Anaerobic Digestion - Process Data Analysis

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Abstract

Energy recovery from waste tends to decrease problems, such as increased energy consumption and waste management, by using waste to produce energy. Anaerobic digestion is one such technology, producing energy without greenhouse gas emissions from biodegradable waste. Although widely used, anaerobic digestion is a complex process and there is some difficulty in predicting and optimising the process, so there is a continuous study of it through mathematical modelling. This work aims to develop a mathematical model based on process data that describes the operation and behaviour of an anaerobic digester over time. The model was developed based on the ADM1 model developed by IWA. The model was calibrated with a set of operation data, and after validation, the same model was tested for a different set of data in order to understand if it remained valid. From the results obtained it was possible to understand that there is a lack of input data, mainly of the substrate composition, so that the model can predict correctly. However, for the existing data, the model obtains acceptable errors and is able to predict the trends. By re-calibrating the model it was possible to conclude, that with low input information, a model that adjusts over time can be beneficial. The best results were obtained when there was information about the initial substrate, such as COD.

Keywords

Waste to energy, Anaerobic Digestion, Municipal solid waste, Mathematical Modelling, ADM1, Operation data.

Contents

1. Introduction

Energy supply and waste management are two of the biggest problems that our planet faces. With the continued growth of the population, industrialisation, improvement of living standards, and high consumption of products and energy, waste production also tends to increase. Although there has been much progress in recent decades, remains a growing problem and it crucial to be solved. [1, 2, 3]

The rapid growth of energy consumption over the years, and the need to match it with energy accumulation and conversion, have led to a transition from biomass (wood) to fossil fuels (coal, natural gas, etc.). This rapid growth had spotlighted energy sources that are ready for immediate use with preferably no pre-process. Energy consumption is expected to continue to grow and the intensive use of fossil fuels results in significant greenhouse gas emissions and, consequently, climate changes. Over the past few decades efforts have been made to solve this problem with developments in renewable energies. Nevertheless, there is still a long way to go since the primary source of energy in the world is still, by far, fossil fuels. [2, 3]

Waste management's beginnings were only towards human excrement and sewage, which caused many health problems. Later progressed to municipal solid waste, which is increasingly worried about gaseous wastes, like CO_2, CH_4 and others (NOx, Sox, etc.), the environment, and public health. [2]

Energy and waste problems are connected in numerous ways, and waste to energy (WTE) can address these two critical issues. WTE is the direct conversion of waste to steam and electricity. Organic waste, mostly composed of biomass, is a renewable resource. It has been used for energy generation since it is a feasible and affordable way to produce energy, mainly in developing countries. It also has the advantage of not emitting carbon dioxide into the environment, thus it is favourably compared to other energy production methods. These types of technology, which are in continuous development, pretend to extract energy in the most efficient way while reducing waste. To produce power at optimal conditions it is necessary to understand the underlying reaction sequences

(mechanisms) and enable the technologies, in order to be as efficient as possible, because there is still much work to be done to understand the whole mechanism. In the last years, the Anaerobic Digestion (AD) of municipal solid waste (MSW), which is a technology of WTE, has become one of the most attractive renewable energy pathways. [2, 3]

AD is a natural biochemical process that degrades complex organic matter in the absence of oxygen, obtaining biogas (mainly CO_2 and CH_4) and digestate as the two main products. Biogas, in addition to methane and carbon dioxide, also contains semi-harmful contaminants such as hydrogen sulphide and ammonia, but in much smaller amounts ($<11\%$ (v/v)). The production of these gases is a product of the sulphur and nitrogen contents of the feedstock, which are also nutrients required by the process microorganisms, so they cannot be eliminated. [1, 3, 4] Some examples of natural environments where it occurs (some low-oxygen niches) are marshes, marine water sediments, etc. AD processes allow the treatment of waste to reduce the volume and load, producing biogas and digestate. [1, 5, 6, 7]

It is predicted that AD will play an increasingly important role in renewable energy production, given that biomass is a renewable resource and due to its circular economy. [3, 8] This process can be used both at the industrial and domestic levels. [1, 6, 7]

AD is a well-establish process and used for several decades. Still, due to the substrate variability, microbial complexity, and complex physical and chemical interactions in the process, the optimal design of digesters for maximum yield and prediction of the performance is still a challenge. There is also a lack of knowledge about the mechanisms of AD. [5, 9]

With the increase of industrial interest, research and development were intensified. Mathematical modelling is one of the most discussed aspects, intending to identify the most relevant models to optimise digesters biogas formation. There is continuous development and testing of new digesters, new combinations of AD substrates, feeding systems, as well as other equipment's. [5, 6]

Mathematical modelling aims to estimate characteristic parameters of the feedstock and process conditions to forecast the system's evolution, the performance obtained, and fermentation speed. It is a helpful tool to improve the design and efficiency of AD systems. [10]

Over the years, the variety and complexity of mathematical models developed have increased. Several models have been developed in the last two decades, and a diversity of approaches to modelling and parameter identification have been used, creating available models with a precise nature. [5, 8, 9, 11]

The first model was proposed by Andrews and Pearson [12], and had in consideration two bacterial groups, namely acid and methane microorganisms, and the substrate was presumed to have dissolved organic substances. [8, 13] The subsequent models considered biogas production using only the methanogenesis step, as other organisms had inhibitor effects. Denac et al. [14] added to this model the conversion of propionate to acetate by including acetogenesis. [8, 13] The last models developed were based on the four populations (hydrolytic, acidogenic, acetogenic and methanogenic microorganisms), predicting the change of VFA, pH-value, and biogas production. [13] The kinetics steps of these models were based on Monod type kinetics [15], which consider a single growth-limiting substrate. [8, 13]

The exponential model was used to describe the cell concentration in its growth phase and rests on the theory that the speed of growth in an instant is proportional to the concentration of existing cells. However, the cell concentration variation is not described accurately as the substrate is consumed and the stationary phase approaches. [5]

