TÉCNICO LISBOA

ANAEROBIC DIGESTION - PROCESS DATA ANALYSIS

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Thesis to obtain the Master of Science Degree in

Chemical Engineering

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Declaração

Declaro que o presente documento é um trabalho original da minha autoria e que cumpre todos os requisitos do Código de Conduta e Boas Práticas da Universidade de Lisboa.

Declaration

I declare that this document is an original work of my own authorship and that it fulfills all the requirements of the Code of Conduct and Good Practices of the Universidade de Lisboa.

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Acknowledgments

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Resumo

A valorização energética de resíduos tende a diminuir problemas, como o aumento do consumo energético e a gestão de resíduos, através da utilização de resíduos para a produção de energia. A digestão anaeróbia é uma destas tecnologias, e produz energia sem emissão de gases de efeito de estufa a partir de resíduos biodegradáveis. Apesar de vastamente utilizada, a digestão anaeróbia apresenta um processo complexo e existe alguma dificuldade na previsão e otimização do processo, pelo que existe um estudo continuo do mesmo através da modelação matemática.

Este trabalho tem como objetivo desenvolver um modelo matemático, baseado em dados do processo, que descreva a operação e comportamento de um digestor anaeróbio ao longo do tempo. O modelo foi desenvolvido com base no modelo ADM1 desenvolvido pela IWA. O modelo foi calibrado com um conjunto de dados da operação, e após validado, o mesmo modelo foi testado para um conjunto de dados diferente de forma a compreender se este se mantinha válido.

Pelos resultados obtidos foi possível compreender que existem falta de dados de entrada, principalmente da composição do substrato, para que o modelo possa prever de forma correta. No entanto, para os dados existentes, o modelo obtém erros aceitáveis conseguindo prever as tendências. Pela recalibração do modelo foi possível concluir, que com pouca informação de entrada, um modelo que se ajuste ao longo do tempo pode ser benéfico. Os melhores resultados são obtidos quando há informação sobre o substrato inicial, como o COD.

Palavras-chave: Valorização energética de resíduos, Digestão anaeróbia, Resíduos sólidos urbanos, Modelação Matemática, ADM1, Dados de operação.

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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.

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Nomenclature

Greek symbols

γ	Kinetic rate
μ	Cell growth rate
ρ	Density
$\rho_{T,i}$	Transfer rate of gas i

Roman symbols

A	Surface area
AD	Anaerobic digestion
C	Composition of the composite
COD	Chemical oxygen demand
DL	Digester level
DM	Dry matter
Ea	Activation Energy
GRS	Grit Removal System
H_i	Henry constant of component i
HRT	Hidraulic retention time
k	Kinetic constant
K_I	Inhibition constant
$k_l a$	Mass transfer constant
k_{SBV}	Surface based hydrolysis constant
K_S	Saturation constant
$L_{P/C}$	Ratio between phosphorus and carbon in lipids

M	Methane production
MSW	Municipal solid waste
$N_{\%Pr}$	Composition of proteins in nitrogen
Ntot	Total nitrogen flow
OLR	Organic Load Rate
$P_{\%Li}$	Composition of lipids in phosphorus
p_i	Partial pressure of component i
$P_{N/C}$	Ratio between nitrogen and carbon in proteins
Ptot	Total phosphorous flow
q	Flow
R	Ideal gas constant
S	Concentration of the soluble component
T	Temperature
t	Time
TS	Total solids
v	Biochemical rate coefficients
V	Volume
VS	Volatile solids
WTE	Waste to Energy
X	Concentration of the particulate component
Y	Yield

Subscripts

aa	Amino acids
ac	Acetate
acet	Acetogenesis
acid	Acidogenesis
bio	Biogas
c	Composite

ch	Carbohydrates
ch4	Methane
co2	Carbon dioxide
dig	Digestate
h2	Hydrogen
hid	Hydrolysis
in	Entering
lag	Lag phase
lcfa	Long chain fatty acids
li	Lipids
met	Methanogenesis
ms	Monosaccharides
out	Exiting
p	Product
pr	Proteins
s	Substrate
vfa	Volatile fatty acids
x	Biomass

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Chapter 1

Introduction

1.1 Topic Overview

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, the waste production also tends to increase. In the last decades, a lot of progress has occurred in many countries. Yet, this is still a day-to-day problem that continues to grow and it is crucial to solve [1–3].

The rapid growth of energy consumption over the years (Figure 1.1), 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.). It had spotlighted energy sources that are ready for immediate use with preferably no pre-process. As we can see in Figure 1.1, energy consumption is expected to continue to grow. 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, as presented in Figure 1.2, it is possible to understand that in 2018 the primary source of energy worldwide was 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 (MSW), which is increasingly worried about gaseous wastes, like CO_2, CH_4 and others (NOx and SOx), 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 referred to before. WTE is the direct conversion of waste to steam and electricity. Organic waste, mostly composed by biomass, is a renewable resource. It has been used for energy generation since it is a feasible and affordable way to produce energy, so it is mainly used 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 [2, 4, 5].

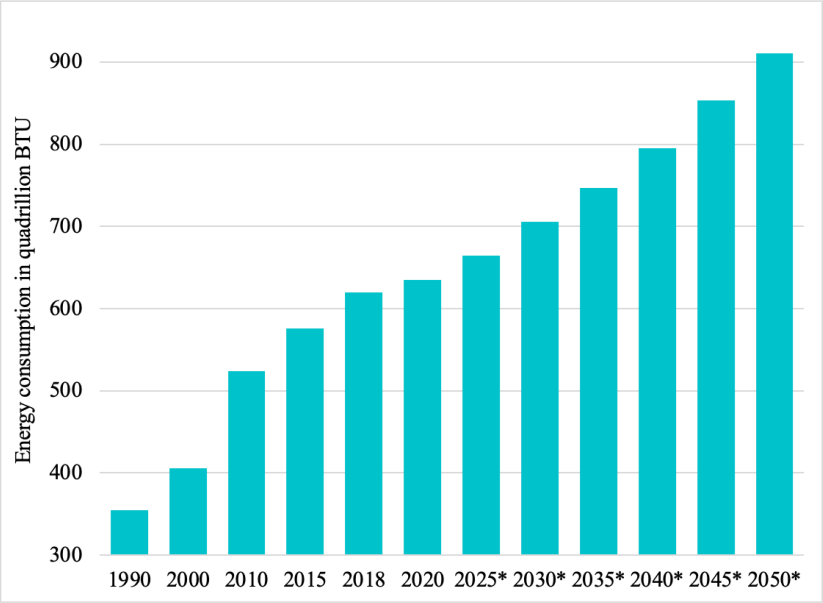

Figure 1.1: Energy consumption worldwide. *represents the projection from 2025. Adapted from: Statista [6]

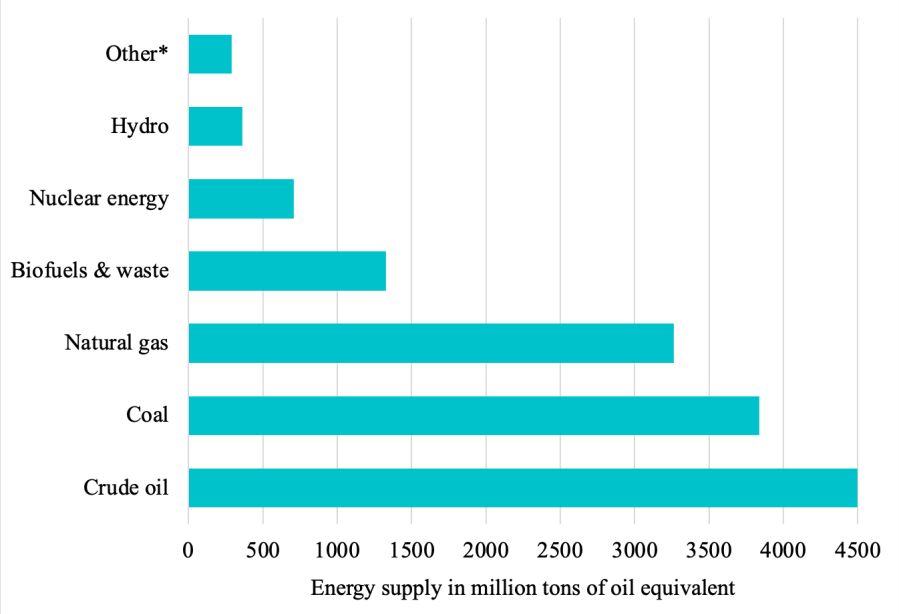

Figure 1.2: Primary energy supply worldwide in 2018. * includes geothermal, solar, wind, heat, tide, wave and ocean energies. Adapted from: Statista [7]

After recycling and composting, MSW treatment meets global standards and integrates WTE as the 3^{rd} step on the hierarchy of the MSW treatment (Figure 1.3). In Europe, the most common solution to the MSW treatment is to combust the remaining waste, after separating recyclable material, in WTE facilities that generate electricity and recover steam [2, 4].

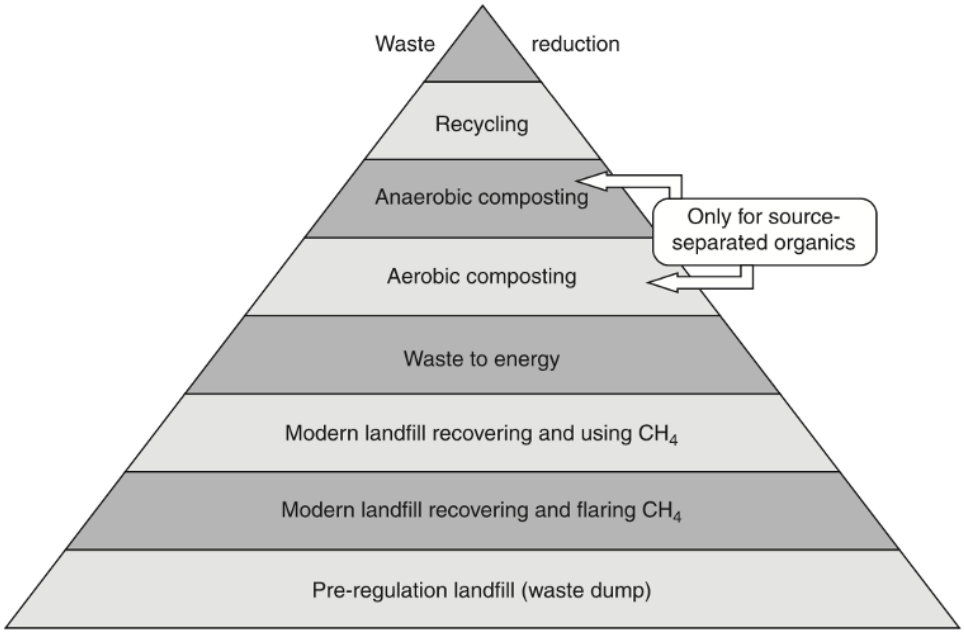

Figure 1.3: Hierarchy of waste management. Reproduced from [2]

WTE is commonly used to convert biomass to sustainable products. There are three types of conversion technologies: thermochemical, physicochemical, and biochemical (Figure 1.4). Physicochemical and biochemical are the most common technologies. Thermal approaches convert biomass into alternative fuel (gasification, liquefaction, pyrolysis, etc.), and biological approaches convert biomass into bioenergy (fermentation and anaerobic digestion). Thermochemical methods are the most used technology of WTE globally. Yet, in the last years, the AD of MSW, that uses biochemical conversion, has become one of the most attractive renewable energy pathways [2, 4, 5].

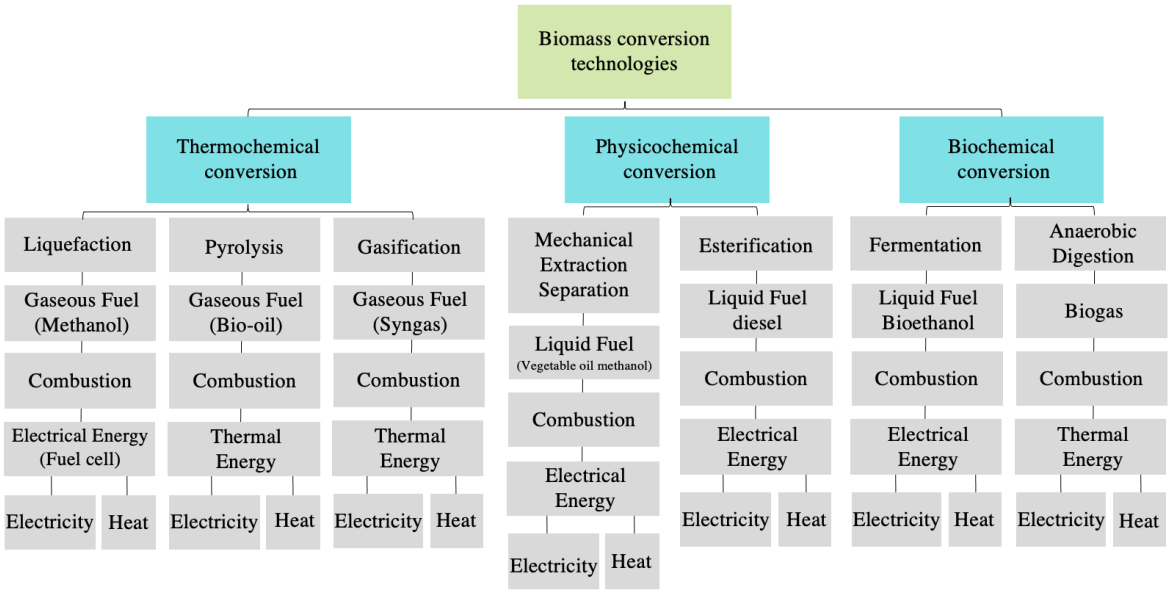

Figure 1.4: Biomass conversion technologies. Adapted from [3]

1.1.1 Anaerobic Digestion

Anaerobic Digestion (AD) is a natural biochemical process where microorganisms decompose organic matter without oxygen. Organic matter is decomposed into biogas, mainly CO_2 and CH_4, and digestate, a mixture of mineral substances (N, P, K, Ca, etc.) and compounds of complex degradation. Some examples of natural environments where it occurs (some low-oxygen niches) are marshes, marine water sediments, ruminants' stomachs, or peat bogs. AD processes allows the treatment of waste to reduce the volume and load, producing biogas and digestate [1, 8–11].

Biogas utilisation for combined heat and power production (CHP) is one of the most used applications. Still, it is also used as a renewable biofuel or feed into the natural gas grid after the upgrade, in some countries. Despite biogas being the aim of AD, digestate is also a valued as it can be used, for example, as a fertiliser instead of using natural manure, as traditionally. Using manure directly as a fertiliser may cause environmental problems, like contamination of waters and air pollution. When using it as feedstock for AD, digestate is obtained, which can then be used as a fertiliser, with no significant loss of nutrients. At the same time, the risks are considerably reduced. AD reduces greenhouse gas emissions by reducing emissions from manure and reducing fossil fuel utilisation [10, 12–14].

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 (Figure 1.5) [5, 15]. This process can be used both at the industrial and domestic levels. Some examples are wastewater treatment facilities for sludge degradation and stabilisation, farms to treat manure, biogas to be used as a cooking and lighting fuel in rural areas (prevalent in China and India), and large facilities to treat MSW and produce energy [1, 9–11].

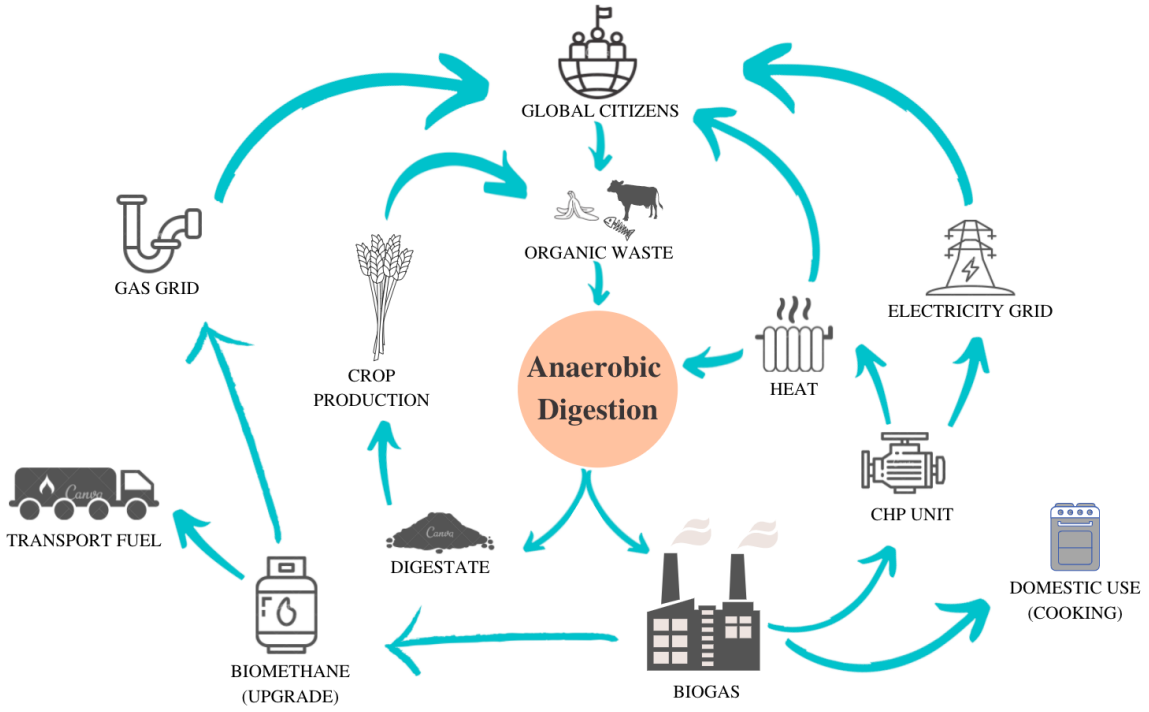

Figure 1.5: The circular economy of Biogas. [2]

AD can use a wide range of feedstock. However, despite the wide range of raw materials, the amount of methane obtained (Methanogenic potential) from each one varies significantly, as it is possible to see in Table 1.1 [9, 13, 16]. The most common feedstocks are animal manure and slurry, organic waste from industries, agricultural residues, forest residues, organic fraction of MSW, sewage sludge, and energy crops (e.g., maize, miscanthus, sorghum, etc.). When combined feedstock is utilised (two or more feedstock types), called co-digestion, it is possible to obtain a higher methane yield and biogas production [1, 13, 14].

Table 1.1: Methanogenic potential from selected feedstock. Adapted from [9, 13]

	DM (%)	VS (% of DM)	Methanogenic potential (L CH_4 / kg VS)	Methanogenic potential (L CH_4 / kg feedstock)
pig slurry	3-8%	70-80%	250-350	6-22
cattle slurry	6-12%	70-85%	200-250	8-25
poultry manure	10-30%	70-80%	300-350	21-84
maize sillage	30-40%	90-95%	250-450	68-170
grass	20-30%	90-95%	300-450	55-128
potatoes	20-30%	90-95%	280-400	54-128
straw	85-90%	80-90%	200-250	136-202
vegetable waste	85-90%	80-90%	200-251	136-203
slaughterhouse residues	35%	90-95%	550-650	173-216
sewage sludge	5-10%	75%	300-400	11-30

AD is a well-establish process and used for several decades. However, there is still a lack of knowledge about the mechanisms of AD due to its high complexity. With the increase of industrial interest, research and development was intensified. Mathematical modelling is one of the most discussed aspects, intending to identify the most relevant models to assist in the optimisation of digesters biogas formation. It is still a challenge to find the optimal design of anaerobic digesters that will maximise methane production due to the significant variability in how it can be produced. However, there is continuous development and testing of new digesters, new combinations of AD substrates, feeding systems, as well as other equipment's [8, 10, 11].

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. The model should be chosen for each case individually, based on availability and characteristics of raw material, the economic aspects of the project, the aim of energy production, operators' training, and others. However, models that can be applied for any application are increasingly being developed and used [8, 9]. There are three main requirements to be met [3]:

- High-quality biogas production and in large quantities;
- Feed with high organic loads;
- Reduction of the hydraulic retention time, guaranteeing a lower digester volume.

1.2 Objectives and Deliverables

This master thesis aims to develop a preliminary mathematical model to describes the operation of anaerobic digesters and predicts the system's evolution over time. This model will have the objective of predicting the behaviour of the digestor, based on operational data of the units in the study, standards models existing in the bibliography, and modifications of these.

The development of a model based on operation data will allow having a good accuracy between the model and the actual operation. It is essential to use operation data with disturbances, and not only steady-state, so that the model can function over a broader range of conditions. Therefore, it is necessary to carry out an analysis of the operational data before using it.

The mathematical model will aim to predict the results of modifications, optimise operational parameters, estimate parameters only periodically measured, and train control staff.

1.3 Industrial context for the thesis

Efacec is a Portuguese company with prominent references worldwide in Energy, Environment & Industry, Mobility and Transports. With over 70 years of the brand is focused on developing products and systems with high added value that improve day to day life. Efacec intends to create a smarter future for a better life while contributing to a sustainable world in the new energy era.

In the Environment & Industry department, where this thesis was developed, integrated solutions are offered, ranging from conception and design to the realisation and operation of systems. Topics such as water treatments or waste treatments and recovery systems are addressed. This thesis fits into the theme of the waste recovery and treatment system that is developed in this department.

1.4 Thesis Outline

Chapter 1 is the introduction of the work, where an overview of the topic is presented in order to better understand how the problem originated and what it intends to solve (Section 1.1). The objectives and deliverables are also presented (Section 1.2), and finally a brief introduction is given to Efacec, the company where the work was carried out (Section 1.3).

Chapter 2 consists of a literature review of the Anaerobic Digestion (Section 2.1) and Anaerobic Digestion mathematical modelling (Section 2.2), addressing the process and its main steps (Section 2.1.1), the key parameters that influence the process (Section 2.1.2), and finally the principals of mathematical modelling are presented, as well as a review of some models, being made a more detailed description to the exponential model (Section 2.2.1), kinetic models (Section 2.2.2) and ADM1 (Section 2.2.3).

Chapter 3 focuses on the implementation of the model, beginning with a description of the general process of the case study (Section 3.1), addressing then on the methods and procedures of the work (Section 3.2), an analysis of the existing data for the implementation of the model was also performed

(Section 3.3), and finally is presented how the model was implemented (Sections 3.4 and 3.5) and how it was fitted and validated (Section 3.6).

