCLUSIONS

The proposed model is valid in a steady state scenario for the conditions initially considered and simulates the anaerobic digestion process with an acceptable error, lower than 10%. The goal of the study was achieved because the model interprets correctly the interdependency of biological conversion processes, equilibrium between chemical species and charge balance, such pH...
calculation, and mass transfer between liquid/gas phases.

Although the adjustment is acceptable, the large changes on the initial kinetic parameters collected in bibliography can lead to an uncertain error. Moreover, the model tends to be rigid in scenarios where simplifications can’t be neglected, like temperature and mixture changes or enhancement of hydrogen partial pressure scenarios, which possibly results in a different steady state condition due to the non-linear system. However, in terms of industrial application, the proposed model represents an opportunity to optimize monitoring and operational process efficiency, support strategic decisions and include sub-models, because the model is scalable.

For future work it is interesting to access other bibliographic kinetic parameters to different scenarios and validate the model in order to maximize the profit of this important industrial tool.

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