Microbial growth and substrate consumption rates (both dependants on the growth-limiting substrate concentration) are the base of the kinetic models. The nutrients on the substrate are presumed to be adequate, and inhibition is also taken into consideration. Several models were developed, presenting complex kinetics and particular applications. [8, 16]

The Anaerobic Digestion Model No.1 (ADM1) was developed by the International Water Association (IWA) Task Group [11] with the objective of creating a model as widely applicable as possible for anaerobic processes. This will not be as accurate as some specific models developed for certain applications because of its generic nature. [16] The components are expressed based on their COD and consider both biochemical and physicochemical processes, assuming perfect substrate mixture. In this model, substrate represents only the degradable COD, since that a significant fraction of the input COD may be anaerobically non-biodegradable. [11, 16]

This master thesis aims to develop a preliminary mathematical model to describe the operation of anaerobic digesters and predict the digestor's behaviour over time. This model will have as bases operational data of the units in the study and standard models existing in the bibliography.

2. Implementation

2.1 Methods and procedure in this work

The numerical model developed during this work was performed using the software *Excel*. The flowchart presented in Figure 1 explains the work path and procedure applied. After selecting the model bases and parameters, the model was formulated based on initial conditions, mainly presenting experimental and theoretical values. Then, based on the first set of data (operation data), the parameters defined initially from theoretical values were estimated by consecutively carrying out simulations until the experimental and theoretical values present similar behaviour. Once the calibration was finished, a second model validation was carried out based on the second data set.

2.2 Assumptions and model description

The model was developed, having in consideration an ideal reactor to describe the apparent behaviour. However, the real

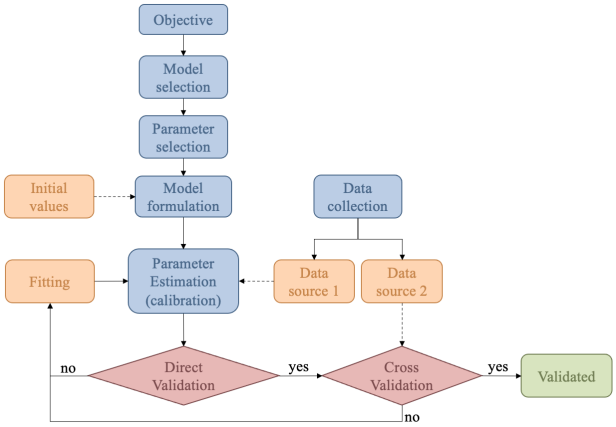

Figure 1. Flowchart of the applied methods and procedures in this work.

digester is not ideal given that temperature and concentration present gradients and other physical and chemical occurrences. Nevertheless, the reactor was considered perfectly agitated, i.e., temperature or concentration gradients were not considered.

The model was developed based on some assumptions and simplified equations of model ADM1 to facilitate the construction and operation (presented below), as there are some limitations in terms of existing data. One of the most relevant limitations is the lack of data characterising the input, such as substrate composition. The information flow existing in the model, i.e., the model input data and results obtained from the model, is as follows: the model receives data on temperature, input flow and digester level, and provides information on biogas flow, COD, Ntot, Ptot and % CO_2 and CH_4 in biogas.

Model assumptions:

- CSTR reactor;
- Mesophilic digestion (reference temperature of 35ºC);
- First-order reactions;
- Constant density (Table 1);
- COD flux (Figure 2);
- Inhibitions were not considered;
- The ratio of 0.47 to CO_2/CH_4.

In addition, some parameters were also arbitrated based on theoretical values for parameters that did not present experimental values, which are presented in Table 1.

The mass balance to the liquid phase was done for each component individually, according to Equation 1, for the components presented in COD flux (Figure 2).

$$\frac{dX_i}{dt} = \frac{q_{in}}{V_{liq}}(X_{i,in} - X_i) + \sum \gamma_j v_{i,j} \quad (1)$$

Table 1. Assumed parameters for the development of the model.

PARAMETER	VALUE	REFERENCE
ρ_{dig} (kg/m^3)	1 000	-
ρ_{bio} (kg/m^3)	1.12	-
$L_{P/C}$	0.02	Based on [17, 18]
$P_{N/C}$	0.26	Based on [17, 19]
$P_{\%Li}$ (%)	0.25	Based on [18, 20]
$N_{\%Pr}$ (%)	0.3	Based on [20, 21]

where q_{in} is the feed flow, V_{liq} is the volume of the liquid part inside the digester, $X_{i,in}$ and X_i are the concentration of each component i in the inlet and in the digester, $v_{i,j}$ is the biochemical rate coefficients, and γ_j is the kinetic rate equations for the components (i).

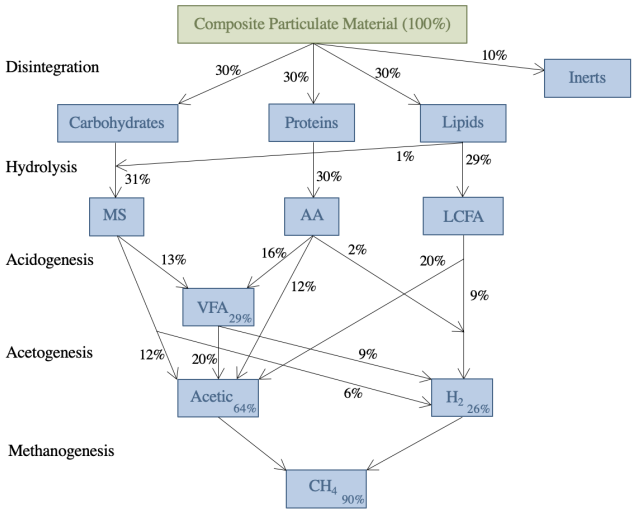

Figure 2. COD flux of a particulate composite considered for the development of the model.