Chapter 4 presents the analysis and discussion of the results obtained, starting with the results of implementing the model (Section 4.1), focusing after in the results obtained in the optimisation of the different parameters of the model, per step (Section 4.2), and the cross-validation with a second set of data to verify the validity of the model (Section 4.3). In addition, an information re-feeding was performed in order to analyse the results obtained (Section 4.4), and was also made a sensitivity analysis of the estimated parameters (Section 4.5).

Chapter 5 gathers the most critical conclusions and achievements obtained throughout the work and some recommendations for future work in developing the model.

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Chapter 2

Literature Review

This chapter consists of a literature review of the Anaerobic Digestion, addresses the process, and explains the main steps. Several factors highly influence the process, so these are also discussed and described. The different categories are also described, as this technology can be applied in different ways. Finally, mathematical modelling and its general principles are discussed and a review of the first models created is presented. A more detailed description of the most common and recent models is also made, with ADM1 being the model taken as the basis.

2.1 Anaerobic Digestion

As previously stated in Chapter 1, AD is a biochemical process that degrades complex organic matter in the absence of oxygen, obtaining biogas 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 ($<$1% (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, 5, 10, 17].

2.1.1 Process

AD occurs through a complex dynamic reaction system with parallel and sequential steps that can be categorised into two main groups [1, 5, 11, 17]:

- Biochemical:Reactions catalysed by enzymes that act on the available organic matter;
- Physicochemical: Ion association/dissociation reactions and gas-liquid transfer, which are not mediated by microorganisms.

The process of AD generates lesser heat than aerobic decomposition, as composting, for example. The energy chemically bonded in the substrate of AD remains mostly in methane of biogas [11].

2.1.1.1 Biochemical Process

The biochemical process is a set of interconnected steps in which the starting material is continuously decomposed into smaller molecules. Each step takes place through the action of specific microorganisms that decompose, successively, the products of the previous steps. In Figure 2.1, a simplified diagram of the AD process is represented, demonstrating the four main stages of the process: hydrolysis, acidogenesis, acetogenesis, and methanogenesis [1, 11].

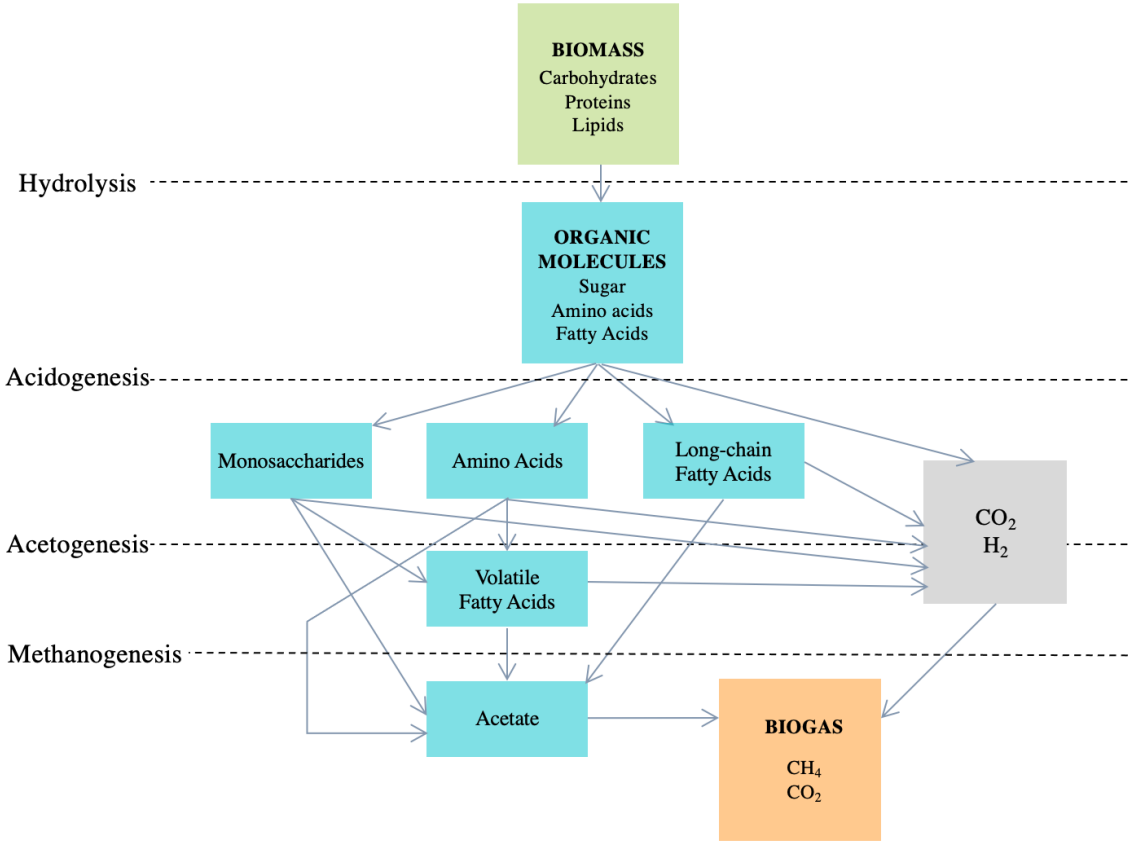


Figure 2.1: Main steps of AD process [1, 3, 5, 9, 11, 12, 15, 17, 18].

These steps run in parallel, both in time and space. Typically, the four steps take place simultaneously at the digester. However, different kinds of microorganisms are carried out, requiring different conditions for optimal growth. The slowest step defines the overall reaction's speed. Nevertheless, it is not consensual whether the slowest one is hydrolysis or methanogenesis. Biogas production is relatively small in the first one, and the highest production is achieved during methanogenesis [1, 9, 11].

The general biochemical reaction can be described by Equation 2.1 [5]:

$$C_cH_hO_oS_s + xH_2O \rightarrow yCH_4 + (c-y)CO_2 + nNH_3 + sH_2S \tag{2.1}$$

where x and y are defined by equations 2.2 and 2.3, respectively:

$$x = \frac{1}{4}(4c - h - 2o + 3n + 2s) \tag{2.2}$$

$$y = \frac{1}{8}(4c + h - 2o - 3n + 2s) \tag{2.3}$$

A well-balanced AD process occurs when there is no accumulation of intermediate products, i.e., complete decomposition of the organic matter into the products of interest, such as methane, carbon dioxide, hydrogen sulphide, and ammonia. The biogas composition produced depends on several factors, like residence time, reactor set-up, temperature, and others. We will discuss the biogas composition factors further in Section 2.1.2 [1, 9–11].

Hydrolysis

In the theoretical first step of the process, hydrolysis, complex and long-chain organic matter (polymers) is broken into lower molecular weight organic compounds, monomers, such as carbohydrates, proteins, and lipids, through the action of hydrolytic microorganisms. The microorganisms involved release hydrolytic exo-enzymes (extracellular) that decompose the material biochemically outside the microbial cells [1, 5, 9].

As referred before, some authors [1, 11] consider this step to be the slowest one due to the formation of toxic or unwanted compounds. The speed of the reaction can also be limited because of the use of substrates in the form of particles. The utilisation of biological, chemical, or mechanical pre-treatments can speed up hydrolysis and increase digestion performance because they can promote the disintegration of the substrate and allow the accessibility of anaerobic microorganisms by liberation of intracellular matter [1, 11].

The hydrolysis of carbohydrates can be described by Equation 2.4 [12]:

$$(C_6H_{10}O_5)_{is} \rightarrow Y_c(C_6H_{10}O_5)_s + (1 - Y_c)CO_2 + (C_6H_{10}O_5)_{in} \tag{2.4}$$

where $(C_6H_{10}O_5)_{is}$ represents insoluble complex carbohydrates, including biodegradable and inert; $(C_6H_{10}O_5)_s$ represent soluble carbohydrates, monosaccharides; $(C_6H_{10}O_5)_{in}$ represent inert carbohydrates; and Y_c is the fraction of biodegradable carbohydrates.

The hydrolysis of lipids can be described by Equation 2.5 [12]:

$$C_{57}H_{107}O_6 + 3H_2O \rightarrow C_3H_8O_3 + 3C_{18}H_{34}O_2 \tag{2.5}$$

where $C_{57}H_{107}O_6$ represents, in a general way, lipids (glycerol-trioleate); $C_3H_8O_33$ represents glycerol; and $C_{18}H_{34}O_2$ represents long-chain fatty acids (LCFA).

The hydrolysis of proteins can be described by Equation 2.6 [12]:

$$(Protein)_{is} \rightarrow Y_p(Aminoacids) + (1 - Y_p)(Protein)_{in} \tag{2.6}$$

where $(Protein)_{is}$ represents complex proteins; $(Protein)_{in}$ represents inert proteins; and Y_p is the fraction of biodegradable protein (only biodegradable fraction is hydrolysed into amino acids, and the inert remains unchanged).

Acidogenesis

The second step of the process converts the monomers, a product of hydrolysis, into compounds, including monosaccharides, long-chain fatty acids (LCFA), amino acids, lactic acid through acidogenic fermentative organisms, and carbon dioxide and hydrogen, which are by-products of the degradation process [1, 5, 9].

This conversion into organic acids creates a drop in the pH system, favouring the performance of acidogenic and acetogenic microorganisms that are better established in an acidic pH (4.5-5.5). This step produces acids that are the main precursors of methane production (that occurs in the last step), making them essential in AD's overall performance [1].

The conversion of monosaccharides to acetate and volatile fatty acids (VFA: propionate and butyrate) can be represented by Equation 2.7 [12]:

$$\begin{aligned} C_6H_{10}O_5 + 0.115NH_3 \rightarrow 0.1115C_5H_7NO_2 + 0.744C_2H_4O_2 + \\ +0.5C_3H_6O_2 + 0.4409C_4H_8O_2 + 0.6909CO_2 + 0.0254H_2O \end{aligned} \tag{2.7}$$

where $C_6H_{10}O_5$, $C_5H_7NO_2$, $C_2H_4O_2$, $C_3H_6O_2$, $C_4H_8O_2$ represents, respectively, monosaccharides, microbial cell formula, acetate, propionate, and butyrate.

The conversion of amino acids to acetate and VFA (propionate, butyrate, and valerate) can be represented by Equation 2.8 [12]:

$$\begin{aligned} CH_{2.03}O_{0.6}N_{0.3}S_{0.001} + 0.3006H_2O \rightarrow 0.017013C_5H_7NO_2 + \\ +0.29742C_2H_4O_2 + 0.02904C_3H_6O_2 + 0.022826C_4H_8O_2 + \\ +0.013202C_5H_{10}O_2 + 0.07527CO_2 + 0.28298NH_3 + 0.001H_2S \end{aligned} \tag{2.8}$$

where $CH_{2.03}O_{0.6}N_{0.3}S_{0.001}$ and $C_5H_{10}O_2$ represents, respectively, amino acids and valerate. The remaining ones were already identified previously.

The conversion of glycerol to VFA (propionate) can be represented by Equation 2.9 [12]:

$$C_3H_8O_3 + 0.04071NH_3 + 0.0291CO_2 \rightarrow 0.04071C_5H_7NO_2 + 0.9418C_3H_6O_2 + 1.09305H_2O \tag{2.9}$$

Acetogenesis

In the third step, the compounds produced in acidogenesis are converted into hydrogen, carbon dioxide, and acetate through acetogenic bacteria. The formation of a large amount of hydrogen from acids causes a decrease in pH. Acetogenic microorganisms grow slowly and are very sensitive to changes in the environment and organic loadings, with the optimum pH for their action being approximately 6 [1].

The conversion of VFA (propionate, butyrate, and valerate) to acetate can be represented by Equations 2.10, 2.11 and 2.12, respectively [12]:

$$C_3H_6O_2 + 1.764H_2O + 0.0458NH_3 \rightarrow 0.0458C_5H_7NO_2 + 0.9345C_2H_4O_2 + 2.804H_2 + 0.902CO_2 \quad (2.10)$$

$$\begin{aligned} C_4H_8O_2 + 1.7818H_2O + 0.0544NH_3 + 0.0544CO_2 \rightarrow \\ 0.0544C_5H_7NO_2 + 1.8909C_2H_4O_2 + 1.8909H_2 \end{aligned} \quad (2.11)$$

$$\begin{aligned} C_5H_{10}O_2 + 0.8045H_2O + 0.0653NH_3 + 0.05543CO_2 \rightarrow 0.0653C_5H_7NO_2 + \\ +0.8912C_2H_4O_2 + 0.02904C_3H_6O_2 + 0.4454CH_4 \end{aligned} \quad (2.12)$$

where CH_4 represent methane.

The conversion of LCFA to acetate can be represented by Equation 2.13 [12]:

$$C_{18}H_{34}O_2 + 15.2398H_2O + 0.1701NH_3 + 0.25CO_2 \rightarrow 0.1701C_5H_7NO_2 + 8.6998C_2H_4O_2 + 14.5H_2 \quad (2.13)$$

Methanogenesis

In the last stage, methanogenic archaea breakdown produces methane from the compounds formed in acetogenesis. Methanogenic organisms are divided into two main groups, where acetotrophic methanogenesis is the primary pathway [1, 10]:

- Acetotrophic - cleaves acetate and methanol into methane (Equation 2.14)
- Hydrogenotrophic - produce methane from hydrogen and carbon dioxide (Equation 2.15)

$$C_2H_4O_2 + 0.022NH_3 \rightarrow 0.022C_5H_7NO_2 + 0.945CH_4 + 0.066H_2O \quad (2.14)$$

$$0.7431CO_2 + 2.804H_2 + 0.01618NH_3 \rightarrow 0.01618C_5H_7NO_2 + 0.6604CH_4 + 1.45H_2O \quad (2.15)$$

Unlike the other microorganisms involved in AD, methanogenic organisms prefer a slightly alkaline environment (pH around 6.5-8). Hydrogenotrophic methanogens are better resistant to environmental changes than acetotrophic methanogens, yet operation conditions severely influence methanogenesis [1, 11].

2.1.1.2 Physicochemical Processes

Physicochemical reactions are those that are not mediated by microorganisms, and within this type of reaction, the ones that occur in anaerobic digesters are [17, 19]:

- Gas-liquid reactions;
- Liquid-liquid exchanges;
- Liquid-solid transformations.

The first two are the most common in AD models because liquid-solid transformations present many difficulties in implementation, despite their importance, which leads most models not to include them. Liquid-solid transformations are fundamental in digesters with high levels of cations that form carbonate precipitates, like Mg^{2+} and Ca^{2+} [19].

The following arguments seek to summarise why the physicochemical system is so crucial for AD models [19]:

- Biological inhibition factors can be explained by physicochemical parameters such as pH, free acids and bases, and dissolved gas concentrations;
- The correct estimation of physicochemical transformations affects the gas flow and carbonate alkalinity;
- The control of reactions carried out from the pH is characterised by the physicochemical state, which is the primary operating cost due to the control being done using strong acid or base.

In AD the most significant acid-base pairs are: NH_4^+/NH_3 (pKa=9.25), CO_2/HCO_3^- (pKa=6.35) and VFA/VFA^- (pKa$\sim$4.8) and H2O/OH-/H+ system (pKw=14.00). Dissociation/association processes presented before are faster when compared to other processes, thus are addressed as equilibrium processes. The three main process gas components are CO_2, CH_4, and H_2 [17, 20].

2.1.2 Process Parameters

Several critical parameters influence AD efficiency. First, it is essential to provide the appropriate conditions for the microorganisms' development, like constant temperature, absence of oxygen, neutral pH, and nutrient feeding, among others. The biggest challenge is that optimal conditions for hydrolysis and acidification are different compared to methanogenesis requirements. The most critical parameters are discussed next [5, 10, 21].

Temperature

Temperature is a crucial parameter in AD since the bacteria are highly affected by temperature variation, affecting biogas production. Three broad ranges of temperature are considered, each favouring a specific type of microorganisms: psychrophilic, mesophilic, and thermophilic. These ranges are directly related to the hydraulic retention time (HTR), as it is possible to understand in Table 2.1 [3, 9, 11].

Table 2.1: Temperature ranges of AD and correspondents' typical HRT [11].

	T (°C)	HTR (days)
Psychrophilic	$< 20°$	70 to 80
Mesophilic	30° to 42°	30 to 40
Termophilic	43° to 55°	15 to 20

The temperature must remain constant since any change of temperature can destabilise the AD process and reduce or stop the microorganism's activity. Thermophilic bacterias are more sensitive to temperature, tolerating fluctuations of only $\pm 1°C$, while mesophilic bacteria tolerate a fluctuation of $\pm 3°C$ [3, 5, 10].

Low temperatures have the advantage of requiring a reduced amount of energy, but in those conditions' methane generation is significantly lower due to low enzymatic and bacterial activity. Enzymatic and bacterial activity increases with temperature, so the processes becomes faster, and it is possible to use reactors with smaller volumes. In the mesophilic and thermophilic ranges, anaerobic bacteria's exhibits the highest activity [3, 5, 10].

Operating in mesophilic conditions provides better stability and lower energy costs than thermophilic conditions, making it the most popular range. Thermophilic conditions also present a risk of inhibition of the process, yet they also present several benefits, such as [11, 18]:

- Retention time is reduced, the process is quicker and a better efficiency is achieved;
- The higher growth rate of methanogenic bacteria;
- Effective pathogens destruction;
- Improved digestibility;
- Easier separation of the liquid and gaseous fraction.

In reality, the operation temperature is chosen based on the feedstock, as they have different amounts of microorganisms and pathogens. The necessary temperature for the process temperature is provided by the floor or wall heating systems inside the digester [11].

pH, VFA and alkalinity

The pH is the measure of acidity/alkalinity of a solution, it stands for one of the most significant parameters in the performance and stability of a digester. The growth of methanogenic microorganisms and the dissociation of some compounds of importance (ammonia, sulphide, and organic acids) are driven by AD subtracts pH values. pH is influenced by alkalinity, VFA, CO_2 production, and concentration of bicarbonate (HCO_3) [11, 18].

AD microorganisms require different optimum pH for their growth, as presented in Table 2.2. Methane formation occurs at an optimum interval between 7.0-8.0, and acidogenic microorganisms usually have an optimum pH with a lower value. These are the microorganisms with more severe difficulty to adapt

to pH once acetogenic microorganisms produce volatile compounds that acidify the environment, which negatively influences the activity of methanogenic microorganisms [1, 11].

Table 2.2: Optimal pH for bacterial groups present in AD [1, 18].

Bacterial Group	Optimum pH
Hidraulitic	$\pm$ 6.0
Acidogenic	4.5-5.5
Acetogenic	$\pm$ 6.0
Methanogenic	6.5-8

In the mesophilic range, the optimum pH is between 6.5 and 8.0, and, at pH lower than 6.0 or higher than 8.3, the process is critically inhibited. At the thermophilic range, the optimum pH is higher once CO_2 solubility in water decreases with temperature, which means that dissolved CO_2 forms carbonic acid by reaction with water. It is important to refer that the feedstock used can also influence the optimum pH [1, 11].

The production of ammonia at the degradation of proteins or ammonia from feedstock can increase the value of pH, whereas the pH value is decreased by the accumulation of VFA. pH is also influenced by the concentration of alkaline and acid components in the liquid phase. The bicarbonate buffer system usually controls the variation of pH inside the digester. The buffer neutralises pH changes until a certain level, and when it is extremely over-past, it changes the pH, inhibiting the AD process. Usually, due to this, the pH value is not independently monitored. The relation between alkalinity and VFA can evaluate the stability of the digester. A stable and well-buffered digester should present an alkalinity/VFA molar ratio of at least 1.4:1 [11, 18, 20].

Ammonia

Ammonia (NH_3) is an essential nutrient to the AD process and fertilisers produced from digestate. It is produced mainly from proteins present in the feedstock. However, despite being important, when in high concentration is an inhibitor of AD, especially when in a thermophilic regime, since free-ammonia concentration is directly proportional to temperature [11].

When the used feedstock is animal slurry, the concentration of ammonia is higher, originated from urine. Methanogenic microorganisms are significantly affected by ammonia, and their concentration should be lower than 80 mg/l [11].

The concentration of free-ammonia can be calculated by the following Equation 2.16 [11]:

$$[NH_3] = \frac{[T - NH_3]}{1 + \frac{[H+]}{k_a}} \tag{2.16}$$

where $[NH_3]$, $[T - NH_3]$ and $[H+]$ are the concentration of free ammonia, total ammonia, and H+, respectively, and k_a the dissociation parameter, with values increasing with temperature. The inhibition of the process increases with temperature and pH since free ammonia will increase. When inhibited by ammonia, pH decreases as a result of an increase in the concentration of VFA. The pH decrease will

partially neutralise the ammonia effect as a consequence of a decrease in free ammonia concentration [11].

C/N ratio

The ratio between the amount of carbon and nitrogen in the organic matter is defined by C/N, which is directly dependent on the type and complexity of the substrate, and it drives the stability and performance of the process. The optimum C/N ratio is a value discussed by several authors [1, 3, 18], commonly accepted values between 20 and 31. The optimal C/N ratio indicates a suitable environment as well as it helps to control proper nutrient balance [1, 3, 18].

Carbohydrates are organic compounds that are quite important for biogas production since they increase the substrate's protein conversion and proteases activity. Nitrogen is required for protein synthesis, and it is used as a nutrient for microorganisms responsible for AD, as referred above. Ammonia is produced from nitrogen compounds in the AD process. The process is severely affected by the lack of carbon and nitrogen [1, 18].

Methanogenic microorganisms require nitrogen to meet their protein requirements. While carbon constitutes the source of energy, nitrogen serves to intensify microbial growth. A high C/N ratio means that high carbon content is available, and methanogenesis quickly consumes nitrogen resulting in low gas yield. On the other hand, a low C/N ratio means that the material is rich in protein, leading to an accumulation of ammonia that inhibits the process [1, 3].

Phosphorus

The phosphorus content in the digestate can be given by total phosphorus or phosphate pentoxide. This is an essential nutrient for the digest to be applied to the soil. The digested substrate should present a minimum of phosphate so that it can be commercialised. This value can vary from country to country, but for example, in Portugal, the minimum is 3% (Decreto-Lei nº 103/2015, de 15 de Junho). Anaerobic digestion does not influence the amount of phosphorus, depending only on the raw material introduced into the digesters [11].

Chemical Oxygen Demand

The chemical oxygen demand (COD) is the amount of oxygen consumed to chemically oxidise organic and contaminants into inorganic end products. During anaerobic digestion, COD decreases with the digestion of organic matter. However, a significant amount of organic matter may still be present in the substrate at the end. The smaller the COD, in the output, the greater the digestion efficiency considering more organic matter was digested [11, 22].