2.3 Model Formulation

The model formulated was based on the ADM1 model, given that it is the most generic and applicable model, and it is a model that can be adapted and easily modified. This is an essential point since the available data and parameters are limited, thus it is necessary to adapt the model. Bellow are presented the initial conditions that were taken into consideration and from where some of the variables were defined. It is important to refer that in the stoichiometry of the disintegration, the values in the table will not be used fixedly but will be one of the parameters fitted in the model calibration.

The mass balances were performed in terms of COD, so it was necessary to know the initial value that the composite presents. This value has not been measured, so it was necessary to estimate it from the available data. This calculation has in consideration the chemical composition of the composite that can vary with the substrate, which is unknown. Hence, the initial COD is a variable parameter. The following composi-

tions of macromolecules, shown in Table 2, were assumed for the chemical composition of the composite. [19] Moreover, Equations 2 and 3 represent the global equations of AD. [22]

Table 2. Chemical composition of the macromolecules proteins, carbohydrates, and lipids. [19]

Proteins	$C_1H_{2.52}O_{0.87}N_{0.26}$
Lipids	$C_1H_2O_1$
Carbohydrates	$C_1H_{2.85}O_{0.575}$

$$C_cH_hO_o + yH_2O \rightarrow xCH_4 + (c-x)CO_2 \quad (2)$$

$$C_cH_hO_o + yO_2 \rightarrow \frac{h}{2}H_2O + cCO_2 \quad (3)$$

where x is defined by Equation 4:

$$x = \frac{c}{2} + \frac{h}{8} - \frac{o}{4} \quad (4)$$

The initial COD calculation process will be demonstrated below for an example where the composite composition is as follows: 99.8% of carbohydrate, 0.18% of proteins, and 0.009% of lipids. It was possible to deduct Equations 5 and 6, which represents the AD of this composite:

$$C_1H_2O_1 + H_2O \rightarrow 0.5CH_4 + 0.5CO_2 \quad (5)$$

$$C_1H_2O_1 + O_2 \rightarrow H_2O + CO_2 \quad (6)$$

From Equation 5, it is possible to confirm that from 1 mol of CH_2O it is obtained 1 mol of gas (CH_4 and CO_2), that according to the constant of perfect gases under atmospheric conditions, 1 mole of gas corresponds to 22.4L of gas. To oxidise 1 kg of composite, 1 kg of oxygen is necessary, which will produce the correspondent to 33.3 moles and 746.7L of gas. So, the methanogenic potential is 0.75 m^3 biogas/kg COD. From equation 7, it is possible to estimate the initial COD of a composite, that will be used as the concentration of composite in terms of COD, $X_{c,in}$:

$$0.75\frac{m^3 gas}{kgCOD} \cdot X_{c,in}\frac{kgCOD}{m^3 feed} \cdot q_{in}\frac{m^3 feed}{day} = q_{bio}\frac{m^3 biogas}{day} \quad (7)$$

where q_{bio} is the biogas flow.
The value of the initial COD was arbitrated (and used fixedly) from an average of feed and biogas flow, and the value obtained was 35 kg/day.
To obtain the amount of nitrogen and phosphorous at the output to compare theoretical and experimental values, it was also necessary to define them from the model components. Thus, equations 8 and 9 represent the mass balance:

$$\frac{dNtot}{dt} = N_{tot,i} - N_{tot} = (q_{in} \cdot \rho_{dig} \cdot N_{\%Pr} \cdot C_{pr}) - N_{tot} \quad (8)$$

where $N_{tot,i}$ and N_{tot} are the inlet total nitrogen flow and total nitrogen flow, respectively, ρ_{dig} is the digestate density, $N_{\%Pr}$ is the composition of proteins in nitrogen and C_{pr} is the composition of the composite in proteins.

$$\frac{dPtot}{dt} = P_{tot,i} - P_{tot} = (q_{in} \cdot \rho_{dig} \cdot P_{\%Li} \cdot C_{li}) - P_{tot} \quad (9)$$

where $P_{tot,i}$ and P_{tot} are the inlet total phosphorus flow and total phosphorus flow, respectively, $P_{\%Li}$ is the composition of lipids in phosphorus and C_{li} is the composition of the composite in lipids.
Moreover, Ntot and Ptot can be calculated from Equations 10 and 11 in the first instance before considering the steady-state. Then, the successive ones are calculated from the variation.

$$N_{tot} = \frac{q_{dig}}{\rho_{dig}} \cdot P_{N/C} \cdot (X_{Pr} + X_{aa}) \quad (10)$$

$$P_{tot} = \frac{q_{dig}}{\rho_{dig}} \cdot L_{P/C} \cdot X_{li} \quad (11)$$

where $P_{N/C}$ is the ratio between nitrogen and carbon in proteins, $L_{P/C}$ the ratio between phosphorus and carbon in lipids, and X_{aa} the concentration of amino acids.
The final COD in the digested was also calculated from theoretical values of the model in order to be possible to compare with the experimental values, from Equation 12:

$$COD = \frac{q_{dig}}{\rho_{dig}}[X_c + X_{ch} + X_{pr} + X_{li} + S_{ms} + S_{aa} + S_{LCFA} + S_{VFA} + S_{ac}] \quad (12)$$

where X_c, X_{ch}, X_{pr}, X_{li} are the concentration of particulate components composite, carbohidrates, proteins and lipids, respectively, and S_{ms}, S_{aa}, S_{LCFA}, S_{VFA}, S_{ac} are the concentration of soluble components monosacharides, amino acids, long chain fatty acids, volatile fatty acids and acetate, respectively.
The temperature variation in the digester was considered using the Arrhenius law, described in Equation 13, which will allow a fitting of the kinetic constants with temperature.