Hidraulic Retention Time

The hydraulic retention time (HRT) is the average time interval that the substrate remains inside the digester. This is an essential parameter for the dimensioning of the digester. HTR depends on the temperature of operation (as referred to before) and the composition of the substrate. HRT can be defined by Equation 2.17 [1, 11, 18]:

$$HRT = \frac{V}{Q_v} \tag{2.17}$$

where V is the digester volume and Qv is the volumetric flow.

The HRT must be high enough so that the number of microorganisms removed with the digestion is not greater than the number of microorganisms produced. A small HRT allows for a good digestate flow but reduces biogas production. Thus, it is essential to adapt it to the specific decomposition rate of the used substrates [1, 11, 18].

Organic Load

The biogas production operation process from AD combines economic and technical considerations to obtain maximum production. To obtain the maximum biogas yield, it would be necessary to complete the digestion of the substrate, which would imply a high retention time and, consequently, a digester with a high volume [11].

For the size of the digester or retention time choice, what happens is to reach a compromise between obtaining the highest possible production and being economically viable. The total organic load indicates how much dry organic matter can be fed to the digester. The parameter uses volume and unit of time, according to Equation 2.18 [11]:

$$OLR = \frac{m \cdot c}{V} \tag{2.18}$$

where OLR is the organic loading rate (kg d^{-1} m^{-3}), m is the substrate feed flow (kg d^{-1}), and c is the concentration of organic matter (%).

The increase in the feed rate causes an increase in biogas production, and if this feed is too intense, there is an overload on the digester caused by the accumulation of inhibitory substances, such as VFA [18].

Total and volatile solids

Total solids (TS) represent the substrate content after being dried at about 105°C, consisting of organic and inorganic matter. During digestion, the amount of TS decreases, reaching an amount of 50% to 80% of the initial content [23]. The type of digestion performed, wet or dry, also influences the final TS content. A solid concentration greater than 40% TS might result in the inhibition of the process as a result of reduced contact area with microorganisms [10, 18, 23].

Volatile solids (VS) represent the fraction of solids that can be oxidised and released as gas after heating to 550°C. The VS are approximately the organic matter fraction, which may represent up to 70% of TS [18, 23].

TS and VS can be distinguished, primarily, by their inorganic matter content. The TS content is crucial for biogas production, as the greater the amount of VS, the richer the biogas. However, the relationship between TS and methane production is not linear and depends on raw material. In the treatment of MSW, the amount of methane will decrease with increasing TS between 10% to 25% [18, 23].

2.1.3 Categories

The AD process can present many different configurations, and the reactor depends on the temperature, feedstock, and feeding type. Therefore, various categories of AD exist, which will be further described in the following sections. Wet or dry digestion and batch or continuous system are two of the most important ones.

Wet or dry digestion

The process for AD can be classified based on the total solid concentration of feed, as wet or dry digestion. The digestion will be considered wet if the content in total solid concentration is lower than 15% and dry if the content in solid concentration is between 20% and 40%. The remaining wet mass is water by definition [11, 18].

During the 1980s, all the AD plants constructed were based on wet system, whereas more recently, the new plants constructed were mainly based on dry process [18].

Wet AD implies higher costs than dry AD due to the digestate de-watering post-treatment and the need for a higher reactor volume. Wet AD also has a lower biogas production rate when compared with the dry process. Dry digestion also allows a higher VFA concentration and OLR than wet digestion, causing a low possibility of process inhibition. However, despite dry AD's economic and energetic advantages, it cannot completely mix the waste and cannot guarantee the ideal contact between microorganisms and substrate [11, 18].

Nevertheless, wet AD presents some advantages, like better flexibility on the type of substrate, the possibility of diluting the inhibitory substances by process water, and the need for less high-level equipment. Comparing, studies show that dry AD has a better cost-effective relation and greater biogas production of both processes [11, 18].

Batch or continuous system

A batch reactor is fed one time with feedstock, and it is closed for a certain period to degrade substrate anaerobically. While the continuous system is uninterruptedly loaded with feedstock but enabling removal of digested and biogas [18].

Some of the benefits of batch digesters are identified as technically simple, low-cost investment, low maintenance required, and minimum energy loss. Biogas re-circulation or mechanical agitators can mix the substrate in continuous systems, keeping the production nearly constant. Studies reported that continuous systems achieved higher methanogenic potential at higher OLR than batch systems [18].

Single-stage and multiple stages

Single-stage digesters have four metabolic phases (hydrolysis, acidogenesis, acetogenesis, and methanogenesis) in one reactor. These digesters present low OLR, a higher retention time, a pH range of 6 to 7, low methane production, are simple to design, build and operate, and are generally less expensive. The main limitation of this type of digester is the presence of acidogenic microorganisms that decrease pH due to quick acidification of substrate, which negatively affects methanogenic microor-

ganisms [10, 18]. In Europe, around 90% of the installed AD use single-stage digesters and the rest two-stage systems [10, 18].

A multi-stage system occurs in two or more separated digesters. In the case of two digesters, the first one is used for hydrolysis, acidogenesis, and acetogenesis, while the second one is mostly used for methanogenesis. The separation in two digesters is made to optimise hydrolysis and fermentative acidification in the first digester and methanogenesis in the second one since each step presents different optimum conditions. The advantages of these systems are increased methane production, a higher OLR, enhanced process stability, better elimination of pathogenic, and an improvement in the efficiency rate of volatile solids removal. High capital investment and operational cost, and complex maintenance are the most significant disadvantages [10, 18].

Co-digestion

Co-digestion is a combined feed of two or more types of organic waste mixed and treated simultaneously. It is usually used to improve the efficiency of AD due to the following benefits [1, 8, 9, 11, 18]:

- Meet the nutritional needs of the microbial community, which enhance process stability and performance;
- Higher methane yield and biogas production;
- Fertiliser generated from nutrient-rich digestate;
- Toxic compounds dilution;
- Increase in biodegradable organic matter;
- Economic advantages due to the need for less equipment (shared equipment).

Anaerobic co-digestion is commonly used nowadays. Animal manure is a suitable co-substrate given that it presents a broad variety of nutrients and high buffer capacity that improve the maximum OLR and offer a more stable environment. Sewage is a great co-substrate due to its low organic load and high active bacteria content. The bacteria present in sewage are favourable for the development of various microorganisms in the AD process [1, 8, 9, 11, 18].

In summary, these co-substrates have some proprieties that present an advantage for AD, such as high water content, low price, high accessibility, and natural content of anaerobic bacteria. However, when used alone, these co-substrates present a low methane yield [1, 8, 9, 11, 18].

2.2 Anaerobic Digestion Mathematical Modelling

AD is a well-established process, but due to the substrate variability, microbial complexity, and the 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. AD mathematical models are valuable tools that enhance the design and efficiency of the systems. They characterise the main aspects of a biological process, establishing distinguished feedstock parameters and processing conditions to forecast the system's evolution [8, 12, 24].

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. This section will present an overview of the existing models in the AD field [8, 12, 15, 19, 25].

The most suitable structure for the models should be chosen based on the following four principles [25]:

- The model should be as simple as possible;
- The parameters with the most significant influence must be presented;
- Unknown parameters must be estimated from experimental data;
- The model must remain valid under expected conditions.

Identifying the parameters is a subtle task due to many existing parameters and the lack of experimental data. The literature shows an absence of a systematic procedure for modelling AD processes. Furthermore, collections of parameter values are being reported without a deep analysis of parameter accuracy and model validity, making it challenging to analyse all the published information [24, 25].

Models that consider that the limiting step changes with variable operating conditions are difficult to model and often cannot describe the process adequately under transient conditions [26].

Models can be classified according to two types:

- dynamic or non-dynamic;
- white-box, grey-box, or black-box.

Dynamic or non-dynamic (steady-state) refers to the time frame of the prediction. Dynamic models can make predictions continuously in time or at regular discrete intervals, while non-dynamic only predict time-independent variables [15].

The second type of classification is driven by the amount of a priori information included [15, 27]. White-boxes are deductive models, which use theoretical information to describe the biochemical reactions of the process. Meanwhile, black-box models are based on experimental data that link input to output without considering any prior knowledge of the biochemical process. Lastly, grey-box or empirical models are the ones that have the parameters set as a physical interpretation but are also adjusted by a parameter estimation procedure. These are the type of models most used for dynamic models, as it is

usually the result of simplifying the process, and since AD is a relatively complex process, they are the most suitable [15, 27].

Dynamic models involve multiple ordinary differential equations (ODE) based on mass-balance considerations and can be generally represented by Equation 2.19. In addition to ODEs, most model structures also present algebraic equations (AE) used to describe balances or other fixed constraints. AE originate mass balances or instantaneous reactions, such as neutralisation reactions, the flow of insoluble gaseous components [15].

$$\frac{dx}{dt} = (x_{in} - x) \cdot D + K \cdot r(x) - F(x) \tag{2.19}$$

where x is the vector of state variables, such as concentration of components, D (d^{-1}) is the dilution rate of feed, K is the stoichiometric or rate-equation matrix, r(x) is the reaction rate matrix, and F(x) the mass-transfer between gas and liquid phase [15].

The first model was proposed by Andrews and Pearson [28], and had in consideration two bacterial groups, namely acid and methane microorganisms, and the substrate was presumed to have dissolved organic substances [15, 26]. The subsequent models considered biogas production using only the methanogenesis step, as other organisms had inhibitor effects. Denac et al [29] added to this model the conversion of propionate to acetate by including acetogenesis [15, 26]. 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 [26]. The kinetics steps of these models were based on Monod type kinetics [30], which consider a single growth-limiting substrate [15, 26].

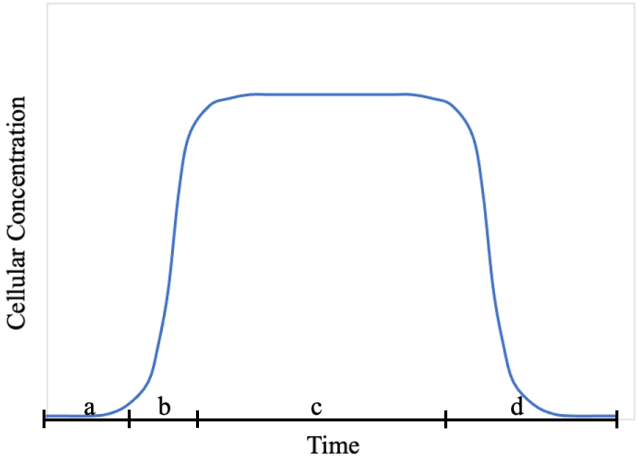


Figure 2.2: Variation of cell concentration over time in a batch reactor. Subtitle: a-*lag phase*; b-*growth phase*; c-*stationary phase*; d-*death phase*. Adapted from [8]

The digestion can be described in the function of the cell concentration. At the beginning of digestion, the amount of microorganisms is reduced, as well as their growth. This initial stage is called the *lag phase*. After that, there is an immediate increase in cell concentration named the *growth phase*. When cells compete for substrate and achieve a point when the cell replications are equal to cell deaths, the *growth phase* ends, and the *stationary phase* begins [8, 30]. The *stationary phase* ends when the

number of deaths is higher than the replication, resulting in a fall of cell concentration, called the *death phase*. In practice, the interesting part of analysing is from the *lag phase* until the *stationary phase*, as it is the part of the process where the most considerable amount of biogas is produced. However, the sigmoid equation does not properly fit generally with the experimental results obtained. In figure 2.2, it is possible to analyse the variation of cell concentration described above [8, 30].

2.2.1 Exponential model

The exponential model is used to describe the cell concentration variation in the *growth phase*. This model rests on theory that the speed of growth in an instant is proportional to the concentration of cells existing , which can be expressed by the Equation 2.20 [8]:

$$\frac{dX}{dt} = \mu \cdot X \tag{2.20}$$

where X is the concentration of cells and μ is the cell growth rate (d^{-1}).

The development of Equation 2.20, leads us to equation 2.21, where it is possible to verify possible to verify that the variation of cells follows an exponential curve in the *growth phase* [8].

$$\mu = \frac{X_2 - X_1}{X_1 \cdot (t - t_{lag})} \tag{2.21}$$

where t_{lag} is the lag time, and t the actual time.

It has been verified that μ varies with time, so this model is not entirely satisfactory. To obtain a better fit, Monod proposed a model in which the cell growth rate is calculated considering the substrate concentration, represented by Equation 2.22. As mentioned above, when it reaches a certain point the cell concentration increases and the growth rate slows down [8].

$$\mu = \frac{\mu_{max} \cdot S}{K_S + S} \tag{2.22}$$

where μ_{max} is the maximum cell growth rate, S is the substrate concentration at a given time and, K_S is the saturation constant [8].

Other models with the same style appeared along with Monod [30], and they all described that the maximum rate in the exponential phase is minimised when the substrate concentration is low [8].

The biomass/substrate yield can be calculated from Equation 2.23, where the variation of cell concentration is proportional to substrate consumption [8].

$$Y_{x/s} = \frac{X_1 - X_0}{S_0 - S_1} \tag{2.23}$$

where S_0 and S_1 are the initial and final cell concentrations.

The product/biomass yield and the methane production (M) can also be calculated, which can be described by the equations 2.24 and 2.25, respectively [8].

$$Y_{p/x} = \frac{P_1 - P_0}{X_1 - X_0} \tag{2.24}$$

$$\frac{dM}{dt} = Y_{p/x} \cdot \frac{dX}{dt} \tag{2.25}$$

Based on Equation 2.25 and by deriving the variation of cell concentration over time, it is possible to achieve Equation 2.26, which indicates the methane production over time. It was also proven that the amount of product obtained follows an exponential growth during the exponential growth of microorganisms [8].

$$M = Y_{p/x} \cdot X_0 \cdot e^{\mu(t - t_{lag})} \tag{2.26}$$

When complemented by the Monod equation, it is still a practical and straightforward model. However, this model is not entirely acceptable given that it does not accurately describe the cell concentration variation as the substrate is consumed and the stationary phase approaches [8].

2.2.2 Kinetic models overview

Microbial growth and substrate consumption rates (both depend 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 can also be taken into consideration [31].

After Monod, it was observed that the acetoclastic methanogenesis step exhibited inhibition at high acetate concentration, whereby the kinetic Equation 2.28, Andrews kinetics, [29] was proposed based on Haldane kinetics (Equation 2.27) [15].

$$\mu = \frac{\mu_{max}}{1 + \frac{K_S}{S} + \frac{S}{K_I}} \tag{2.27}$$

$$\mu = \frac{\mu_{max}}{1 + \frac{K_S}{S} + \frac{VFA}{K_I}} \tag{2.28}$$

where VFA is the concentration of VFA and, K_I is the inhibition constant.

With the development of knowledge about the process of anaerobic digestion, it was realised that several factors influence it efficiency, such as overload and toxic components. These inhibitions are included in the recent models and are directly related to pH, which can be calculated from the H^+ concentration (Equation 2.29) [15]:

$$H^+ = HCO_3^- + VFA^- + LCFA^- + OH^- + An^- - Cat^+ - NH_4^+ \tag{2.29}$$

where An^- and Cat^+ are the concentration of anion and cation, respectively.

The solubility of CO_2 (Equation 2.30) has to be considered to obtain the real pH and biogas production rates [15].

$$r_{CO2} = k_l a(\frac{p_{CO2}}{H_{CO2}} - [CO_2]) \tag{2.30}$$

where $k_l a$ is the mass-transfer constant, p_{CO2} the partial pressure of CO_2 , H_{CO2} the Henry constant, and $[CO_2]$ the concentration of unionised CO_2 in the liquid phase.

Most of the natural substrates are particulated, for which the digestion of dissolved organics is not a common situation. Therefore, hydrolysis will solubilise the particulates before acidogenic and methanogenic steps. Hydrolysis limits the rate in most part of situations [15]. In literature [15, 32], several kinetic equations are reported for hydrolysis as a first-order reaction, but the kinetic constant depends on various factors, including composition or particle size distribution. [15, 32]

TA kinetic equation described the coverage of particles with bacteria that secrete hydrolytic exo-enzymes, Equation 2.31, developed by Sanders et al. [15, 32].

$$\mu = k_{SBK} \cdot A \tag{2.31}$$

where k_{SBK} is the surface based hydrolysis constant and A is the surface area available for hydrolysis.

Hobson developed a model that had in consideration the surface-based kinetics, from which Vavilin et al. [32] describes that this kind of kinetics can also depend on the particle shape [15]. Hydrolysis can be described in two phases: in the first stage, the particulates are colonised by bacteria, which later excrete the hydrolytic enzymes; in the second stage, the surface covered by the bacteria is degraded. This degradation takes place at a constant depth per unit of time and can be described by the Contois kinetic expression (Equation 2.32) [15].

$$\mu = \mu_{max} \cdot X \frac{S}{K_S X + S} \tag{2.32}$$

For low S/X, this expression will represent the first-order kinetics for the substrate, while for a high S/X, this expression will represent the first-order kinetics for the biomass [15].

The subsequent models addressed specific applications of AD, i.e., specific types of substrates, being that it is possible to divide into four main groups: wastewater, sludge, manure and solid waste [15].

2.2.3 ADM1

The Anaerobic Digestion Model No. 1 (ADM1) was developed by the International Water Association (IWA) Task Group [19] with the objective of creating a model as widely applicable as possible for anaerobic processes, a generic model. This model is the most used in the research area. However, this will not be as accurate as some specific models developed for certain applications because of its generic nature [19, 31, 33]. This model has already been implemented by several authors in different areas, such as, industrial applications [34], distillery waste [35], dairy manure [36], sewage sludge [37], solid waste [38], agricultural biogas plant [39], swine manure [40], among others.

ADM1 is a structural model that describes both biochemical and physicochemical processes, as-

suming a perfect substrate mixture [19, 27]. The components are expressed based on their COD and consider both biochemical and physicochemical processes. Substrate represents only the degradable COD since a great fraction of the input COD may be anaerobically non-biodegradable [19, 31].

This model is based on the four steps of the AD process described and their equations in Section 2.1.1: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. In Figure 2.1, there are schematically presented all the biochemical reactions assumed in this model. The disintegration of biomass is not considered a step of the AD process, but it will be treated in the same way in this model, having its own kinetic. ADM1 considers microorganisms as part of the complex organic matter. This model includes [12, 31]:

- 19 biochemical processes: 1 process of disintegration of complex organic matter; 3 processes of hydrolysis of carbohydrates, proteins, and lipids; 8 processes of uptake of sugars, amino acids, LCFA, VFA, acetate, and hydrogen; and 7 processes of decay of sugars, amino acids, LCFA, VFA, acetate, and hydrogen;
- 6 acid/base equilibrium in association with pH calculation;
- 3 gas-liquid transfer processes;
- Inhibitions.

In ADM1, the stoichiometric yield coefficients of the 19 processes referred to before are represented in the form of a matrix,where the inherent inhibition of the process, such as by pH, ammonia, and hydrogen, is considered. Substrate uptake kinetics is used to describe variable change and inhibition of microorganisms, so the Monod-type kinetics is used, not Michalis-Menten. In Appendix A.1, the matrices created by IWA are represented. Disintegration and hydrolysis are assumed to follow first-order kinetics, while the remaining steps are Monod-type kinetics [12, 15, 19].

A total of 32 differential equations can be used to calculate the dynamic states of AD components. The mass balance for a continuous anaerobic digester on a given substrate is described by Equation 2.33 [19]:

$$\frac{dS_i}{dt} = \frac{q_{in} \cdot S_{in}}{V} - \frac{q_{out} \cdot S_{liq}}{V} + \sum \rho_j v_{i,j} \tag{2.33}$$

where S_i is the soluble concentration substrate, S_{in} is the initial concentration of the soluble substrate, q_{in} and q_{out} the inflow and outflow, respectively, V is the digester volume, and $\sum \rho_j v_{i,j}$ the sum of biochemical rate coefficients ($v_{i,j}$) and kinetic rates (ρ_j)for the process, which are presented in Appendix A.1.

Liquid-gas transfer equations (also taken into account in this model) can be generally described by Equation 2.34, and the differential equations for the gas phase with a constant gas volume by Equation 2.35 [19].

$$\rho_{T,i} = k_L a(S_{liq,i} - 16K_{H,i}p_{gas,i}) \tag{2.34}$$

$$\frac{dS_{gas,i}}{dt} = -\frac{q_{gas} \cdot S_{gas,i}}{V_{gas}} + \rho_{T,i}\frac{V_{liq}}{V_{gas}} \tag{2.35}$$

where $\rho_{T,i}$ and $p_{gas,i}$ are the transfer rate and pressure of gas i; and $k_L a$ is a gas-liquid transfer coefficient.

Temperature is an important parameter, which mainly influences the physicochemical system due to changes in equilibrium coefficients and also in biochemical parameters. If the heat of reaction is considered independent of temperature, the influence of temperature in a given parameter can be described by Equation 2.36 [19]:

$$K_2 = K_1 \cdot e^{\Theta(T_2 - T_1)} \tag{2.36}$$

where K is the given parameter and Θ is defined by Equation 2.37:

$$\Theta = \frac{\Delta H^\circ}{R}(\frac{1}{T_1} - \frac{1}{T_2}) \tag{2.37}$$

Figure 2.3 represents the model concept of a single-tank continuous digester with constant liquid volume, including inputs, reaction kinetics, and output [12, 19].

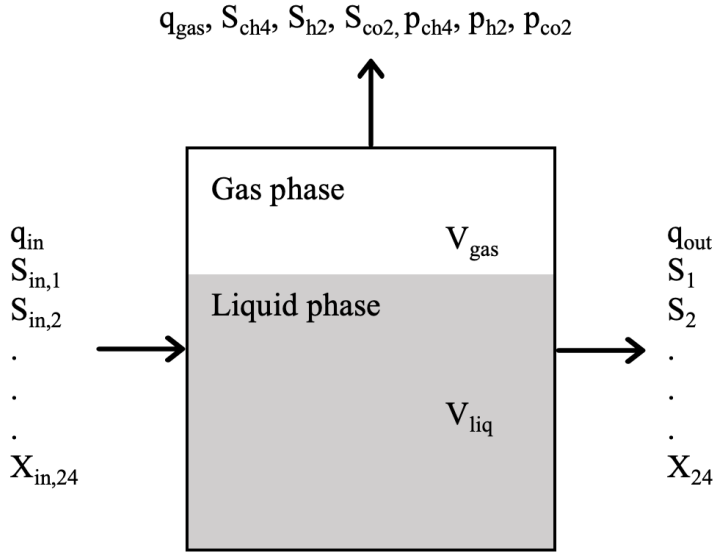


Figure 2.3: Schematic of a single-tank continuous digester. Where q, V, p represents, respectively flow, volume and pressure; X and S represent, respectively, particulate and soluble components concentration. Adapted from [19].

ADM1 provide some advantages, such as [12]:

- Increased model application for full-scale designs;
- Will allow more consistent and more straightforward presentation and application of future modifications and add-ons;
- Process optimisation;

- Opportunity to implement AD research in industrial applications, providing a reasonable basis for other model development and validation studies.

Below are listed some of the limitations in the ADM1 model that have been acknowledged in the literature [24, 31]:

- The need to extensively characterise the substrate and the various bacterial groups may make it less practical for full-scale simulation;
- Assuming that disintegration happens before hydrolysis can introduce error into the complex matter;
- Conversion and distribution of S, P, and N are underdeveloped;
- Even though the ADM1 application in different substrates has been successful, modelling the liquid-solid transformations like the precipitation and solubilisation of ions is not considered in the model.

ADM1 model has the advantage of being a possible base for further modifications and developments [15, 41]. The main issues that are taken into account in the subsequent models (based on ADM1) are co-digestion, characterisation of substrates and solids or particular waste digestion. Co-digestion presents substrates that have a composition that is heterogenic and changes dynamically, providing parameter estimation problems. Efforts were made to take into consideration the toxic effects of inhibitory substances from co-substrates and intermediates [15, 31].

Other issues were also considered in extensions or modifications, such as degradation of new soluble, fermentable substrates, organic contaminants degradation, organic solid waste disintegrating using a surface-based kinetics model, and VFAs inhibition [31].

Chapter 3

Implementation

This chapter aims at presenting the methods used to examine the case study, beginning with a description of the process in study, and then with the methods and procedures used through this work. Is presented the data analysis of the existing data as well as the choice of data sets. And finally, the development of the mathematical model and materials used, being presented the assumptions and description of the model, how the model was formulated and how the dynamic model fitting and validation was performed.

3.1 Case-study: General AD process description

The plant feed is made of different raw materials that need different pre-treatments depending on their composition and presenting distinct lines of treatment. In the plants under study, the raw materials used are MSW and cattle and chicken manure. Therefore, the pre-treatment can be divided into mechanical and biological treatments.

MSW line has both mechanical and biological pre-treatment, starting with the mechanical, subdivided into wet and dry pre-treatment. Initially, in the dry pre-treatment, the waste goes through a bag opener, then the separation of waste with less than 80 mm, moving then to magnetic separation, before reaching the pulpers. After this separation, in the pulpers, there is a wet pre-treatment process that aims to: remove heavy non-biodegradable contaminants (stones, glass, and metals) and light (textiles, plastics, and others) and disintegrate biodegradable waste to optimise the anaerobic digestion process, obtaining a biodegradable suspension. The suspension produced also contains ”sands” with a diameter of up to 10 mm, which then passes through a Grit Removal System (GRS), where sand with a diameter greater than 250 μm will be removed.

The following stage is the biological pre-treatment, where initially it is necessary to carry out a thickening of the suspension coming from the GRS, as the suspension from the GRS has an average of 7% of total solids, increasing the total solids content, after thickening, to about 10%. Thickening is carried out to use smaller digestion tanks and increase the organic load present. Before entering the digesters, the suspension is stored in tanks to be fed to the digesters continuously and regularly, as the necessary

condition for anaerobic digestion. In the digesters, there is production of biogas, part of which is reintroduced in the digesters, that improves the mixture inside the digester and optimises the digestion. The biological process is carried out at approximately 35°C in mesophilic conditions.

The cattle and chicken manure line has a much simpler pre-treatment, only needing to go through a GRS to eliminate ”sands”, stones, and bones and then going to the digesters following the same process described for the MSW line.

Once the digestion is finished, the digested product undergoes dehydration, changing from a total solids content of approximately 0.5% to 2% to 30% to 35%. The dehydrated digestate can then undergo different treatments. In these cases, composting or aeration thanks are used. The general AD process is presented schematically in Figure 3.1.

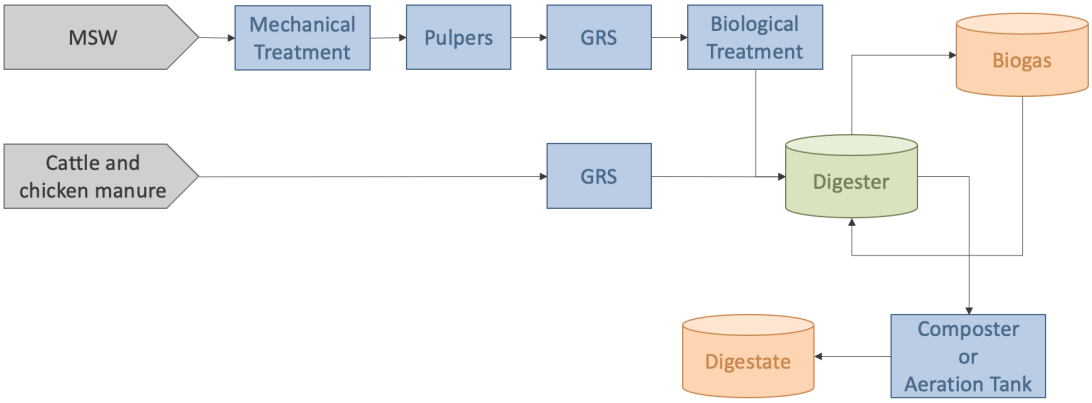


Figure 3.1: Schematic description of the AD process.

3.2 Methods and procedure in this work

The numerical model developed during this work was performed using the software *Excel*. The flowchart presented in Figure 3.2 explains the work path and procedure applied. After selecting the model and parameters, the model is formulated based on initial conditions, mainly presenting theoretical values and experimental ones. Then, based on the first set of 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.

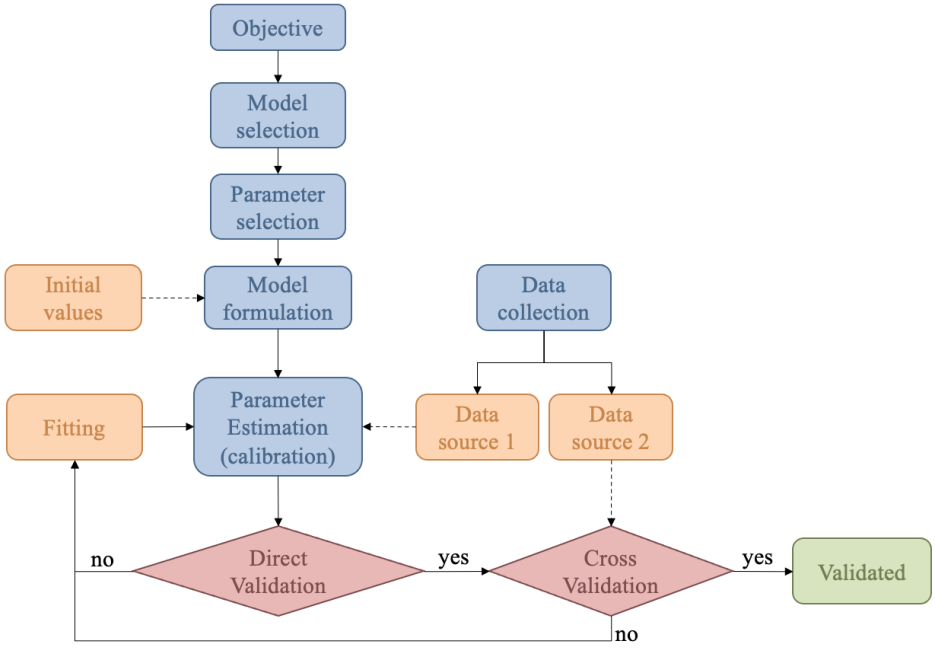


Figure 3.2: Flowchart of the applied methods and procedures in this work.

3.3 Data analysis

Efacec collected the data used for the model developed over a period of ten months, with the parameters being measured daily. For the construction of the model, a set of process parameters were selected that had relevance to anaerobic digestion and a significant number of consecutive days of data. In Table 3.1, the list of the chosen parameters is presented, as well as the method of analysis used for its determination.

Table 3.1: Methods of analysis or measurement of the experimental parameters used. In COD, Ntot and Ptot the standards for the methods are indicated, not the specific methods.

PARAMETER	MEASURE
T (°C)	Temperature sensor (digester's exit)
q_{in} (m^3/day)	Flowmeter
COD (kg/day)	ISO 15705:2002
Ntot (kg/day)	UNI EN 25663:1995 + ISO 7150-1:1984
Ptot (kg/day)	APAT CNR IRSA 4110 A1 Man 29 2003
q_{bio} (m^3/day)	Flowmeter
DL (m^3)	Floater
% CO_2	-
% CH_4	-

COD was the only parameter that was measured weekly, being calculated an approximated daily value by and Efacec. These approximated values were used as if they were experimental values for model calibration and validation.

From the data provided by Efacec, two sets of data were chosen in order to use the first one (with a smaller number of days) to calibrate the model and the second one (with a more significant number

of days) to carry out the cross-validation. For the first set of data set, the reactor's start-up data was chosen, as the theoretical model on which the model is based represents the start-up (the moment when there are more variations on the values of the parameters). The second data set has a more significant number of days of data to verify that the model holds for a wide range of conditions and variations. For the data choice, it was considered that it is important to have disturbances and consecutive days of data. The data sets referred to are presented below in Figures 33.4 to 3.6. The red dots represent unused data, which has been considered unreliable since they present very low values with no possible explanation.

The plant features two parallel digesters with similar functions. The parameters measured by the chemical analysis of the digester, such as COD, Ntot and Ptot, are measured for the set of the two digesters. For the remaining parameters, although they are measured separately, the value of all the digesters is taken.

Data set 1

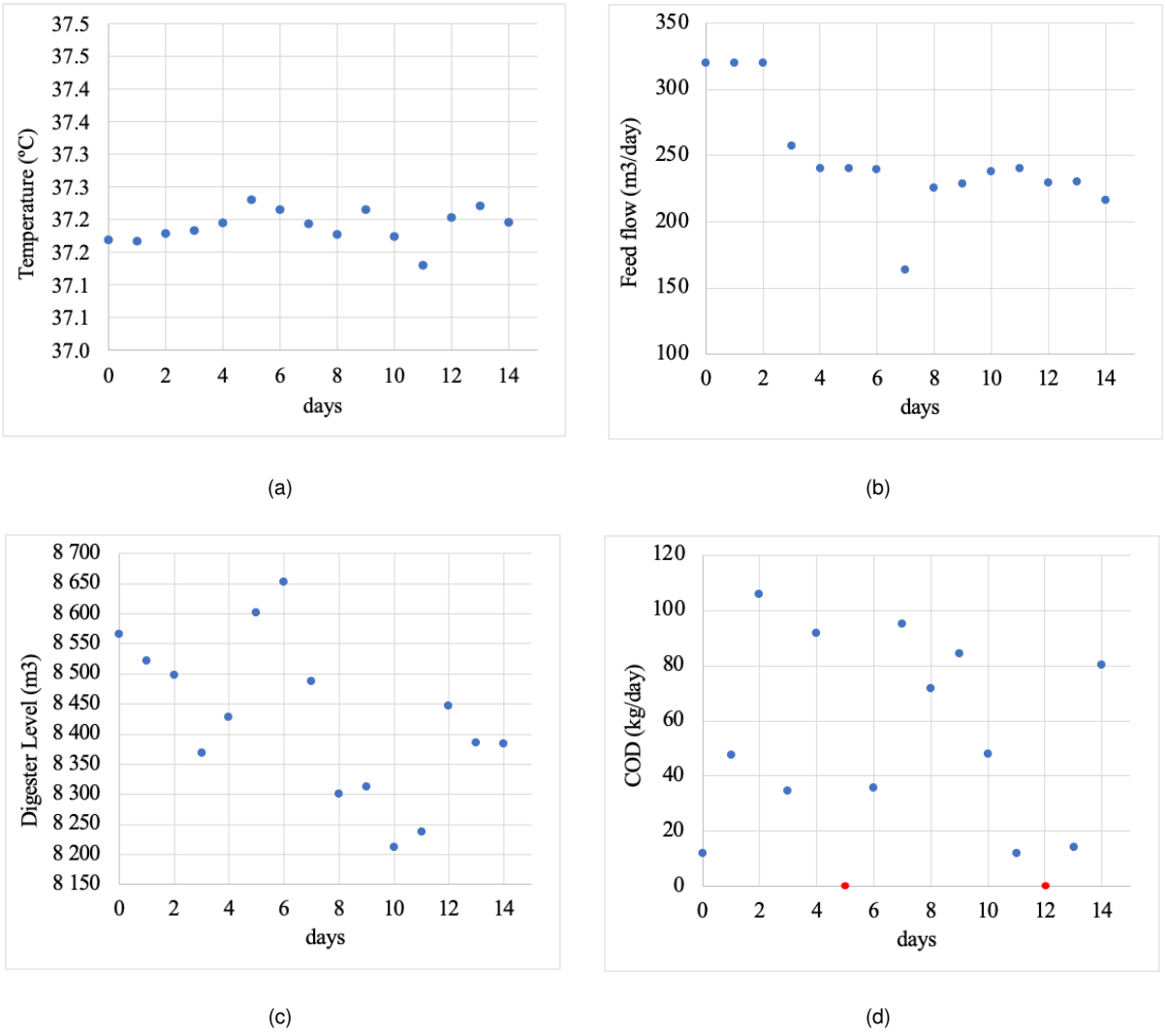


Figure 3.3: Variation of a) temperature (°C), b) feed flow (m^3/day), c) digester level (m^3) and d) COD (kg/day), during a period of 15 days from the start-up (data set 1). Dots marked in red represent unused data, as it has been considered unreliable.

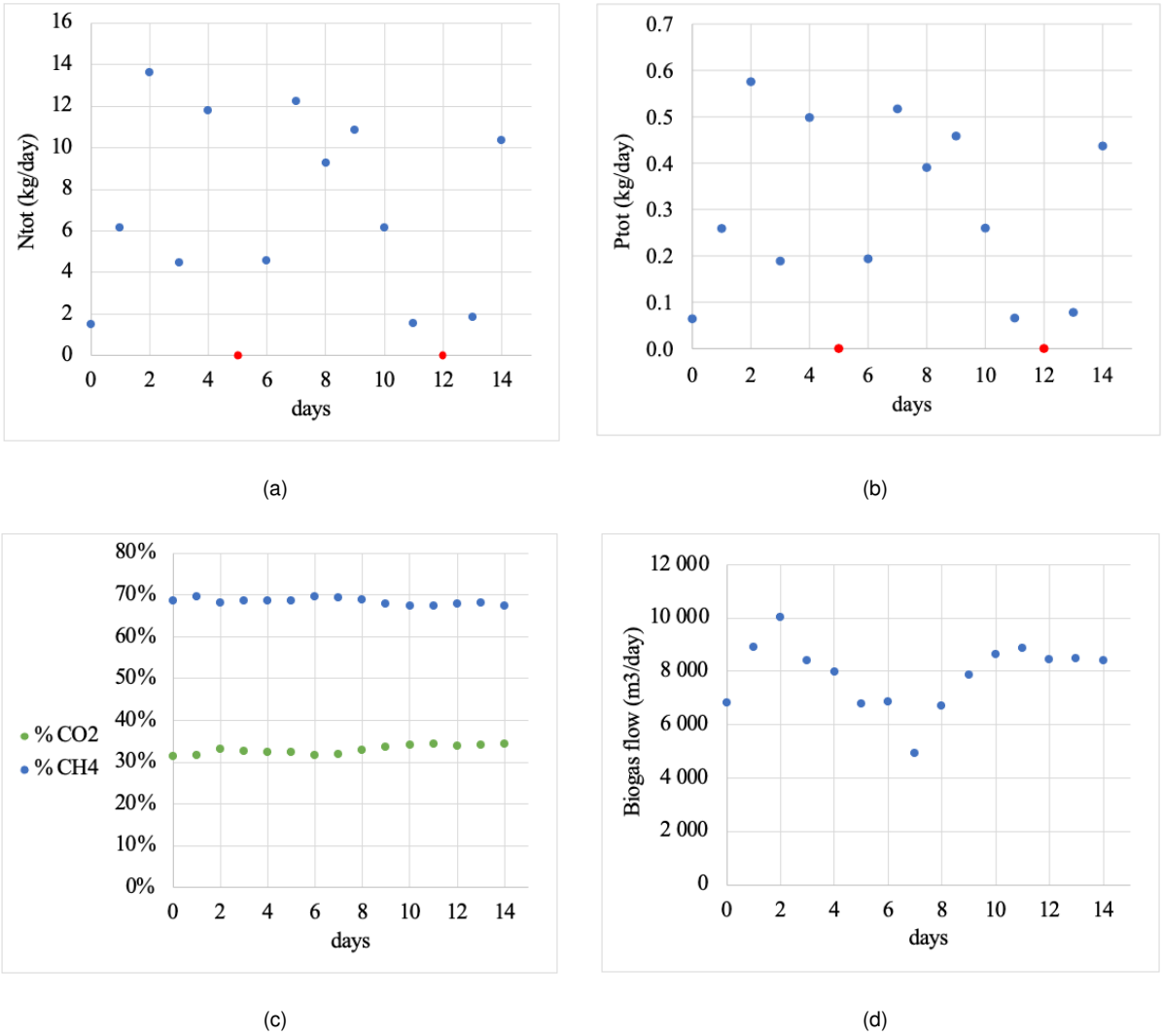


Figure 3.4: Variation of a) Ntot (kg/day), b) Ptot (kg/day), c) % of CO_3 and CH_4 in biogas and d) biogas flow (m^3/day), during a period of 15 days from the start-up (data set 1). Dots marked in red represent unused data, as it has been considered unreliable.

By analysing the two sets of data, it is possible to see that temperature variations are minimal, less than 1°C. Therefore, temperature calibration is not expected to be very reliable due to a lack of data. Nevertheless, it will be analysed in order to verify the results, i.e. the model will be fitted with this data. Furthermore, it is crucial to understand that the model will only correspond to the mesophilic regime since the bacteria's developed in each regime are different.

From the data analysis and process information, it was possible to conclude that the start-up of the digester was not carried out with empty but already contained slurry, as biogas production began immediately. However, in the theoretical model, the start-up was initially considered with an empty digester, so it was necessary to impose a steady state for this to correspond to reality.

Data set 2

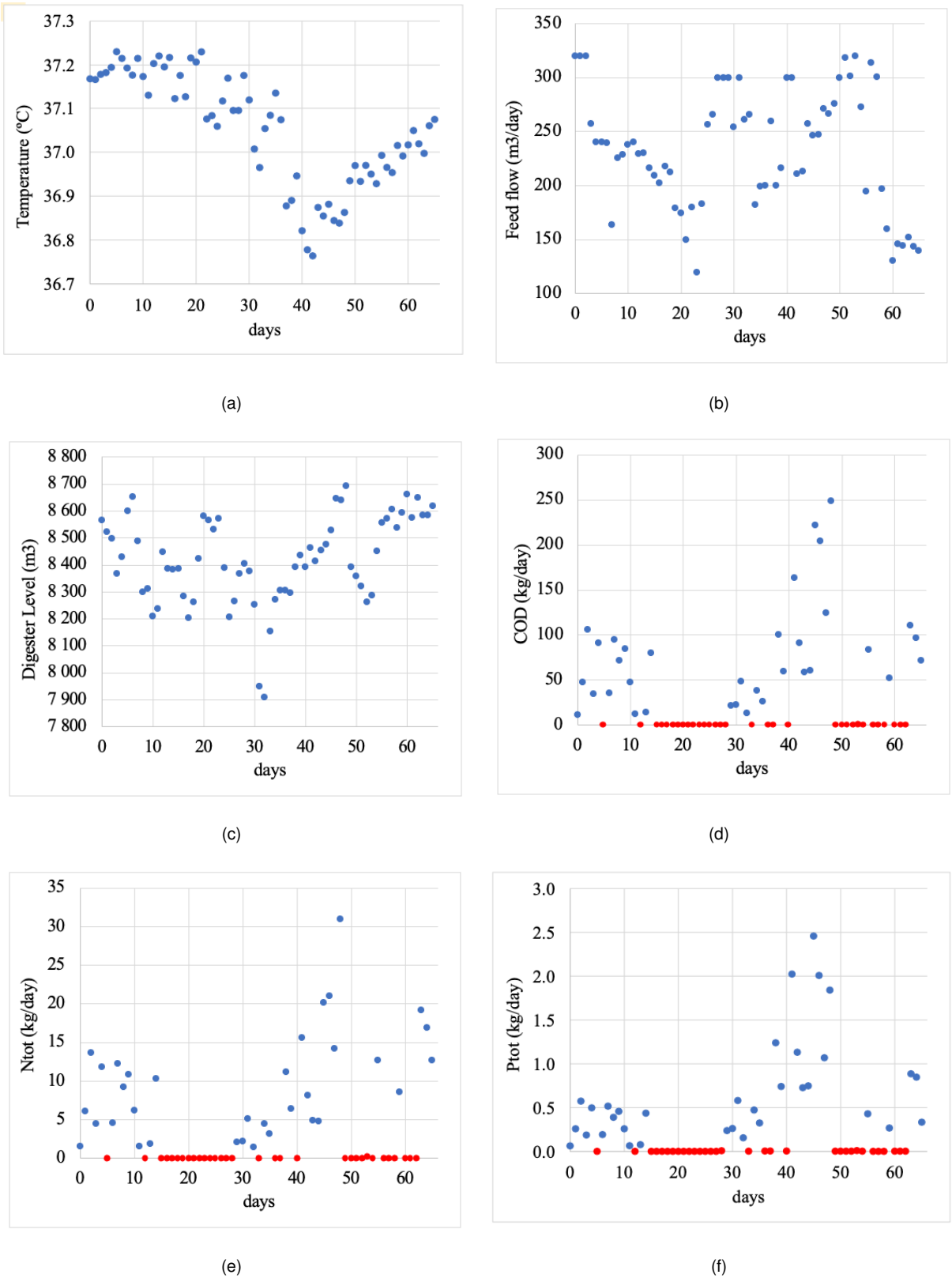
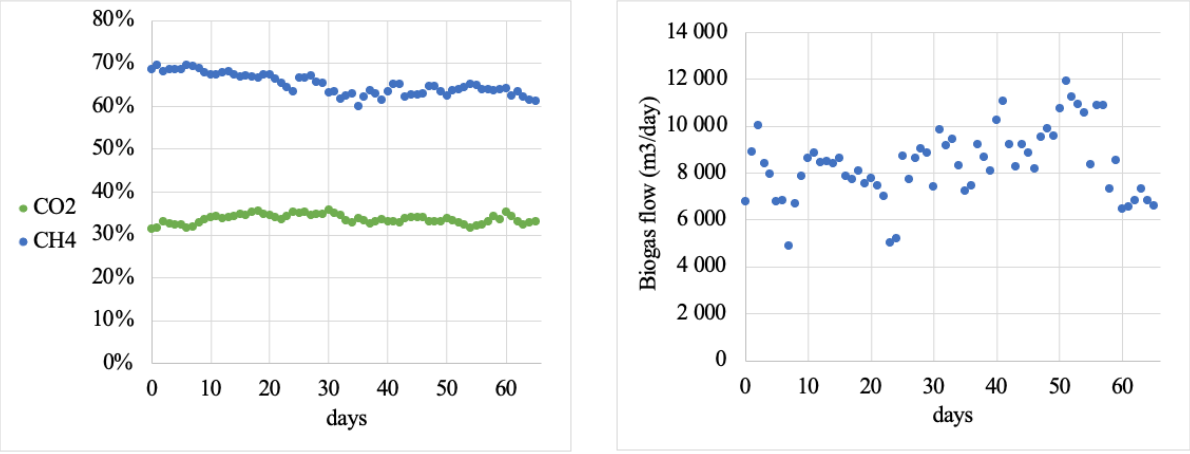


Figure 3.5: Variation of a) temperature (°C), b) feed flow (m^3/day), c) digester level (m^3), d) COD (kg/day), e) Ntot (kg/day) and f) Ptot (kg/day), during a period of 66 days from the start-up (data set 2). Dots marked in red represent unused data, as it has been considered unreliable.