$$k = k_{ref} \cdot exp\left[-\frac{Ea}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right] \quad (13)$$

where k and k_{ref} are the kinetics constant at a given temperature and at a reference temperature, respectively, Ea is the activation energy, R is the ideal gas constant, and T and T_{ref} are the given temperature and the reference temperature, respectively.
The COD flux defined does not consider the production of CO_2, as it only considers the production of CH_4 and H_2 gases. Therefore, the concentration of CO_2 was defined as a function of CH_4. Furthermore, from the experimental data of these parameters over a year, it was possible to verify that they present an approximately constant ratio, so it was defined in this way (Equation 14).

$$S_{CO_2} = 0.47S_{CH_4} \quad (14)$$

The amount of biogas exiting the digester (q_{bio}) was calculated (Equation 15) having in consideration the production of the three components considered (CH_4, H_2 and CO_2) and the volume of biogas inside the digester, that is the biogas retained inside the digester.

$$q_{bio} = biogas\ produced - biogas\ retained \quad (15)$$

Initial values

For the model formulation, literature values were considered that later will be fitted with the calibration of the model. Table 3 presents the values that were assumed for the kinetic constants. [11] It is essential to mention that the kinetic constants referred to in the table are to a reference temperature of 308.15K and will be fitted for the actual temperature, as will be further explained. [11] The initial values of the Ea for each reaction was 20 Kcal/mol, and the composition of the composite was 30% of carbohydrates, proteins and lipids, and 10% of inerts. [11]

Table 3. Initial values for the kinetic constants. [11]

PARAMETER	VALUE	UNIT
k_{dis}	0.40	
$k_{hid,ch}$	0.25	
$k_{hid,pr}$	0.20	
$k_{hid,li}$	0.10	
$k_{acid,ms}$	30	d^{-1}
$k_{acid,aa}$	50	
$k_{acid,LCFA}$	6	
$k_{acet,VFA}$	20	
$k_{met,ac}$	20	
$k_{met,h2}$	20	
$Ea_{acet,VFA}$	20	
$Ea_{met,ac}$	20	
$Ea_{met,h2}$	20	

2.4 Dynamic model fitting and validation

Once the model is defined, it is necessary to carry out the calibration and validation with the first set of data and then the cross-validation with the second set.

The calibration of the model was made through the use of the *Solver* tool of *Excel* to minimise the squared difference between experimental and theoretical values. This process was carried out through several consecutive and iterative steps until the results were stable:

- Step 1 – fitting of the composite composition;
- Step 2 - fitting of the kinetic constants at the reference temperature;
- Step 3 - fitting of the activation energy of each reaction.

The third step, the fitting of the activation energy of each reaction, depends on the digesters temperature. Despite not being expected good results from this fitting, since the temperature data present little variation, this was performed in order to analyse the results.

For the validation, the difference between the experimental and theoretical values was compared, and the relative error of the model regarding each parameter in the analysis was calculated. Then, in the cross-validation, the same was done as in the validation, together with an addition of a new calibration in order to assess the possibility of improvement.

3. Results and Discussion

3.1 Model Formulation

The model was formulated with the initial values presented in Table 3. The results obtained are graphically represented in Figure 3.

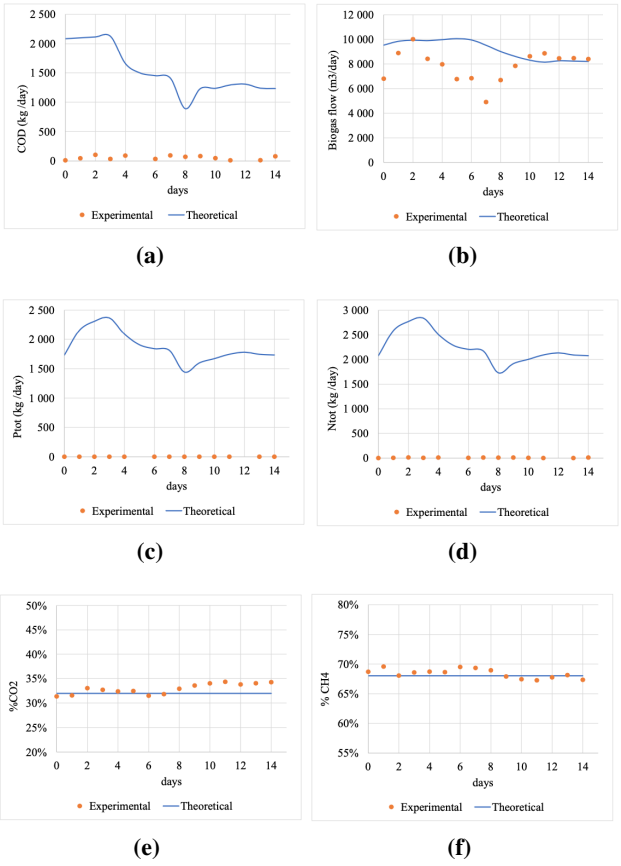

Figure 3. Comparison between experimental and theoretical values of a) COD, b) biogas flow, c) Ptot, d) Ntot, e)% of CO_2 and f)% of CH_4 in biogas, after model formulation (at initial conditions).

The results obtained make it possible to understand that the theoretical model with the literature values conditions is quite far from reality. The closest parameters are $\%CO_2$ and $\%CH_4$, which already present a behaviour very close to reality, with an

error between 1.2% and 4.3%. However, despite having values similar to reality, these parameters do not show variations, since the CO_2 concentration is not defined by the kinetics in the model but rather as a proportion of CH_4.

3.2 Model Calibration and validation

As mentioned, for the validation of the model, the three steps presented above (composite composition, kinetic constants and activation energy calibration) were performed iteratively until stable results were obtained. The results are presented in Figure 4, and Table 4 contains the obtained errors.