(a) (b)

Figure 3.6: Variation of a)% of CO_3 and CH_4 in biogas and b) biogas flow (m^3/day), during a period of 66 days from the start-up (data set 2).

COD, Ntot and Ptot have shown at first sight high variations (Figure 3.4) not justified by the flow input. However, it is important to verify that the variations are similar in the three parameters, which indicates that they might have a correlation between them, likely at the composition of the feed. Data from two other plants (Figure 3.7) was analysed in order to verify if this variation also existed, having been verified the same type of behaviour. In addition to this variation being created by changes in feed, some analysis errors may also be associated.

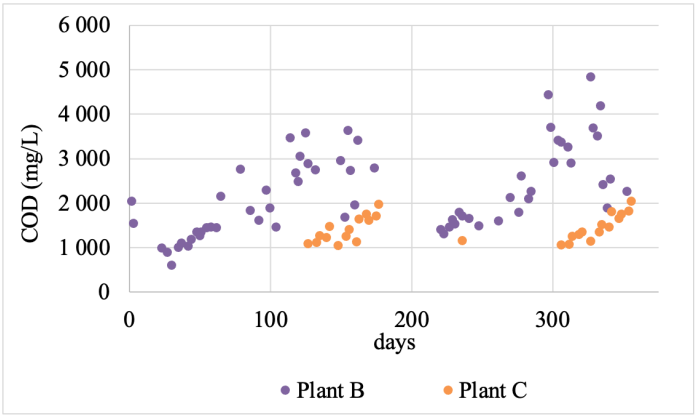


Figure 3.7: COD variation in plant B and C.

3.4 Assumptions and model description

The model was developed, having in consideration an ideal reactor to describe the apparent behaviour. However, the real 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., there were no considered temperature or concentration gradients, and the system is represented in Figure 3.8.

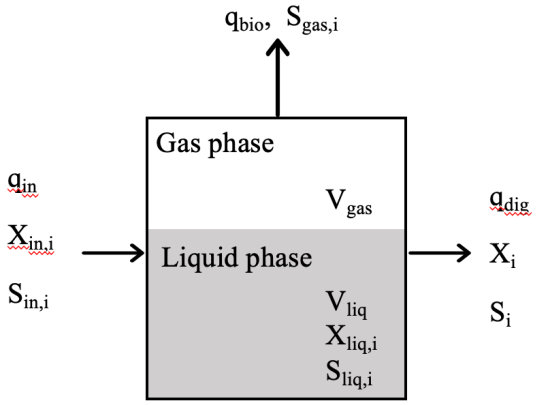


Figure 3.8: Schematic of a single thank digester considered for this model.

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. This information flow is schematically presented in Figure 3.9.

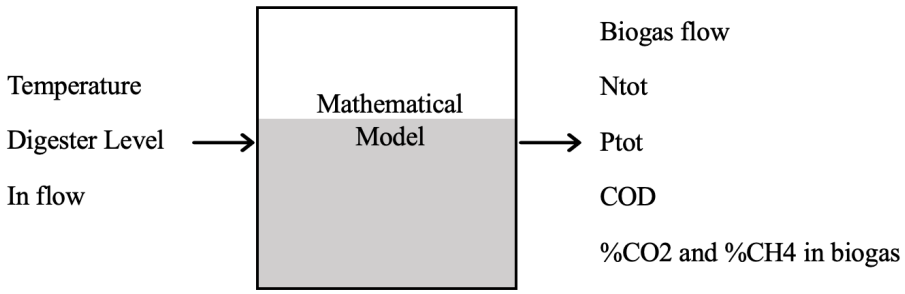


Figure 3.9: Schematic representation of the information flow in the model.

Model assumptions:

- CSTR reactor;
- Mesophilic digestion (reference temperature of 35°C);
- HRT constant;
- First-order reactions;
- Constant density (Table 3.2);
- COD flux (Figure 3.10);
- Inhibitions were not considered;
- The ratio of 0.47 to CO_2/CH_4.

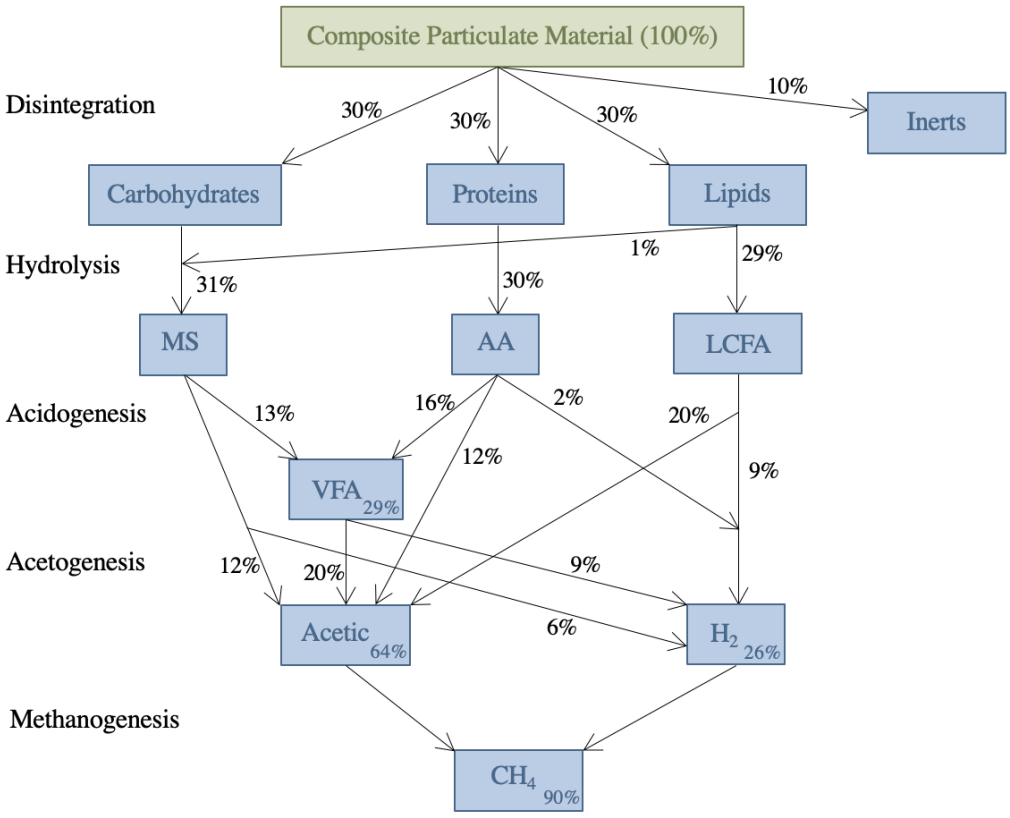


Figure 3.10: COD flux of a particulate composite considered for the development of the model.

In addition, some parameters were also arbitrated based on theoretical values for parameters that did not present experimental values, which are presented in Table 3.2. Finally, a sensitivity analysis of the assumed parameters was made to understand the influence these can have on the model results, which will be presented in the Results (Chapter 4).

Table 3.2: Assumed parameters for the development of the model.

PARAMETER	VALUE	REFERENCE
ρ_{dig} (kg/m^3)	1000	-
ρ_{bio} (kg/m^3)	1.12	-
$L_{P/C}$	0.02	Based on [42, 43]
$P_{N/C}$	0.26	Based on [42, 44]
$P_{\%Li}$ (%)	0.25	Based on [43, 45]
$N_{\%Pr}$ (%)	0.3	Based on [45–47]

3.4.1 Mass Balances

The mass balances for each component were described from equation 2.33, and can be represented by equations 3.1 to 3.10.

$$\frac{dX_c}{dt} = \frac{q_{in}}{V_{liq}}(X_{c,in} - X_c) + \sum \gamma_j v_{i,j} \tag{3.1}$$

$$\frac{dX_{ch}}{dt} = \frac{q_{in}}{V_{liq}}(-X_{ch}) + \sum \gamma_j v_{i,j} \tag{3.2}$$

$$\frac{dX_{pr}}{dt} = \frac{q_{in}}{V_{liq}}(-X_{pr}) + \sum \gamma_j v_{i,j} \tag{3.3}$$

$$\frac{dX_{li}}{dt} = \frac{q_{in}}{V_{liq}}(-X_{li}) + \sum \gamma_j v_{i,j} \tag{3.4}$$

$$\frac{dX_i}{dt} = \frac{q_{in}}{V_{liq}}(-X_i) + \sum \gamma_j v_{i,j} \tag{3.5}$$

$$\frac{dS_{ms}}{dt} = \frac{q_{in}}{V_{liq}}(-X_{ms}) + \sum \gamma_j v_{i,j} \tag{3.6}$$

$$\frac{dS_{aa}}{dt} = \frac{q_{in}}{V_{liq}}(-X_{aa}) + \sum \gamma_j v_{i,j} \tag{3.7}$$

$$\frac{dS_{lcfa}}{dt} = \frac{q_{in}}{V_{liq}}(-X_{lcfa}) + \sum \gamma_j v_{i,j} \tag{3.8}$$

$$\frac{dS_{vfa}}{dt} = \frac{q_{in}}{V_{liq}}(-X_{vfa}) + \sum \gamma_j v_{i,j} \tag{3.9}$$

$$\frac{dS_{ac}}{dt} = \frac{q_{in}}{V_{liq}}(-X_{ac}) + \sum \gamma_j v_{i,j} \tag{3.10}$$

$$\frac{dS_{h2}}{dt} = \sum \gamma_j v_{i,j} \tag{3.11}$$

$$\frac{dS_{ch4}}{dt} = \sum \gamma_j v_{i,j} \tag{3.12}$$

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). The nomenclature of the components is presented in Table 3.3.

Table 3.3: Nomenclature of the components of the model.

Symbol	Description
Xi	Concentration of soluble component i
Si	Concentration of particulate component i
components (i)	
c	composite
ch	carbohydrates
pr	proteins
li	lipids
i	inerts
ms	monosaccharides
aa	amino acids
lcfa	long chain fatty acids
vfa	volatile fatty acids
ac	acetate
h2	hydrogen
ch4	methane

3.5 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. All reactions were assumed to be first order, and the Matrix method [1] represents the kinetic equations (Table 3.4). 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.

[1] Matrix method represents the reaction terms for each component, subdivided by processes.

Table 3.4: Biochemical rate coefficients ($v_{i,j}$) and kinetic rate equations (γ_j) for the components. (i=1-12; j=1-10)

Component (i) $\rightarrow$		**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**Rate**
Process (j) $\downarrow$		X_c	X_{ch}	X_{pr}	X_{li}	X_I	S_{ms}	S_{aa}	S_{LCFA}	S_{VFA}	S_{ac}	S_{h2}	S_{ch4}	**(γ_j; kg COD m^3 d^{-1})**
1	Disintegration	-1	0.30	0.30	0.30	0.10								$k_{dis}\ X_c$
2	Hydrolysis of carbohydrates		-1				1							$k_{hid,ch}\ X_h$
3	Hydrolysis of proteins			-1				1						$k_{hid,pr}\ X_{pr}$
4	Hydrolysis of lipids				-1		0.03		0.97					$k_{hid,li}\ X_{li}$
5	Acidogenesis of monosaccharides						-1			0.47	0.39	0.19		$k_{acid,ms}\ S_{ms}$
6	Acidogenesis of amino acids							-1		0.53	0.40	0.07		$k_{acid,aa}\ S_{aa}$
7	Acidogenesis of LCFA								-1		0.69	0.31		$k_{acid,LCFA}\ S_{LCFA}$
8	Acetogenesis of VFA									-1	0.69	0.31		$k_{acet,VFA}\ S_{VFA}$
9	Methanogenesis of acetate										-1		1	$k_{met,ac}\ S_{ac}$
10	Methanogenesis of hydrogen											-1	1	$k_{met,ac}\ S_{ac}$

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 compositions of macromolecules, shown in Table 3.5, were assumed for the chemical composition of the composite [44]. Moreover, Equations 3.13 and 3.14 represent the global equations of AD [48].

Table 3.5: Chemical composition of the macromolecules proteins, carbohydrates, and lipids. [44]

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

$$C_cH_hO_o + yH_2O \rightarrow xCH_4 + (c-x)CO_2 \tag{3.13}$$

$$C_cH_hO_o + yO_2 \rightarrow \frac{h}{2}H_2O + cCO_2 \tag{3.14}$$

where x is defined by Equation 3.15:

$$x = \frac{c}{2} + \frac{h}{8} - \frac{o}{4} \tag{3.15}$$

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 3.16 and 3.17, which represents the AD of this composite:

$$C_1H_2O_1 + H_2O \rightarrow 0.5CH_4 + 0.5CO_2 \tag{3.16}$$

$$C_1H_2O_1 + O_2 \rightarrow H_2O + CO_2 \tag{3.17}$$

From Equation 3.16, 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 3.18, it is possible to estimate the initial COD of a composite, that will be used as the concentration of composite in terms of COD, $X_{c,in}$:

$$0.75\frac{m^3gas}{kgCOD} \cdot X_{c,in}\frac{kgCOD}{m^3feed} \cdot q_{in}\frac{m^3feed}{day} = q_{bio}\frac{m^3biogas}{day} \tag{3.18}$$

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.

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 3.19:

$$COD = \frac{q_{dig}}{\rho_{dig}} [X_c + X_{ch} + X_{pr} + X_{li} + S_{ms} + S_{aa} + S_{LCFA} + S_{VFA} + S_{ac}] \tag{3.19}$$

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 3.20 and 3.21 represent the mass balance:

$$\frac{dNtot}{dt} = N_{tot,i} - N_{tot} = (q_{in} \cdot \rho_{dig} \cdot N_{\%Pr} \cdot C_{pr}) - N_{tot} \tag{3.20}$$

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.

$$\frac{dPtot}{dt} = P_{tot,i} - P_{tot} = (q_{in} \cdot \rho_{dig} \cdot P_{\%Li} \cdot C_{li}) - P_{tot} \tag{3.21}$$

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 3.22 and 3.23 in the first instance before considering the steady-state. Then, the successive ones are calculated from the variation.

$$N_{tot} = \frac{q_{dig}}{\rho_{dig}} \cdot P_{N/C} \cdot (X_{Pr} + X_{aa}) \tag{3.22}$$

$$P_{tot} = \frac{q_{dig}}{\rho_{dig}} \cdot L_{P/C} \cdot X_{li} \tag{3.23}$$

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 temperature variation in the digester was considered using the Arrhenius law, described in Equation 3.24, which will allow a fitting of the kinetic constants with temperature.

$$k = k_{ref} \cdot exp\left[-\frac{Ea}{R}(\frac{1}{T} - \frac{1}{T_{ref}})\right] \tag{3.24}$$

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 3.25).

$$S_{CO_2} = 0.47 S_{CH_4} \tag{3.25}$$

The amount of biogas exiting the digester (q_{bio}) was calculated (Equation 3.26) 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.

$$q_{bio} = biogas\ produced - biogas\ retained \tag{3.26}$$

Initial values

For the model formulation, literature values were considered that later will be fitted with the calibration of the model. Table 3.6 presents the values that were assumed [19]. 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 [19]. The initial value of the activation energy was considered to be 20 Kcal/mol for all the reactions.

Table 3.6: Initial values for the parameters of the model. [19]

PARAMETER	VALUE	UNIT
C_{ch}	30	%
C_{pr}	30	
C_{li}	30	
C_I	10	
kk_{dis}	0.40	d^{-1}
$k_{hid,ch}$	0.25	
$k_{hid,pr}$	0.20	
$k_{hid,li}$	0.10	
$k_{acid,ms}$	30	
$k_{acid,aa}$	50	
$k_{acid,LCFA}$	6.0	
$k_{acet,VFA}$	20	
$k_{met,ac}$	20	
$k_{met,h2}$	20	

3.6 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.

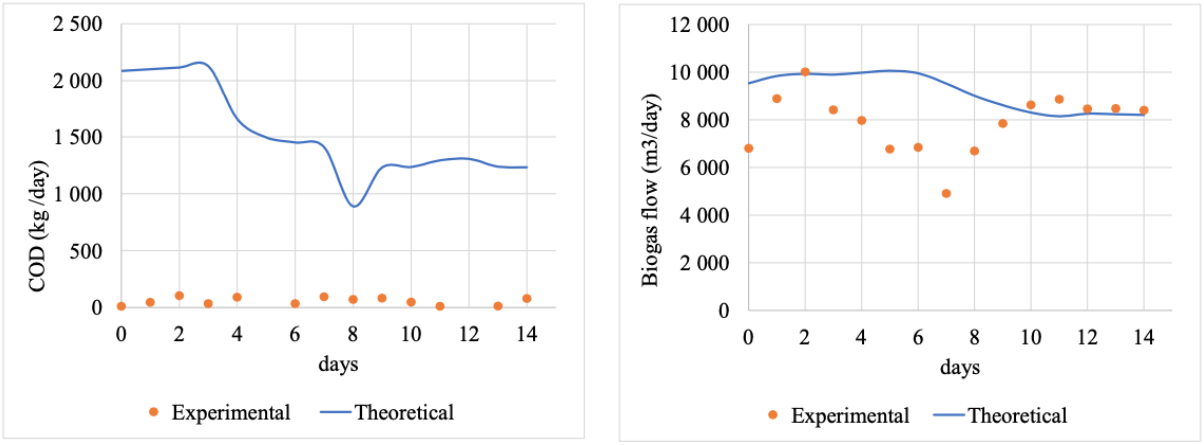
Chapter 4

Results

During this work, the implementation of mathematical models that describe anaerobic digestion was studied, and the ADM1 model was chosen as the basis of the model developed. This chapter contains an analysis of the results obtained, starting with the results of implementing the model, focusing after in the results obtained in the optimisation of the different parameters of the model, per step, and the cross-validation with a second set of data to verify the validity of the model. In addition, an information re-feeding was performed in order to analyse the results obtained, and was also made a sensitivity analysis of the estimated parameters.

4.1 Model Formulation

The model was formulated according to what was indicated in in Chapter 3. The parameters that will be fitted in the calibration of the model were defined based on literature values presented (initial values) in Table 3.6. The results obtained are graphically represented in Figures 4.1 and 4.2.



(a) (b)

Figure 4.1: Experimental and theoretical values of a) COD and b) biogas flow, after the 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.

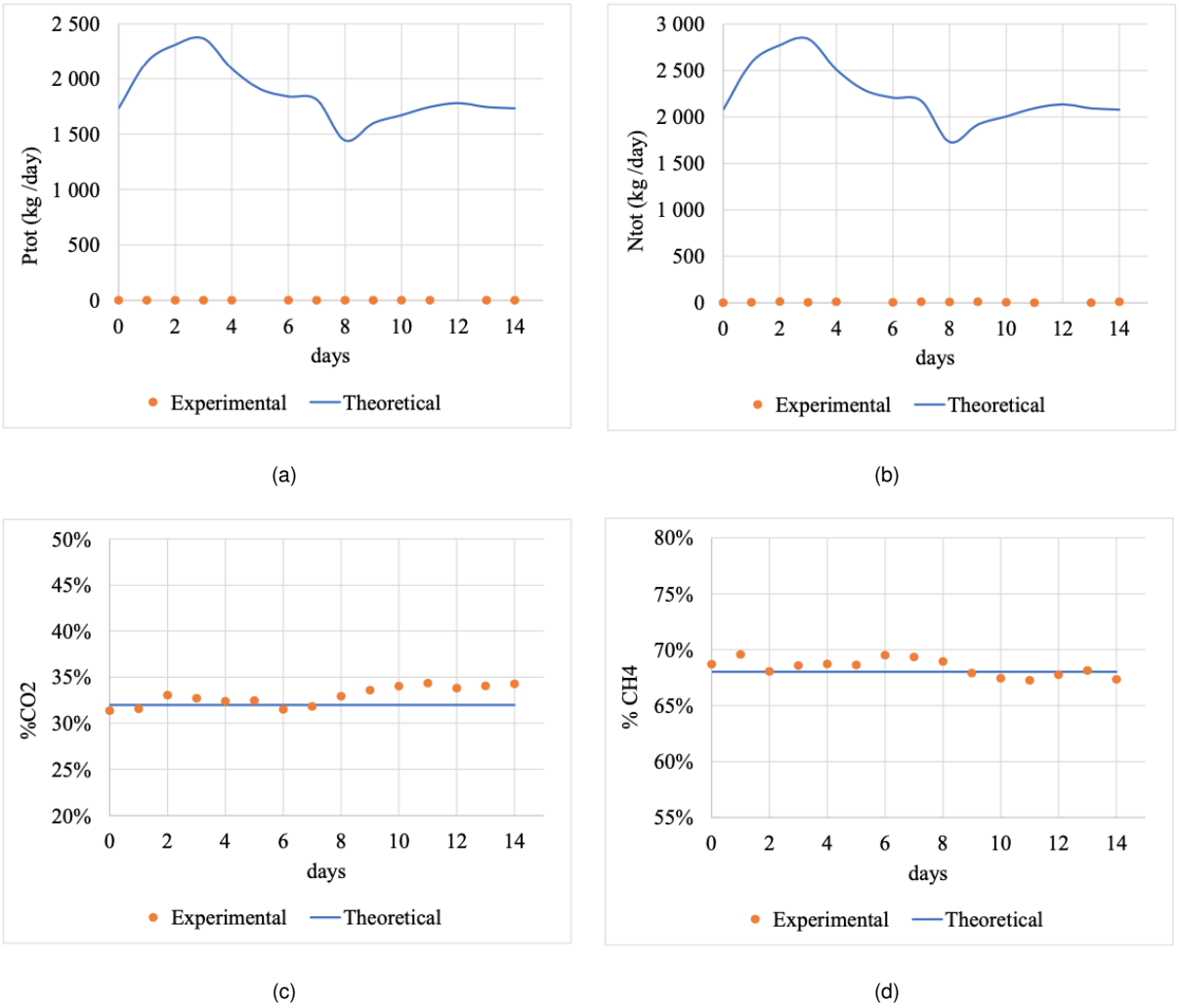


Figure 4.2: Comparison between experimental and theoretical values of a) Ptot and b) Ntot, c)% of CO_2 and d)% of CH_4 in biogas, after model formulation (at initial conditions).

4.2 Model Calibration and validation

As mentioned before, the model was calibrated in 3 steps (calibration of the composite composition, kinetic constants, and activation energy) that were carried out iteratively until stability in the results was achieved. The parameters optimised in these steps, and the respective values are summarised in Table 4.1 below. In addition, the errors obtained and representative graphs of the model are also be presented by each step.

Table 4.1: Final value of the parameters of the model after each step of the calibration.

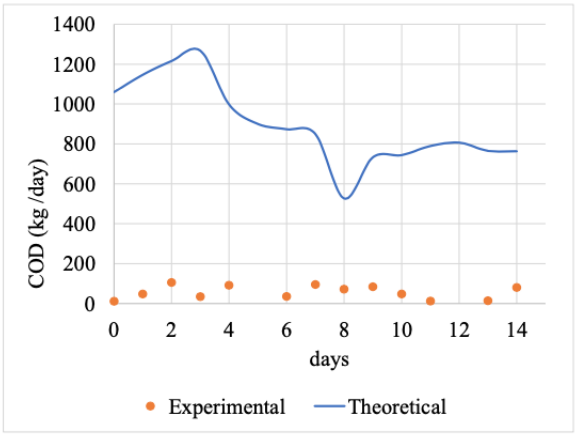
PARAMETER	UNIT	Initial Conditions	Calibration of Composite composition	Calibration of Kinetic Constants	Calibration of Activation Energy	Calibration of data set 1
C_{ch}	%	30	57.58	57.58	57.58	69.80
C_{pr}		30	0.10	0.10	0.10	0.11
C_{li}		30	5.07E-03	5.07E-03	5.07E-03	5.18E-03
C_I		10	42.31	42.31	42.31	30.09
kk_{dis}	d^{-1}	0.40	0.40	10.7	10.7	400
$k_{hid,ch}$		0.25	0.25	14.8	14.8	198
$k_{hid,pr}$		0.20	0.20	0.09	0.09	0.12
$k_{hid,li}$		0.10	0.10	0.56	0.56	3.69
$k_{acid,ms}$		30	30	145	145	268
$k_{acid,aa}$		50	50	0.13	0.13	0.18
$k_{acid,LCFA}$		6	6	1.83	1.83	12.1
$k_{acet,VFA}$		20	20	13.3	13.3	387
$k_{met,ac}$		20	20	11.0	11,0	2.32
$k_{met,h2}$		20	0	0	0	0
Ea_{dis}	Kcal/mol	20	20	20	-2.76	-2.61
$Ea_{hid,ch}$		20	20	20	46.8	42.5
$Ea_{hid,pr}$		20	20	20	54.2	54.2
$Ea_{hid,li}$		20	20	20	123	125
$Ea_{acid,ms}$		20	20	20	25.5	20.9
$Ea_{acid,aa}$		20	20	20	17.9	17.1
$Ea_{acid,LCFA}$		20	20	20	17.5	17.6
$Ea_{acet,VFA}$		20	20	20	-2.18	-2.22
$Ea_{met,ac}$		20	20	20	-0.65	-0.70
$Ea_{met,h2}$		20	20	20	20	20

4.2.1 Composite composition

The results obtained after composite composition calibration are presented in Figure 4.3, and Table 4.2 contains the obtained errors.

Table 4.2: Error between the experimental and theoretical data after the calibration of the composition of the composite.

Error	COD (kg/day)	q_{bio} (m^3/day)	Ptot (kg/day)	Ntot (kg/day)	% CO_2	% CH_4
Quantity	872	2 646	0.18	4.16	1.40	0.83
Percentage value (%)	1 546	17.9	57.1	57.3	4.3	1.2



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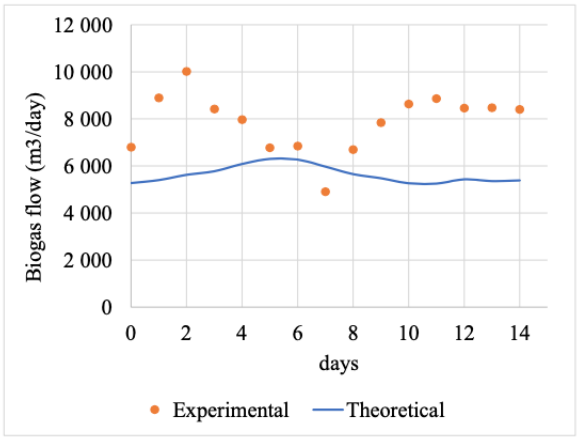

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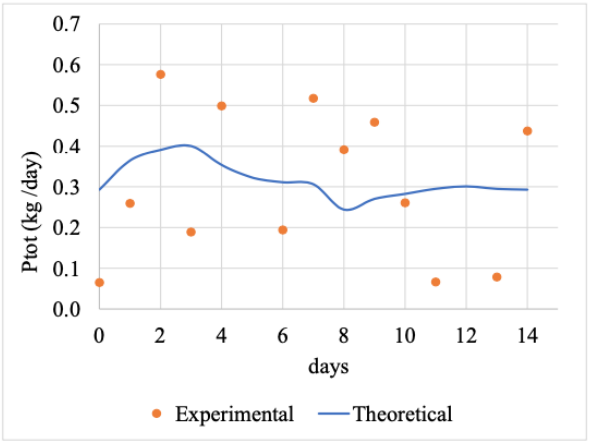

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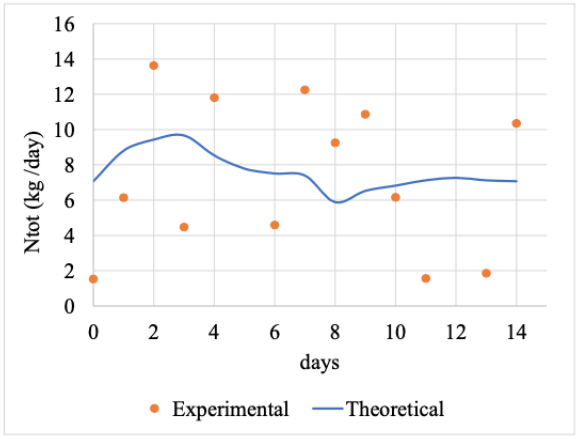

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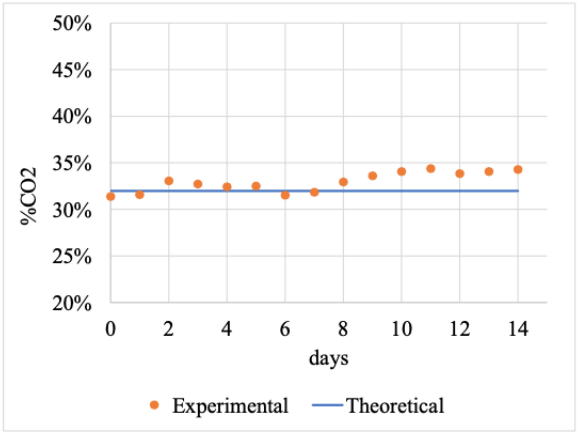

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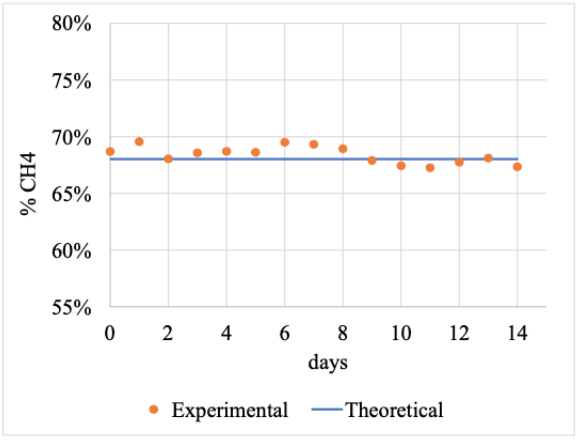

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Figure 4.3: Comparison between experimental and theoretical values of a) COD, b) biogas flow, c) Ptot, d) Ntot, e) % of CO_2 and f) % of CH_4 after the calibration of the composite composition.

In this calibration step, it is possible to verify a significant improvement in Ntot from an error of 31 012% to 57.3%, and Ptot from 613 797% to 57.1%, and in some cases, a behaviour of the model similar to the experimental one. For example, in the first three days in the experimental data, there is an increase of the values of Ntot and Ptot, as well as in the model data. This increase can be justified with the input

data imposed on the model. In Figure 3.4, we can verify that despite the feed flow remaining constant in these three days, the level inside the digester decreases, which justifies the output of a more significant amount of the components referred to in the parameters. Analysing the graphics, it is possible to verify that these two components present many fluctuations in the experimental data, which can be justified by some reasons, like the variation of the composition of the feed. However, since we do not have this type of data available as input parameters, the model will not be able to make this type of prediction, but only a prediction related to feed and level inside the digester.

The biogas flow also presents an improvement of about 9% for an error of about 18%. However, it still does not show similar behaviour to the experimental one.

4.2.2 Kinetic constants

The results obtained after the calibration of the kinetic constants are presented in Figure 4.4, and in Table 4.3 contains the obtained errors.

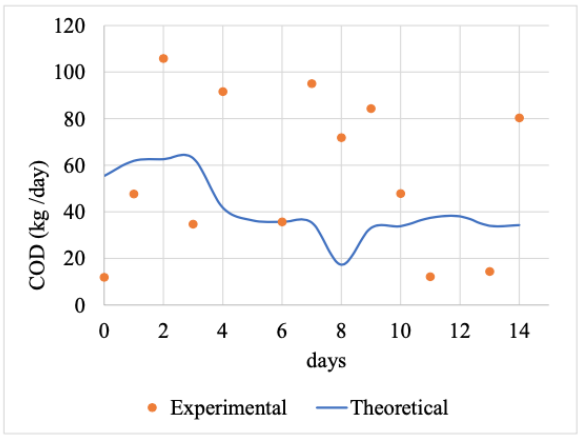
Table 4.3: Error between the experimental and theoretical data after the calibration of the kinetic constants.

Error	COD (kg/day)	q_{bio} (m^3/day)	Ptot (kg/day)	Ntot (kg/day)	% CO_2	% CH_4
Quantity	39.0	1 750	0.18	4.18	1.40	0.83
Percentage value (%)	69.1	11.9	57.8	57.6	4.3	1.2

The calibration of the kinetic constants presents a relevant improvement in the COD and biogas flow. COD shows an error decrease from 1 546% to 69.1%. Thus, the model correct trend predictions, but only in some cases, such as between days 7 to 9, due to the high fluctuation of the experimental data. Similar to Ntot and Ptot, these fluctuations are not justified in the input data, as they can possibly derive from the input composition. Thus, the model will not be able to predict them. Nevertheless, similar behaviour can be found in some moments, such as between days 1 and 3 or between days 7 and 9, when the disturbances may have been caused mainly by feeding and storage and not by the composition.

Despite the previous step already presenting a reduced error, biogas flow still did not present similar behaviour. With the calibration of the kinetics constants, the error reduces again, up to 11.9%, presenting a behaviour more similar to the experimental one, however not at all moments. By analysing Figure **??**b, it is possible to understand that the error can be in part associated with the forecast with a delay of 1 day by the model. The remaining parameters have minor changes.

In the calibration of the model, it was not possible to fit the kinetic constant of reaction 10, the methanogenesis of hydrogen, and the model can only obtain results if this constant is null, which means that the reaction does not occur. For these reasons, and because there is actually a conversion of hydrogen to methane, complete conversion was assumed in the model.



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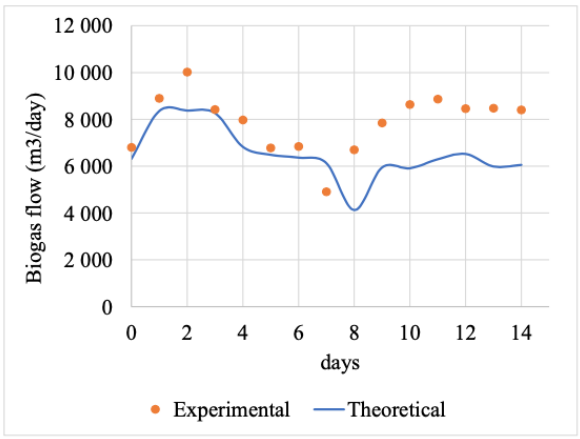

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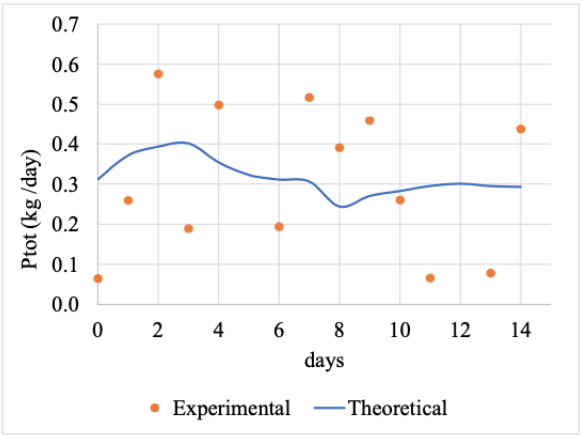

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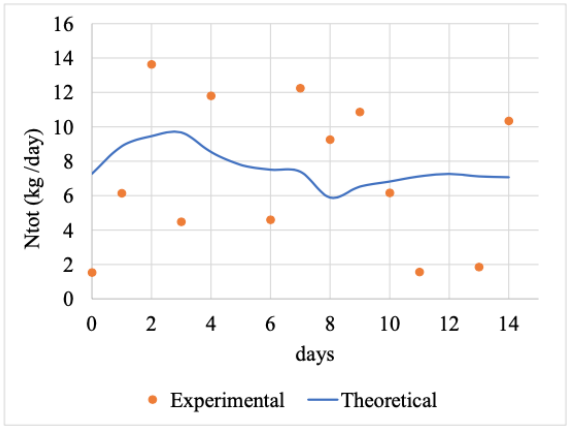

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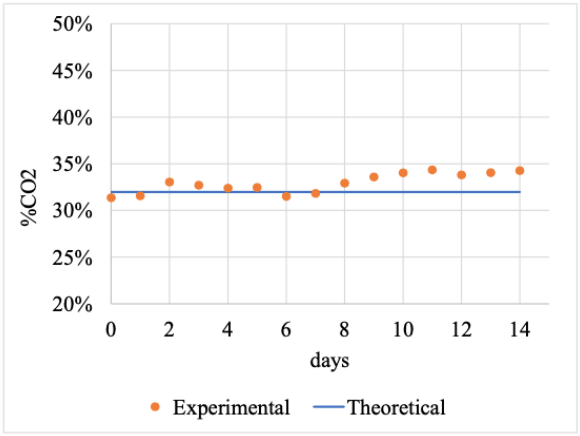

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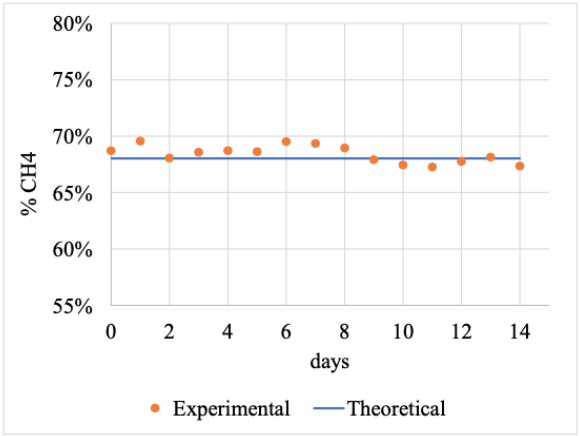
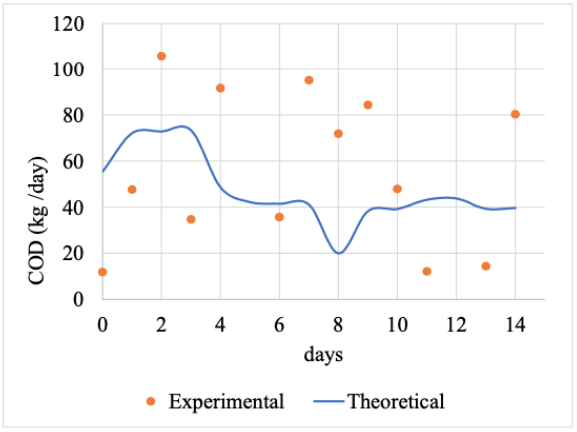


(f)

Figure 4.4: 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 biogas, after the calibration of the kinetic constants.

4.2.3 Activation Energy

The results obtained after the calibration of the kinetic constant are presented in Figure 4.5, and in Table 4.4 the obtained errors.



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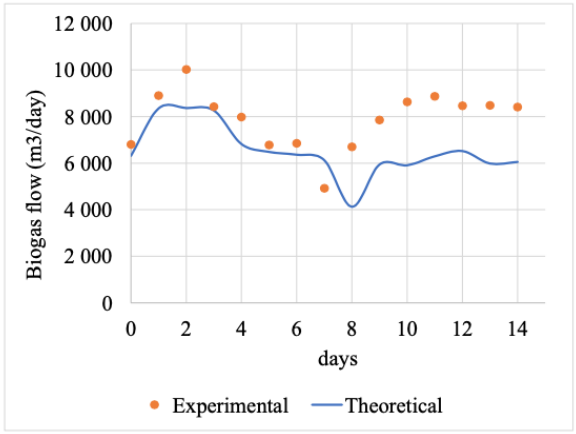

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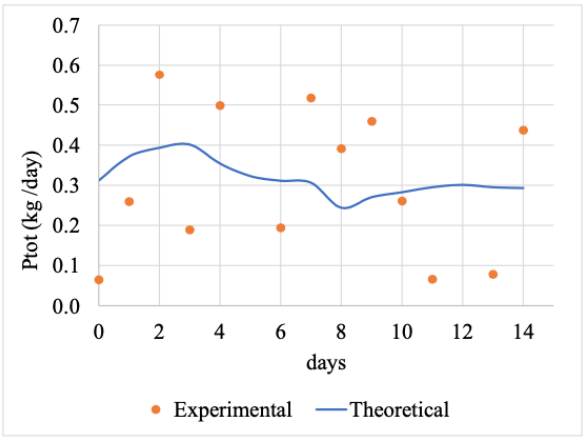

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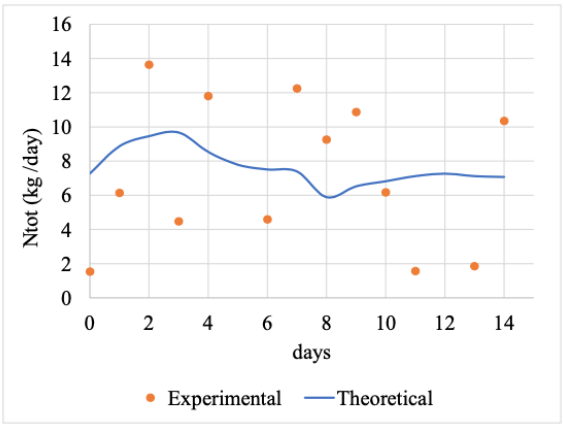

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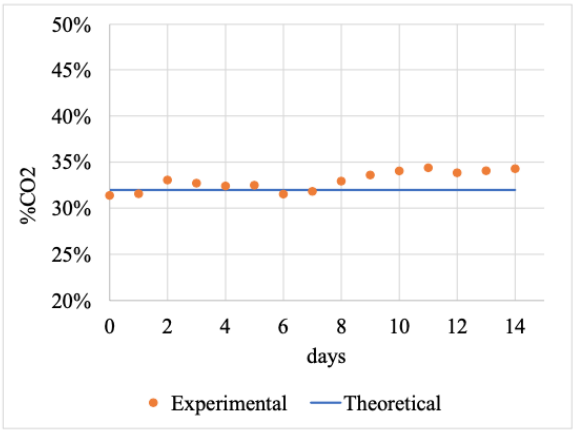

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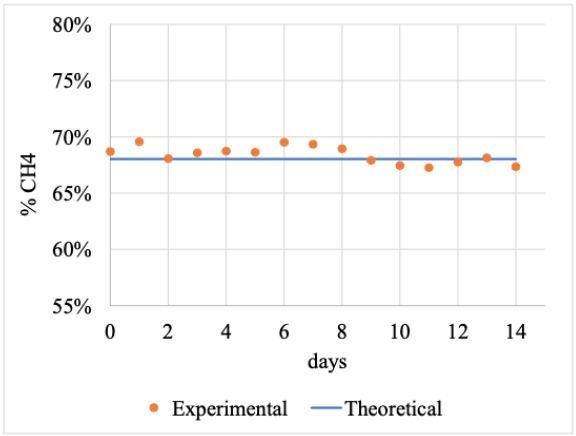

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Figure 4.5: Comparison between experimental and theoretical values of a) COD, b) biogas flow, C) Ptot, d)Ntot, e)% of CO_2 and e)% of CH_4 in biogas, after the calibration of the activation energy.

The last step of the calibration (activation energy calibration) is the step with the minor significance in the model, given that the activation energy is related to the temperature. As mentioned before, the temperature has a reduced variation in the presented data, so the prediction capacity is very limited.

Although not very significant, COD slightly improved, presenting an error of 65.9% instead of 69.1% and a better forecast of trends than in the previous step, although only in a few periods due to high fluctuations. The remaining parameters do not present significant improvements.

Table 4.4: Error between the experimental and theoretical data after the calibration of the activation energy (last calibration).

Error	COD (kg/day)	q_{bio} (m^3/day)	Ptot (kg/day)	Ntot (kg/day)	% CO_2	% CH_4
Quantity	37.2	1 753	0.18	4.18	1.40	0.83
Percentage value (%)	65.9	11.9	57.8	57.6	4.3	1.2

4.2.4 Validation

As mentioned, for the validation of the model, the three steps presented above (calibration of the composite composition, kinetic constants and activation energy) were performed iteratively until stable results were obtained. The results are presented in Figure 4.6, and Table 4.5 contains the obtained errors.