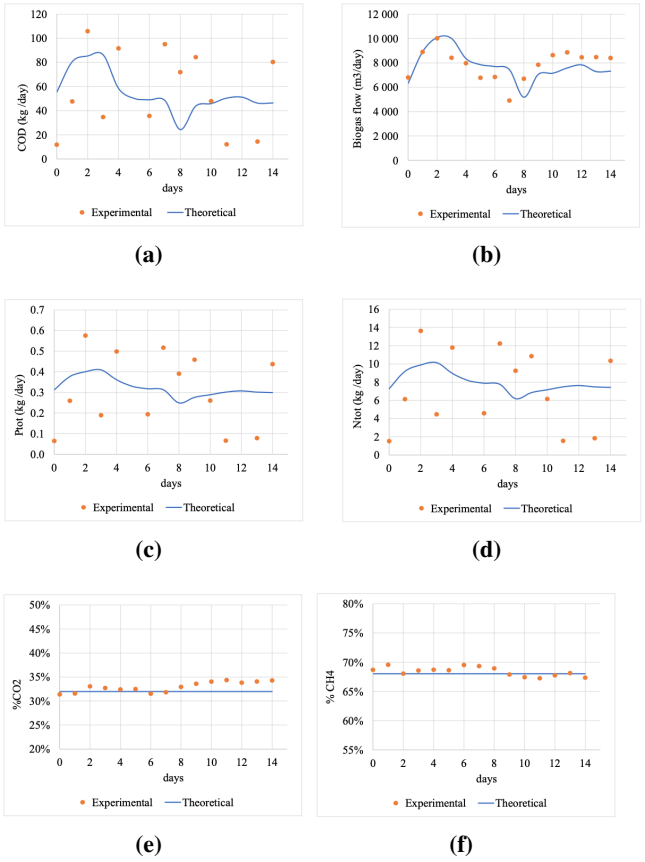

Figure 4. Comparison between experimental and theoretical values of a) COD, b) biogas flow, c) Ptot, d)Ntot, e)% of CO_2 and f)% of CH_4 in biogasafter the calibration with data set 1.

Table 4. Error between the experimental and theoretical data after the calibration with data set 1.

Error	COD (kg/day)	q_{bio} (m^3/day)	Ptot (kg/day)	Ntot (kg/day)	%CO_2 and %CH_4
Quantity	36.22	1 183	0.18	4.20	<1.4
Percentage value (%)	64.2	8.0	57.8	57.8	<4.3

Relevant operating disturbances can be changes in average residence times, working temperature or even in the raw material feeding, and only the flow rate and temperature are considered in the model. Therefore, it would have been essential to have some characterisation of the raw material, for example, of close analysis and potential for biogas production. Since there is no such data, an analysis was carried out in order to understand the fluctuation existing in the parameters when the supply is stationary, that is, the variation of the parameters that are influenced by factors that are not considered in the model. This fluctuation is the error that can be considered acceptable in the model.

For the conclusions of this analysis to be as accurate as possible, two periods in which the feed flow is stationary were analysed. In Figure 5, the first period is present, between days 182 and 190, and in Figure 6, the second one, between days 326 and 340. The fluctuations of each parameter are also summarised in Table 5.

Table 5. Fluctuations of Ptot, Ntot and COD parameters during two distinct stationary periods.

Period (days)	Δ Ptot (kg/day)	Δ Ntot (kg/day)	Δ COD (kg/day)
182-190	1.1	43.2	123.7
326-340	1.5	14.3	40.1

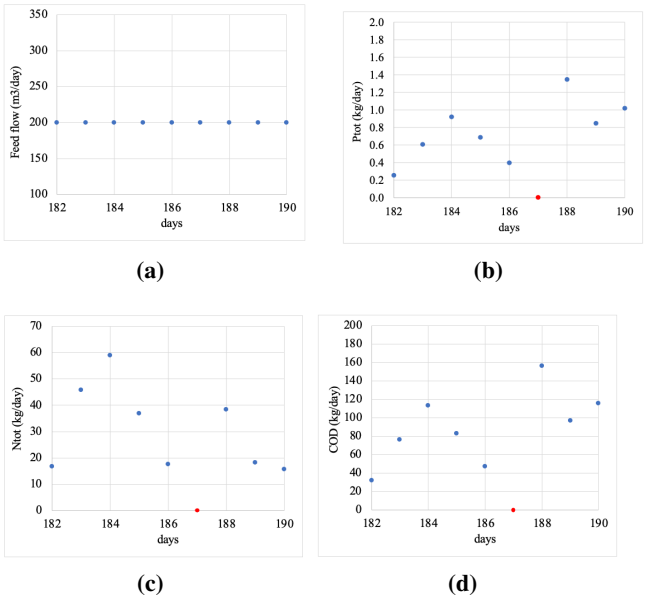

Figure 5. Experimental values of the parameters a) feed flow, b) Ptot, c) Ntot and d) COD between the days 182 and 190. Dots marked in red represent unused data to calculate the fluctuation, as it has been considered unreliable.

From the results obtained, it is possible to verify that the fluctuation of the values is very significant, presenting values higher than the error presented by the model, namely: Ptot presented an error of 0.18 kg/day and a minimum fluctuation of 1.1 kg/day; Ntot with an error of 4.20 kg/day and a minimum fluctuation of 14.3 kg/day; and COD with an error

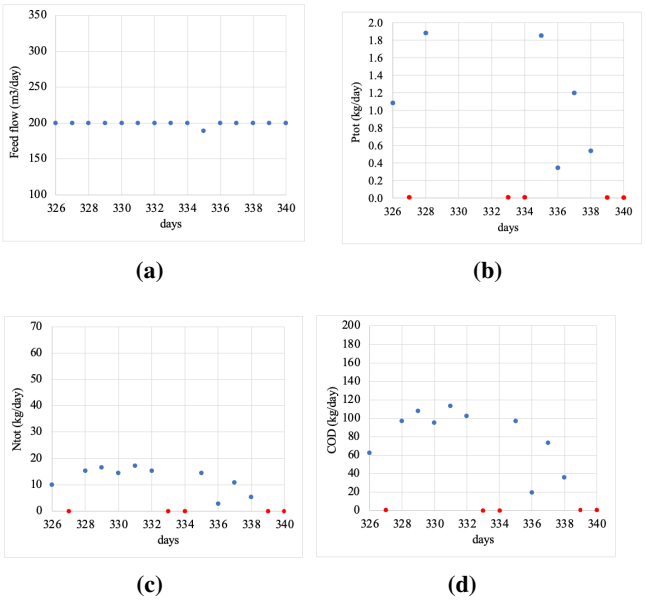

Figure 6. Experimental values of the parameters a) feed flow, b) Ptot, c) Ntot and d) COD between the days 326 and 340. Dots marked in red represent unused data to calculate the fluctuation, as it has been considered unreliable.