Table 4.5: 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	% CH_4
Quantity	36.22	1 183	0.18	4.20	1.4	0.83
Percentage value (%)	64.2	8.0	57.8	57.8	4.3	1.2

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 4.7, the first period is present, between days 182 and 190, and in Figure 4.8, the second one, between days 326 and 340. The fluctuations of each parameter are also summarised in Table 4.6.

Table 4.6: 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

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 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.

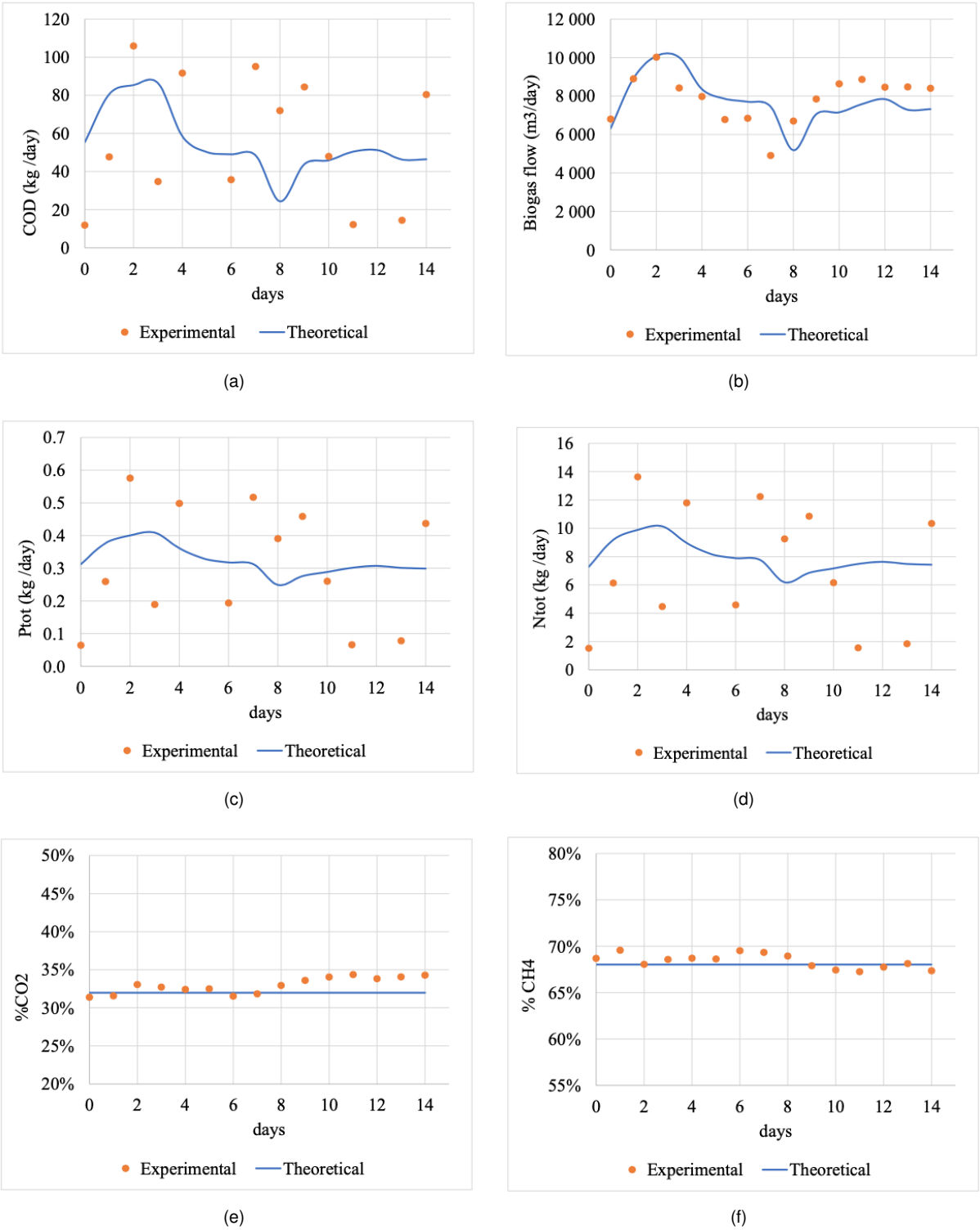


Figure 4.6: Comparison between experimental and theoretical values of a) COD, b) biogas flow, c) Ptot, d)Ntot, e)% of CO_2 and f)% of CH_4 in biogas after the calibration with data set 1.

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 % of 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.

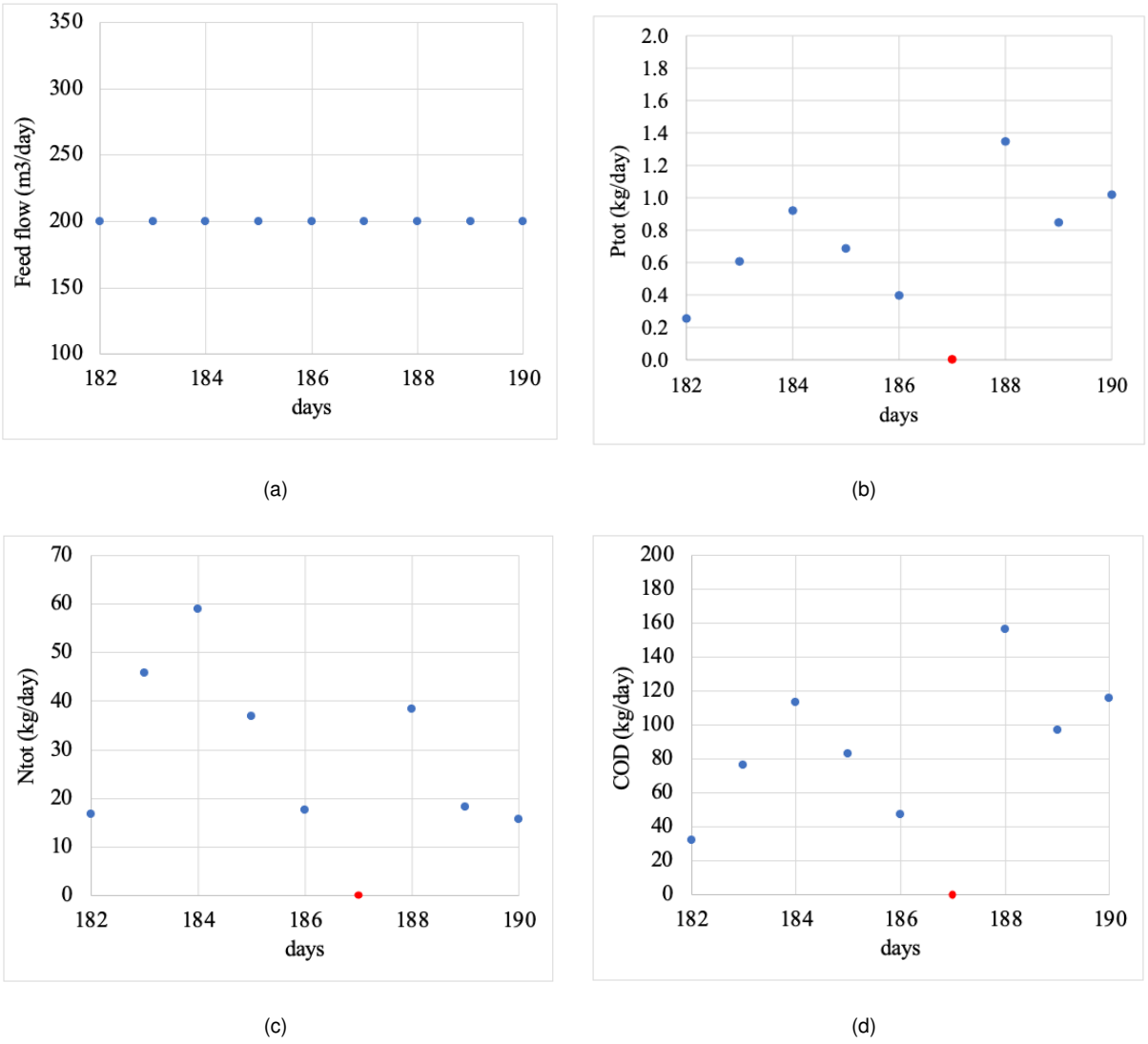


Figure 4.7: Experimental values of the parameters a) feed flow, b) Ptot, c) Ntot and d) COD between the days 182 and 190. Dots marked in red represent unused data to calculate the fluctuation, as it has been considered unreliable.

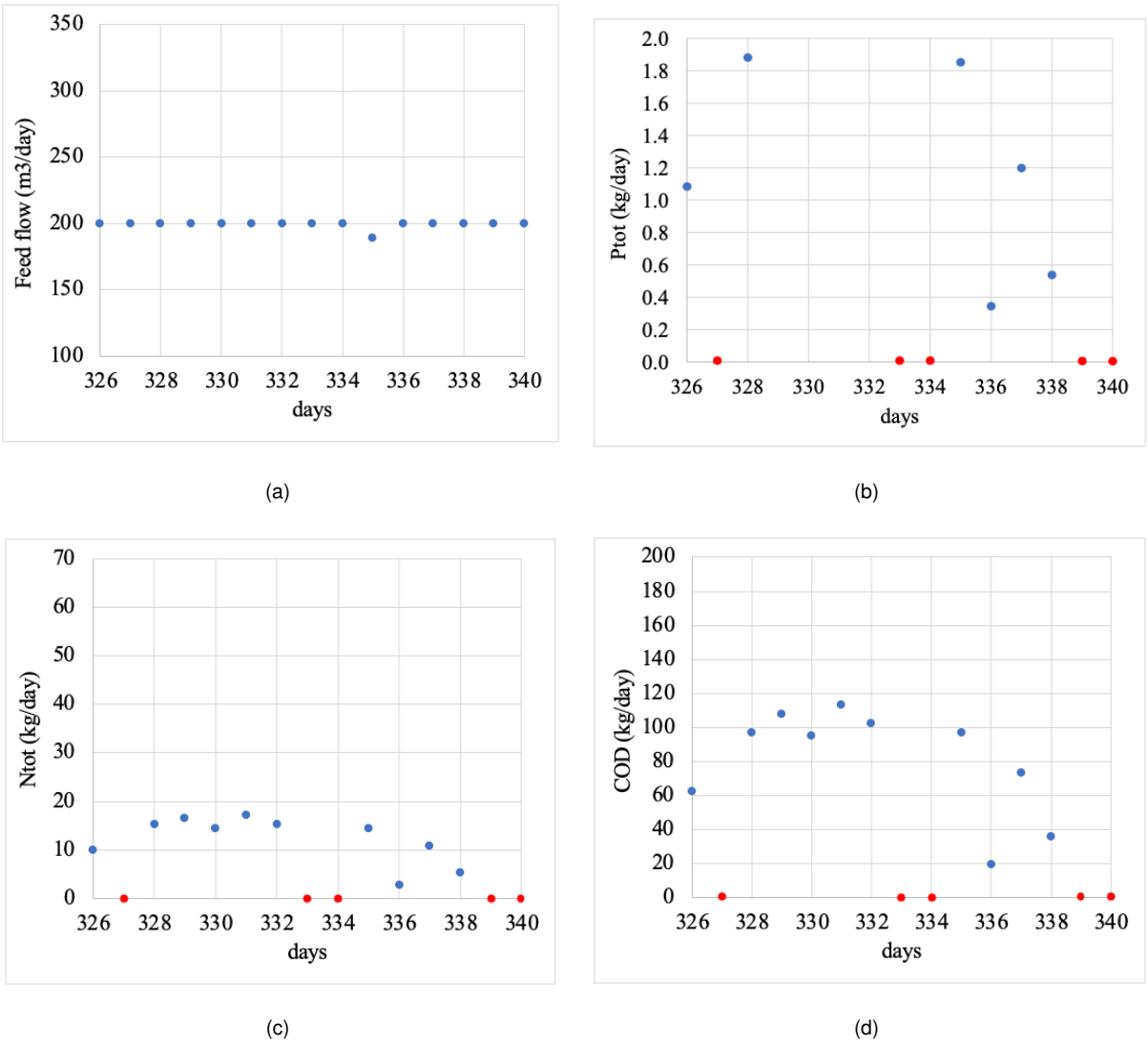


Figure 4.8: Experimental values of the parameters a) feed flow, b) Ptot, c) Ntot and d) COD between the days 326 and 340. Dots marked in red represent unused data to calculate the fluctuation, as it has been considered unreliable.

4.3 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 4.9, and in Table 4.7 the obtained errors.

Table 4.7: 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	% CH_4
Quantity	65.93	1 632	0.70	7.32	1.97	3.82
Percentage value (%)	84.5	19.4	104.3	77.6	5.9	5.9

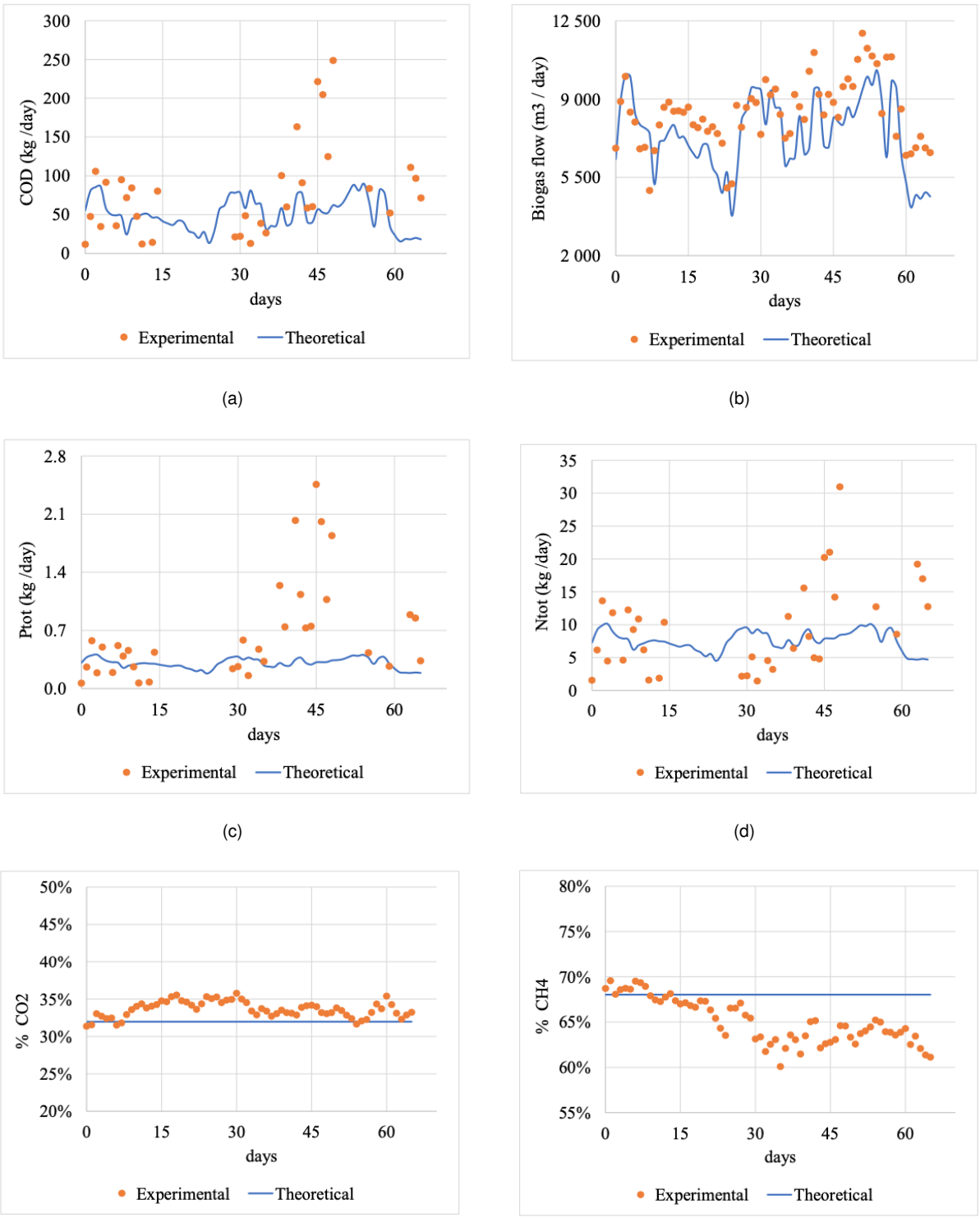


Figure 4.9: Comparison between experimental and theoretical values of a) COD, b) biogas flow, c) Ptot, d) Ntot, e)% of CO_2 and f)% of CH_4 in biogas, for the cross-validation with data set 2.

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. This hypothesis will be analysed below.

The model continues to predict the trends of biogas flow fairly 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.

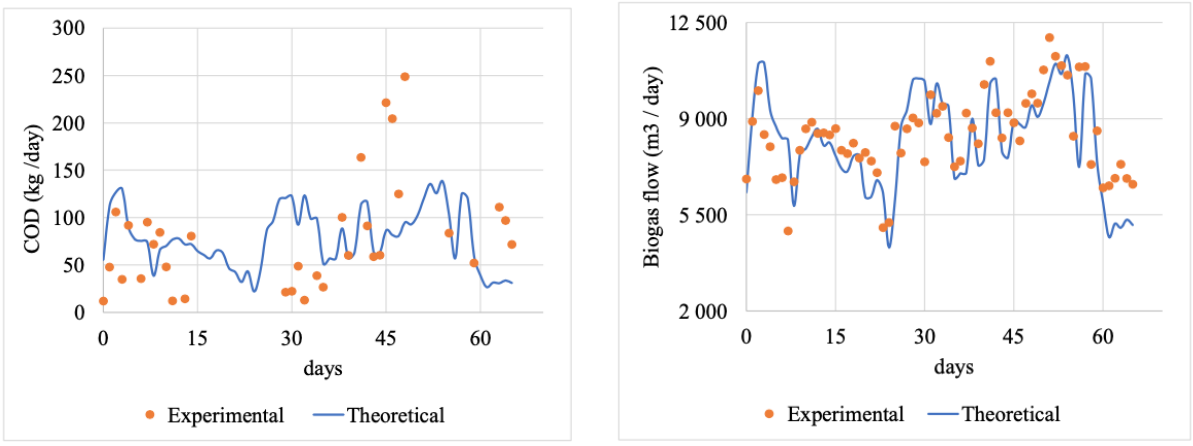
COD, Ntot and Ptot also show a significant increase in error. However, when evaluating the error concerning the previously studied fluctuation, only the COD is not within the minimum fluctuation but rather within the maximum fluctuation. Ptot presents an error of 0.7 kg/day and a minimum fluctuation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

Therefore, 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%.

4.3.1 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 4.10 and 4.11, and Table 4.8 contains the obtained errors.

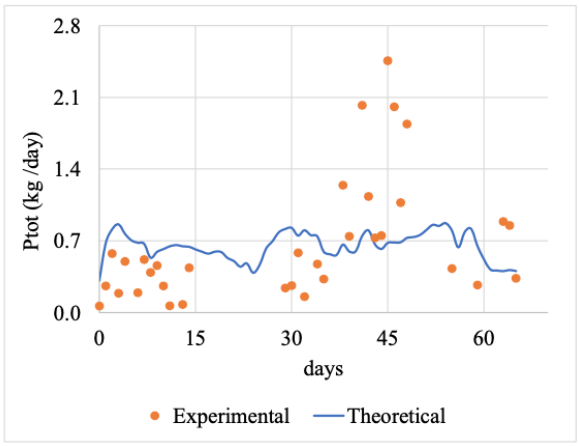


(a) (b)

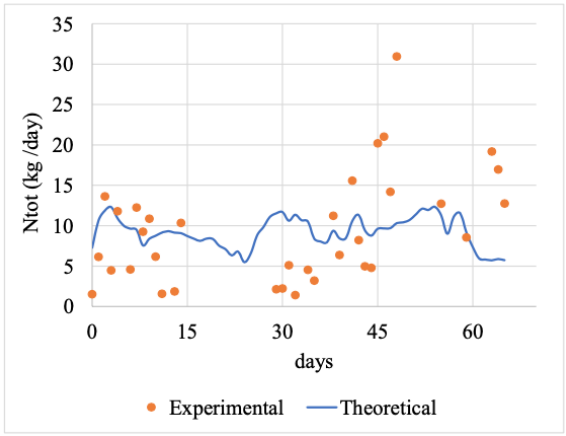
Figure 4.10: Comparison between experimental and theoretical values of a) COD and b) biogas flow, after the re-calibration of the model for data set 2.

Table 4.8: 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	% CH_4
Quantity	64.19	1 397	0.60	7.22	1.97	3.82
Percentage value (%)	82.3	16.6	89.8	76.5	5.9	5.9



(a)



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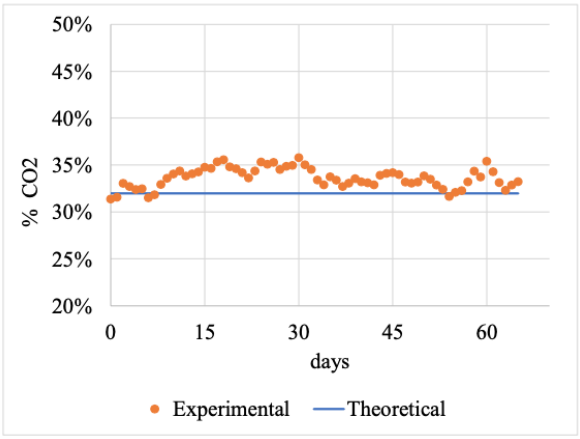

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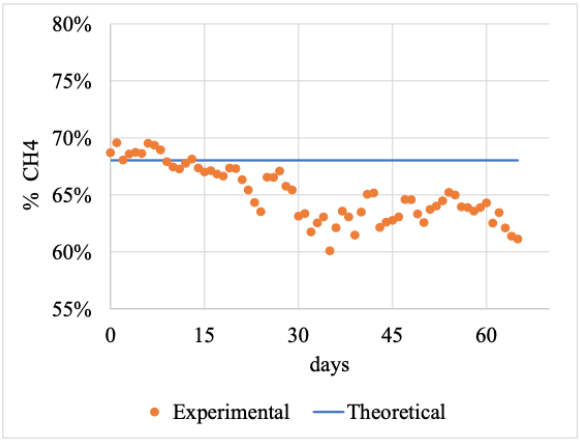


(d)

Figure 4.11: Comparison between experimental and theoretical values of a)Ptot, b)Ntot, c)% of CO_2 and d)% 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 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.

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.

4.4 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 3.18, becoming one more variable information in the model's input.