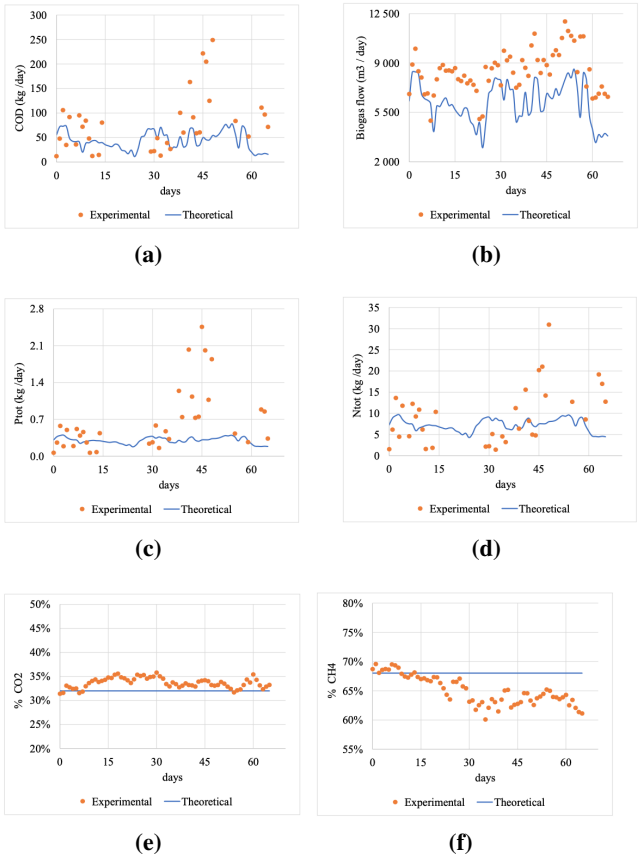

Figure 7. Comparison between experimental and theoretical values of a) COD, b) biogas flow, c) Ptot, d) Ntot, e)% of CO_2 and f)% of CH_4 in biogas, for the cross-validation with data set 2.

of 36.22 kg/day and a minimum fluctuation of 40.1 kg/day. Therefore, it is possible to conclude that the model fits the experimental data in COD, Ntot and Ptot parameters since the theoretical predictions are within the data fluctuation range.

The biogas flow presents a good forecast by the model, taking into account the available data and correctly predicting most trends. However, it has an error of about 8.0% in the forecast. As mentioned before, it can be, in part, associated with the 1-day delay forecast and the lack of data in the model's input data regarding the substrate composition.

The parameters $\%CO_2$ and $\%CH_4$ in biogas have a reduced error, but since only the amount of CH_4 is calculated and CO_2 is obtained from a ratio with CH_4, their relative amounts in the biogas remain constant, showing no variation with experimental values. Nevertheless, even if CO_2 was calculated, its prediction and CH_4 would never be accurate as they depend on the composition of the inlet, such as COD, Ntot and Ptot.

3.3 Cross-validation

The cross-validation was carried out in order to verify if the model was also able to make a correct prediction for a different and more extensive set of data, having been used data set 2 for this verification. The results obtained are presented in Figure 7, and in Table 6 the obtained errors.

Cross-validation of the model allowed us to realise that, despite a more significant forecast error, the model continues to be valid since it predicts the trends and all the parameters within an acceptable and explainable error. However, the results presented may demonstrate that a model with fitting over time could be favourable.

The model continues to predict the trends of biogas flow correctly, with a 19.4% error associated, as before, even though it had a forecast delay of 1-day and does not consider the substrate's composition. This error increase in the amount of biogas demonstrates a need for additional data in the model's input. In addition, it opens up the possibility that a model that fits overtime may be advantageous for the case.

COD, Ntot and Ptot also show a significant increase in error. However, when evaluating the error concerning the previously studied fluctuation, only the COD is not within the minimum fluctuation but rather within the maximum fluctuation. Ptot presents an error of 0.7 kg/day and a minimum fluctuation of 1.1 kg/day; Ntot presents an error of 7.32 kg/day and a minimum fluctuation of 14.3 kg/day; and COD with an error of 65.93 kg/day and a minimum and maximum fluctuation of 40.1 and 123.7 kg/day.

It is possible to conclude that the model fits the experimental data in Ntot and Ptot parameters since the theoretical predictions are within the minimum data fluctuation range, and COD also fits, although it is only within the upper value of fluctuation. However, some errors can be considered as well. The parameters % of CO_2 and $\%CH_4$ in biogas present a more

considerable error, although it remains lower than 6%.

Table 6. Error between the experimental and theoretical data for data set 2 (cross-validation of the model).

Error	COD (kg/day)	q_{bio} (m^3/day)	Ptot (kg/day)	Ntot (kg/day)	$\%CO_2$ and $\%CH_4$
Quantity	65.93	1 632	0.70	7.32	< 3.82
Percentage value (%)	84.5	19.4	104.3	77.6	5.9

Re-calibration

A re-calibration of the model was made with data set 2 to analyse the differences obtained. The results are presented in Figures 8, and in Table 7 contains the obtained errors.

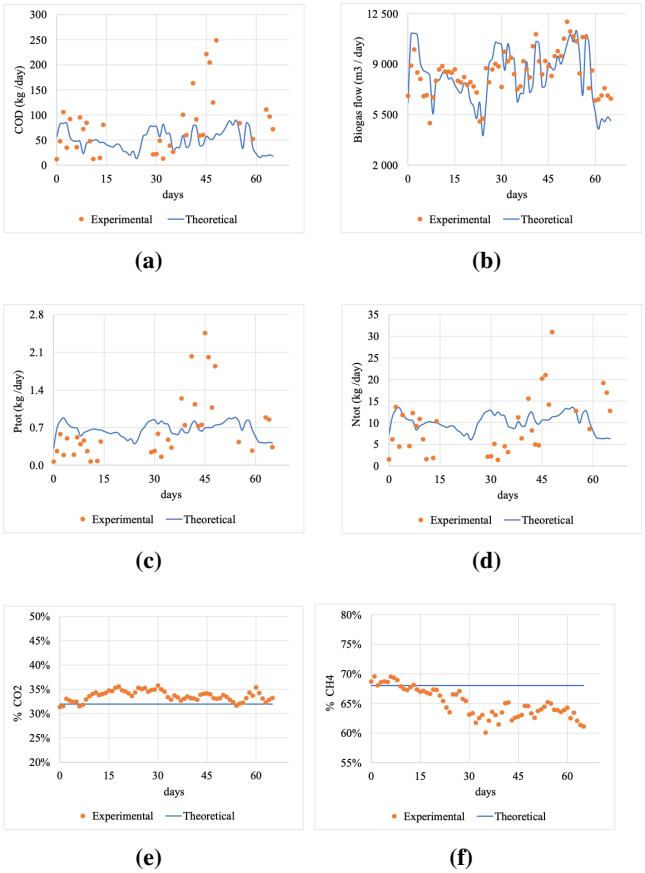

Figure 8. Comparison between experimental and theoretical values of a) COD, b) biogas flow, c)Ptot, d)Ntot, e)% of CO_2 and f)% of CH_4 in biogas, after the re-calibration of the model for data set 2.

From the re-calibration results, it is possible to conclude that the model presents improvements in almost all the parameters. It is also possible to conclude that a model with fitting over time would improve the prediction capacity, as there is a lack of data in the model input.

Table 7. Error between the experimental and theoretical data after the re-calibration of the model for data set 2.

Error	COD (kg/day)	q_{bio} (m^3/day)	Ptot (kg/day)	Ntot (kg/day)	$\%CO_2$ and $\%CH_4$
Quantity	64.19	1 397	0.60	7.22	< 3.82
Percentage value (%)	82.3	16.6	89.8	76.5	5.9

As referred before, COD, Ptot and Ntot vary with the composition of the substrate, so for this model, it is expected that there is an improvement in the fitting of the composition for each different set of data. However, if the feed composition were one of the input variables, this would not be expected to happen.

3.4 Information re-feeding

Information re-feeding was performed in order to understand if the model would obtain better results if it had more data. In this way, the initial substrate COD was calculated from Equation 7, becoming one more variable information in the model's input.

The results obtained after the information re-feeding are presented in Figures 9 and 10 for data set 1 and data set 2 (before the re-calibration), respectively, and in Table 8, the obtained errors.

Table 8. Error between the experimental and theoretical data after the information re-feeding, for data set 1 and data set 2.

Error	COD (kg/day)	q_{bio} (m^3/day)	Ptot (kg/day)	Ntot (kg/day)	$\%CO_2$ and $\%CH_4$
data set 1					
Quantity	36.9	1 129	0.18	4.18	<1.40
Percentage value (%)	65.4	7.7	57.8	57.6	<4.2
data set 2					
Quantity	57.9	1 226	0.60	7.28	< 3.82
Percentage value (%)	74.3	14.6	89.8	77.2	5.9

From the results obtained is possible to conclude that the prediction of the model presents a significant improvement. For data set 1, the improvement is only significant for the biogas flow, showing an improvement from 11.9% to 7.7% of error between experimental and theoretical data. Analysing the graphs it is possible to verify that the model predicts the biogas flow fairly correctly, which was not the case before at all moments. The error obtained is directly related to the 1-day forecast delay. If the forecast did not present a 1-day delay, the error between experimental and theoretical data would only be 0.1%, which demonstrates the accuracy of the forecast.

On the other hand, data set 2 presents significant improvements in COD, Ptot, Ntot, and biogas flow. The improvement

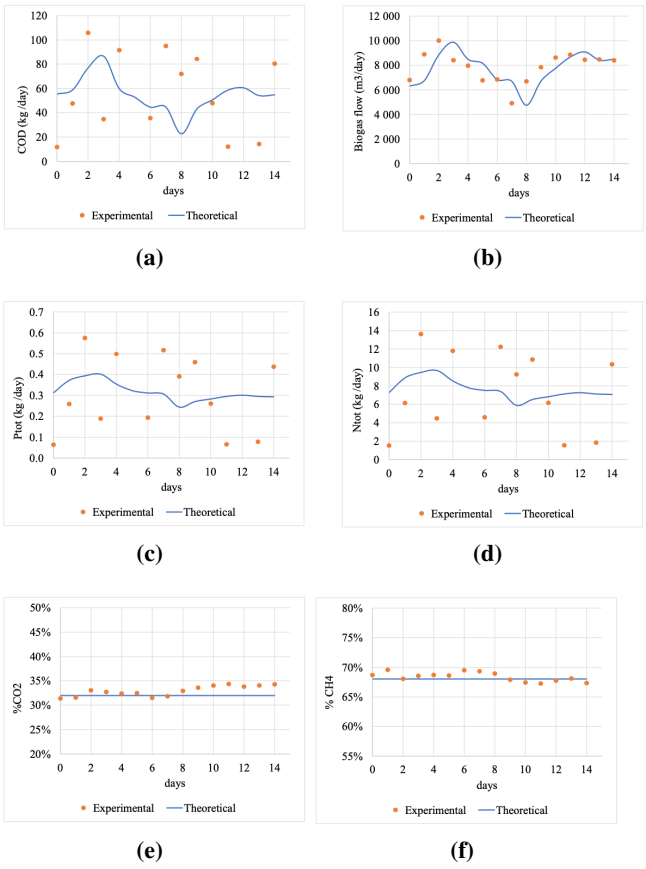

Figure 9. Comparison between experimental and theoretical values of a) COD, b) biogas flow, c) Ptot, d) Ntot, e)% of CO_2 and f)% of CH_4 in biogas for data set 1 after the re-feeding of information.