The results obtained after the information re-feeding are presented in Figures 4.12 and 4.13 for data set 1 and data set 2 (before the re-calibration), respectively, and in Table 4.9, the obtained errors.

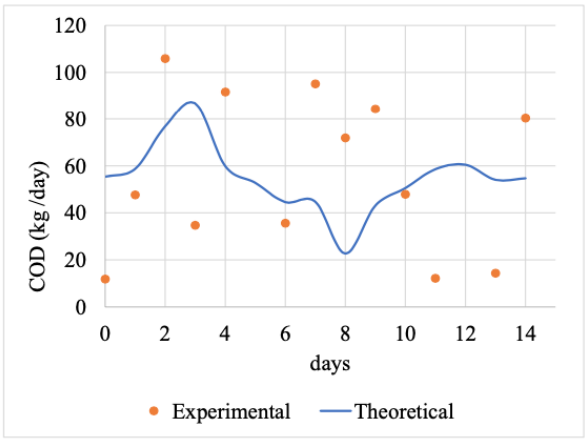
Table 4.9: Error between the experimental and theoretical data after the information re-feeding, for data set 1 and data set 2.

Error	COD (kg/day)	q_{bio} (m^3/day)	Ptot (kg/day)	Ntot (kg/day)	% CO_2	% CH_4
data set 1						
Quantity	36.9	1 129	0.18	4.18	1.40	0.83
Percentage value (%)	65.4	7.7	57.8	57.6	4.2	1.2
data set 2						
Quantity	57.9	1 226	0.60	7.28	1.97	3.82
Percentage value (%)	74.3	14.6	89.8	77.2	5.9	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 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.



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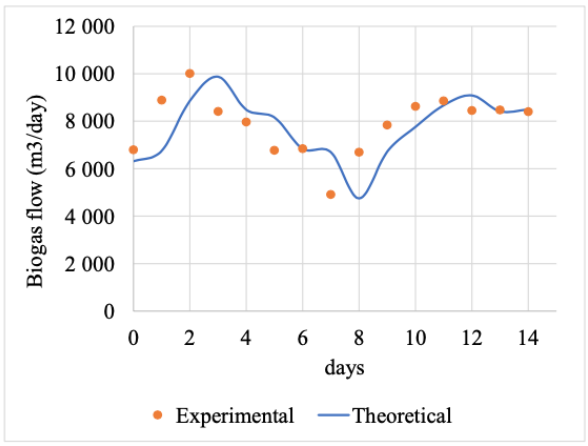

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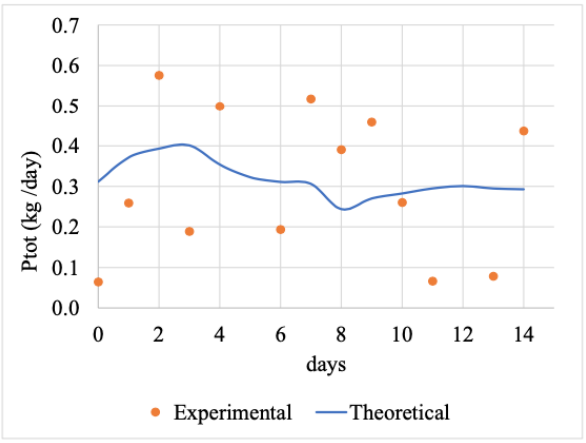

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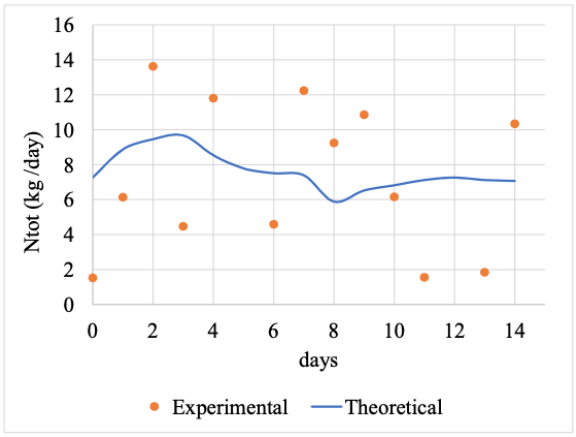

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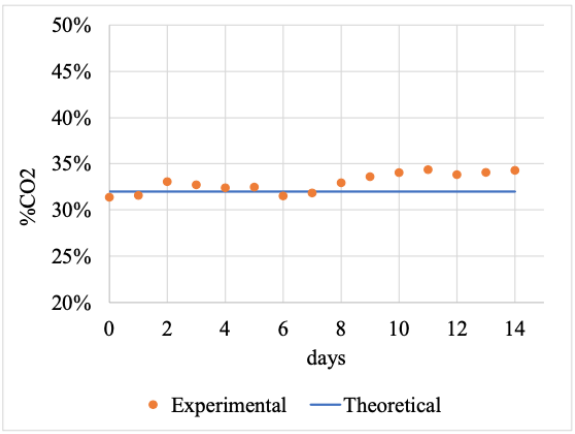

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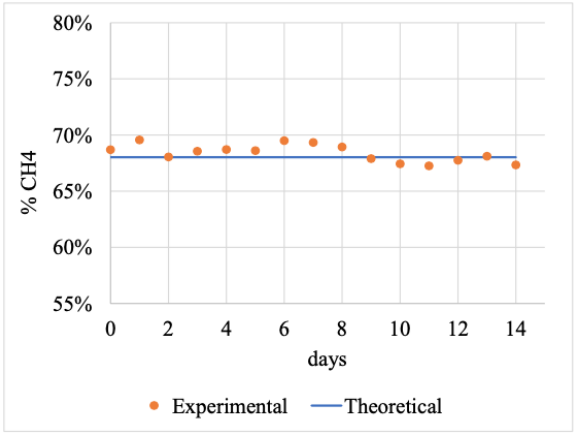
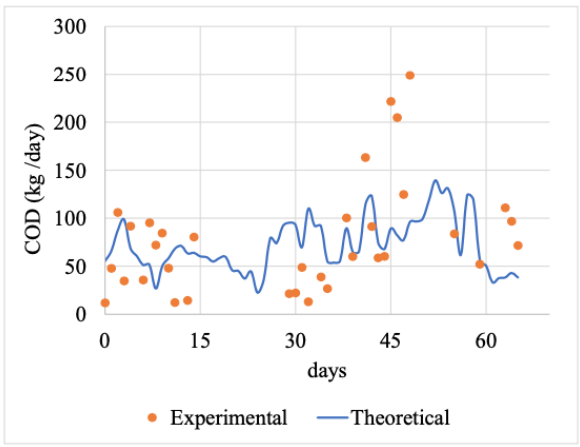
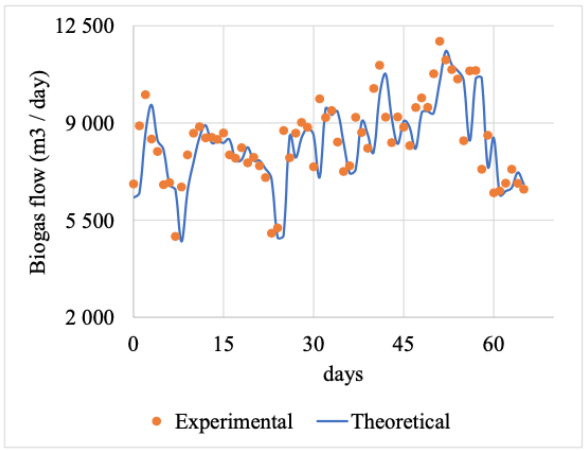


(f)

Figure 4.12: 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.



(a)



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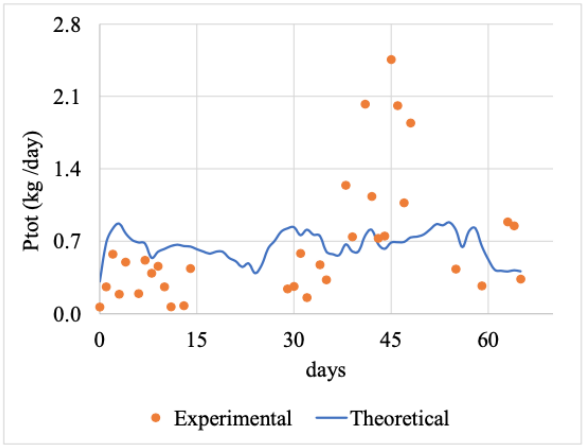

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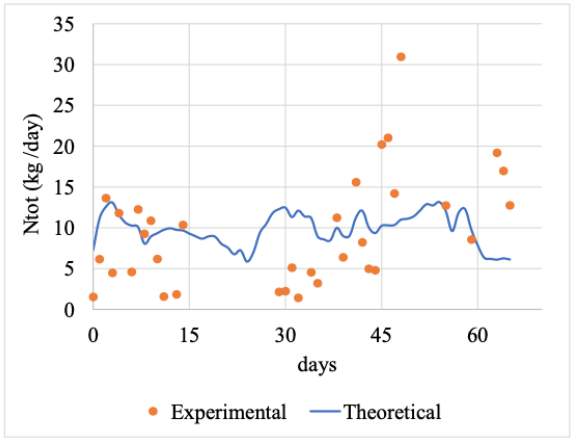

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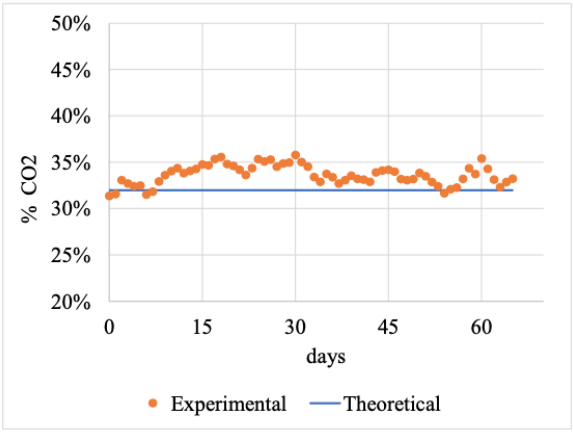

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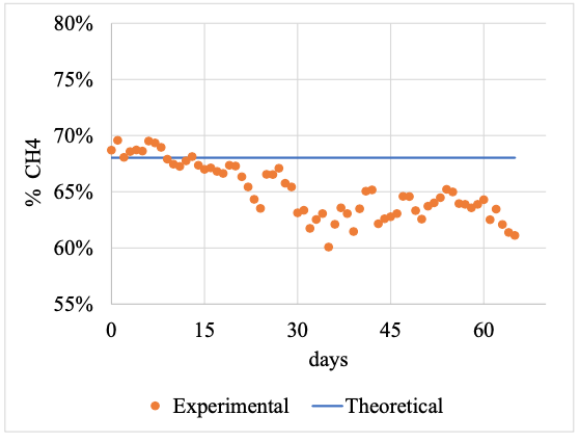

(f)

Figure 4.13: 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.

4.5 Sensitivity analysis for the assumed parameters

A sensitivity analysis for the assumed parameters was performed in order to understand how much impact these parameters have on the model since they were assumed and may not present the actual value. In this way, a variation of more or less 10% to the assumed parameters was performed, and the variation in the output parameters of the model was analysed. The results obtained for this sensibility analysis are presented in Table 4.10.

In general, there is no significant impact on the results if slightly different values had been arbitrated. It can be verified that the most significant impact is caused in Ntot and Ptot, of which there is no input data, so it is natural that when increasing/decreasing the input, the output responds in the same way. Biogas flow also has some sensitivity to density, which would also be expected as they are directly proportional.

Table 4.10: Sensibility analyses of the assumed parameters in the model.

Assumption Defined Parameters		Δ COD	Δ q_{bio}	Δ Ntot	Δ Ptot	Δ % CH_4	Δ % CO_2
ρ_{dig} (kg/m^3)	900 (-10%)	-0.40%	0.00%	-10.01%	-9.99%	0.00%	0.00%
	1 000	-	-	-	-	-	-
	1 100 (+10%)	+0.32%	0.00%	+8.23%	+8.22%	0.00%	0.00%
ρ_{bio} (kg/m^3)	1.01 (-10%)	0.00%	-10.95%	0.00%	0.00%	0.00%	0.00%
	1.12	-	-	-	-	-	-
	1.23 (+10%)	0.00%	-8.88%	0.00%	0.00%	0.00%	0.00%
$P_{\%Li}$	0.023 (-10%)	0.00%	0.00%	0.00%	-9.98%	0.00%	0.00%
	0.025	-	-	-	-	-	-
	0.028 (+10%)	0.00%	0.00%	0.00%	+8.21%	0.00%	0.00%
$N_{\%Pr}$	0.027 (-10%)	0.00%	0.00%	-9.99%	0.00%	0.00%	0.00%
	0.030	-	-	-	-	-	-
	0.033 (+10%)	0.00%	0.00%	+8.22%	0.00%	0.00%	0.00%

Chapter 5

Conclusions and Future Work

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 there was no 1-day forecast error, 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, just as is done with the output COD used for the calibration.

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. Therefore, the total conversion of hydrogen was assumed. For CO_2, a proportion relative to CH_4 was also assumed, 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. Unfortunately, it was not possible to perform this work due to time constraints.

The data analysis enables us to conclude that there are reactor disturbances, both in terms of the feed flow variation and the input feed composition. Furthermore, the variation in the substrate's composition when the feed was constant presented high fluctuations in Ptot, Ntot and COD analysis.

The prediction of COD, Ntot and Ptot show a more significant error. However, it is within the expected data fluctuation. As mentioned before, 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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Appendix A

Mathematical Modelling

A.1 ADM1

Figures A.1 and A.2 represent the kinetics assumed in model ADM1. [19]

Component →	i	1	2	3	4	5	6	7	8	9	10	11	12	Rate (ρ_j, kg COD.m^{-3}.d^{-1})
j ↓ Process		S_{su}	S_{aa}	S_{fa}	S_{va}	S_{bu}	S_{pro}	S_{ac}	S_{h2}	S_{ch4}	S_C	S_N	S_I	
		Monosaccharides (kgCOD m^{-3})	Amino Acids (kgCOD m^{-3})	Long chain fatty acids (kgCOD m^{-3})	Total valerate (kgCOD m^{-3})	Total butyrate (kgCOD m^{-3})	Total propionate (kgCOD m^{-3})	Total acetate (kgCOD m^{-3})	Hydrogen gas (kgCOD m^{-3})	Methane gas (kgCOD m^{-3})	Inorganic Carbon (kmoleC m^{-3})	Inorganic nitrogen (kmoleN m^{-3})	Soluble inerts (kgCOD m^{-3})	
1	Disintegration												$f_{si,xc}$	$k_{dis}X_c$
2	Hydrolysis Carbohydrates	1												$k_{hyd,ch}X_{ch}$
3	Hydrolysis of Proteins		1											$k_{hyd,pr}X_{pr}$
4	Hydrolysis of Lipids	$1-f_{fa,li}$		$f_{fa,li}$										$k_{hyd,li}X_{li}$
5	Uptake of Sugars	-1				$(1-Y_{su})\,f_{bu,su}$	$(1-Y_{su})\,f_{pro,su}$	$(1-Y_{su})\,f_{ac,su}$	$(1-Y_{su})\,f_{h2,su}$		$-\sum_{i=1-9,11-24} C_i Y_{i,5}$	$-(Y_{su})\,N_{bac}$		$k_{m,su}\frac{S_{su}}{K_S+S}X_{su}I_1$
6	Uptake of Amino Acids		-1	$(1-Y_{aa})\,f_{va,aa}$	$(1-Y_{aa})\,f_{bu,aa}$	$(1-Y_{aa})\,f_{pro,aa}$	$(1-Y_{aa})\,f_{ac,aa}$	$(1-Y_{aa})\,f_{h2,aa}$			$-\sum_{i=1-9,11-24} C_i Y_{i,6}$	$N_{aa}-(Y_{aa})\,N_{bac}$		$k_{m,aa}\frac{S_{aa}}{K_S+S_{aa}}X_{aa}I_1$
7	Uptake of LCFA			-1				$(1-Y_{fa})\,0.7$	$(1-Y_{fa})\,0.3$			$-(Y_{li})\,N_{bac}$		$k_{m,fa}\frac{S_{fa}}{K_S+S_{fa}}X_{fa}I_2$
8	Uptake of Valerate				-1		$(1-Y_{c4})\,0.54$	$(1-Y_{c4})\,0.31$	$(1-Y_{c4})\,0.15$			$-(Y_{c4})\,N_{bac}$		$k_{m,c4}\frac{S_{va}}{K_S+S_{va}}X_{c4}\frac{1}{1+S_{bu}/S_{va}}I_2$
9	Uptake of Butyrate					-1		$(1-Y_{c4})\,0.8$	$(1-Y_{c4})\,0.2$			$-(Y_{c4})\,N_{bac}$		$k_{m,c4}\frac{S_{bu}}{K_S+S_{bu}}X_{c4}\frac{1}{1+S_{va}/S_{bu}}I_2$
10	Uptake of Propionate						-1	$(1-Y_{pro})\,0.57$	$(1-Y_{pro})\,0.43$		$-\sum_{i=1 \atop 9,11\ 24} C_i Y_{i,10}$	$-(Y_{pro})\,N_{bac}$		$k_{m,pr}\frac{S_{pro}}{K_S+S_{pro}}X_{pro}I_2$
11	Uptake of Acetate							-1		$(1-Y_{ac})$	$-\sum_{i=1-9,11-24} C_i Y_{i,11}$	$-(Y_{ac})\,N_{bac}$		$k_{m,ac}\frac{S_{ac}}{K_S+S_{ac}}X_{ac}I_3$
12	Uptake of Hydrogen								-1	$(1-Y_{h2})$	$-\sum_{i=1-9,11-24} C_i Y_{i,12}$	$-(Y_{h2})\,N_{bac}$		$k_{m,h2}\frac{S_{h2}}{K_S+S_{h2}}X_{h2}I_1$
13	Decay of X_{su}													$k_{dec,Xsu}X_{su}$
14	Decay of X_{aa}													$k_{dec,Xaa}X_{aa}$
15	Decay of X_{fa}													$k_{dec,Xfa}X_{fa}$
16	Decay of X_{C4}													$k_{dec,Xc4}X_{c4}$
17	Decay of X_{pro}													$k_{dec,Xpro}X_{pro}$
18	Decay of X_{ac}													$k_{dec,Xac}X_{ac}$
19	Decay of X_{h2}													$k_{dec,Xh2}X_{h2}$
														Inhibition factors (3.7): $I_1 = I_{pH}I_{IN,lim}$ $I_2 = I_{pH}I_{IN,lim}I_{h2}$ $I_3 = I_{pH}I_{IN,lim}I_{NH3,Xac}$

Figure A.1: Biochemical rate coefficients ($v_{i,j}$) and kinetic rate equations (ρ_j) for particulate components (i = 1-12; j = 1–19). Reproduced from Anaerobic Digestion Model No. 1 (ADM1) [19].

Component →	i	13	14	15	16	17	18	19	20	21	22	23	24	Rate (ρ_j, kg COD.m^{-3}.d^{-1})
Process ↓		X_c	X_{ch}	X_{pr}	X_{li}	X_{su}	X_{aa}	X_{fa}	X_{c4}	X_{pro}	X_{ac}	X_{h2}	X_I	
j		Composites (kgCOD m^{-3})	Carbohydrates (kgCOD m^{-3})	Proteins (kgCOD m^{-3})	Lipids (kgCOD m^{-3})	Sugar degraders (kgCOD m^{-3})	Amino acid degraders (kgCOD m^{-3})	LCFA degraders (kgCOD m^{-3})	Valerate and butyrate degraders (kgCOD m^{-3})	Propionate degraders (kgCOD m^{-3})	Acetate degraders (kgCOD m^{-3})	Hydrogen degraders (kgCOD m^{-3})	Particulate inerts (kgCOD m^{-3})	
1	Disintegration	-1	$f_{ch,xc}$	$f_{pr,xc}$	$f_{li,xc}$								$f_{I,xc}$	$k_{dis}X_c$
2	Hydrolysis Carbohydrates		-1											$k_{hyd,ch}X_{ch}$
3	Hydrolysis of Proteins			-1										$k_{hyd,pr}X_{pr}$
4	Hydrolysis of Lipids				-1									$k_{hyd,li}X_{li}$
5	Uptake of Sugars					Y_{su}								$k_{m,su}\frac{S_{su}}{K_S+S}X_{su}I_1$
6	Uptake of Amino Acids						Y_{aa}							$k_{m,aa}\frac{S_{aa}}{K_S+S_{aa}}X_{aa}I_1$
7	Uptake of LCFA							Y_{fa}						$k_{m,fa}\frac{S_{fa}}{K_S+S_{fa}}X_{fa}I_2$
8	Uptake of Valerate								Y_{c4}					$k_{m,c4}\frac{S_{va}}{K_S+S_{va}}X_{c4}\frac{1}{1+S_{bu}/S_{va}}I_2$
9	Uptake of Butyrate								Y_{c4}					$k_{m,c4}\frac{S_{bu}}{K_S+S_{bu}}X_{c4}\frac{1}{1+S_{va}/S_{bu}}I_2$
10	Uptake of Propionate									Y_{pro}				$k_{m,pr}\frac{S_{pro}}{K_S+S_{pro}}X_{pro}I_2$
11	Uptake of Acetate										Y_{ac}			$k_{m,ac}\frac{S_{ac}}{K_S+S_{ac}}X_{ac}I_3$
12	Uptake of Hydrogen											Y_{h2}		$k_{m,h2}\frac{S_{h2}}{K_S+S_{h2}}X_{h2}I_1$
13	Decay of X_{su}	1				-1								$k_{dec,Xsu}X_{su}$
14	Decay of X_{aa}	1					-1							$k_{dec,Xaa}X_{aa}$
15	Decay of X_{fa}	1						-1						$k_{dec,Xfa}X_{fa}$
16	Decay of X_{c4}	1							-1					$k_{dec,Xc4}X_{c4}$
17	Decay of X_{pro}	1								-1				$k_{dec,Xpro}X_{pro}$
18	Decay of X_{ac}	1									-1			$k_{dec,Xac}X_{ac}$
19	Decay of X_{h2}	1										-1		$k_{dec,Xh2}X_{h2}$

Inhibition factors (3.7):
$I_1 = I_{pH}I_{IN,lim}$
$I_2 = I_{pH}I_{IN,lim}I_{h_2}$
$I_3 = I_{pH}I_{IN\_lim}I_{NH3,Xac}$

Figure A.2: Biochemical rate coefficients ($v_{i,j}$) and kinetic rate equations (ρ_j) for particulate components (i = 13–24; j = 1–19). Reproduced from Anaerobic Digestion Model No. 1 (ADM1) [19].

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