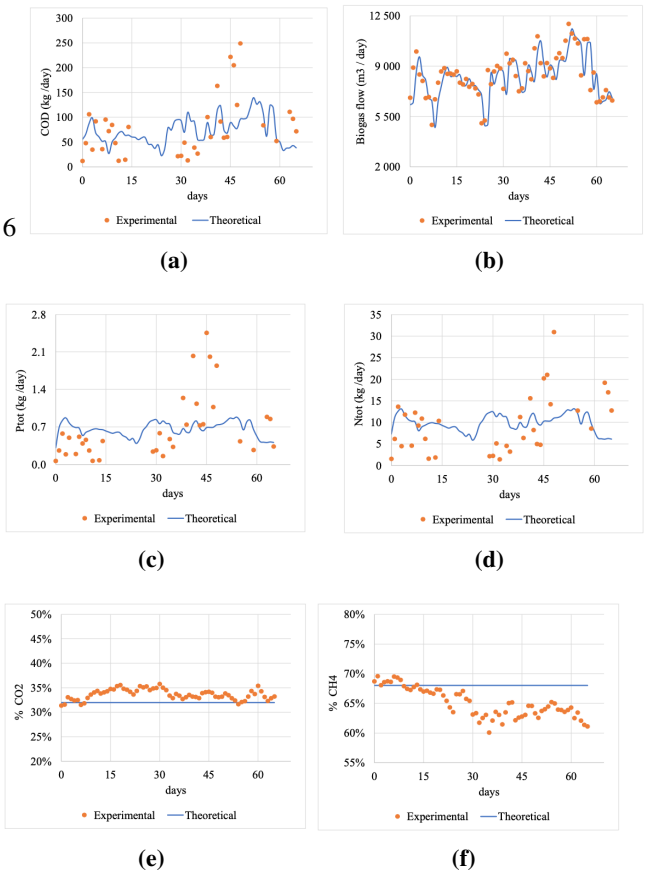

Figure 10. Comparison between experimental and theoretical values of a) COD, b) biogas flow, c) Ptot and d) Ntot, e)% of CO_2 and f)% of CH_4 in biogas for data set 2 after the re-feeding of information.

obtained for these four parameters indicates that possibly if the model would have as an input the initial COD, a model with fitting over time would not be necessary since the results obtained are similar to those obtained after the fitting. As mentioned before, COD, Ntot and Ptot present a significant error due to a lack of data on the composition of the substrate. However, they are within the data fluctuation, so the model fits the experimental data. As for data set 1, the biogas flow is correctly predicted in terms of trends and presents an error of 14.6% associated with the 1-day delay forecast. If there was no 1-day forecast error, the error between experimental and theoretical data would only be 1.9%, demonstrating the forecast's accuracy.

In conclusion, using the initial COD as an input parameter significantly improves the model prediction, confirming once again that the model would predict more correctly if it had more input data, such as substrate composition.

4. Conclusions

The model presented a good performance, predicting within an acceptable error, taking into account the received data. The biogas trends were predicted partly correctly, with some errors associated with missing input composition since it was observed that this deviation was eliminated with the information re-feeding. In terms of biogas quantity, the prediction also presents minor errors, which were almost eliminated when the COD at the reactor inlet was introduced in the data input of the model. However, the forecast of biogas flow always presents a delay of 1-day, if this was eliminated, the error between experimental and theoretical data would be 2% maximum, which demonstrates the accuracy of the forecast. In future, one way to improve biogas forecasting would be to have experimental data from the initial COD, even if they were periodic analysis, and then the remaining day's approximations would be based on the type of feedstock entering.

The model cannot correctly predict the relative amount of gases, and it was not possible to calibrate the kinetic constant of the methanogenesis reaction of hydrogen. Both the amount of H_2 and CO_2 were obtained by assumptions and not by kinetics, so it does not represent an accurate amount of this gas either. This is the point that needs more work in the future, which is to insert kinetics that correctly predict the amount of

the gases.

The prediction of COD, Ntot and Ptot show a more significant error. However, it is within the expected data fluctuation. As mentioned, the data analysis was performed by selecting intervals of days with constant feedstock flow to understand the fluctuation of these variables. Despite the fluctuation, at certain moments, it is possible to identify a correct trend prediction, which seems to be associated with days without variation in the input composition. Therefore, it was possible to conclude that this fluctuation is high and that the model predicts within this range. The fluctuation of COD, Ntot and Ptot parameters is associated with the variation in feedstock composition, so in order for the model to predict these variables correctly, it is necessary to have data about the composition in the model's input data. The chemical analysis of the substrate could give this information in order to obtain its composition. However, this process can be time consuming and expensive, so a more effective way to do it would be to characterise the waste coming from different places and related collection days, such as hotels, restaurants, shopping malls, houses, and so on, as these variables will affect their composition. The waste characterisation is, in these terms, a possible approach to enable approximate predictions of parameters related to substrate composition.

By re-calibrating the model, it was possible to conclude that a model that fits over time can be beneficial when there is no data about the substrate composition in the model's input. However, when comparing with a model with more input data regarding the substrate composition, there is no need to fit over time since it already presents good results.

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