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# Simplified mechanistic model for the two-stage anaerobic degradation of sewage sludge

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Two-phase anaerobic systems are being increasingly implemented for the treatment of both sewage sludge and organic fraction of municipal solid waste. Despite the good amount of mathematical models in anaerobic digestion, few have been applied in two-phase systems. In this study, a three-reaction mechanistic model has been developed, implemented and validated by using experimental data from a long-term anaerobic two-phase (TPAD) digester treating sewage sludge. A sensitivity analysis shows that the most influential parameters of the model are the ones related to the hydrolysis reaction and the activity of methanogens in the thermophilic reactor. The calibration procedure highlights a noticeable growth rate of the thermophilic methanogens throughout the evaluation period. Overall, all the measured variables are properly predicted by the model during both the calibration and the cross-validation periods. The model's representation of the organic matter behaviour is quite good. The most important disagreements are observed for the biogas production especially during the validation period. The whole application procedure underlines the ability of the model to properly predict the behaviour of this bioprocess.

**Keywords:** biogas; modelling; sensitivity analysis; temperature phased; thermophilic

## Nomenclature

| | |
|---|---|
| $S_0$ | particulate organic matter |
| $S_1$ | soluble organic matter |
| $S_2$ | acetic acid equivalent |
| $X_1$ | acidogens concentration |
| $X_2$ | methanogens concentration |
| IC | inorganic carbon |
| $Z$ | total alkalinity |
| $r_H$ | hydrolysis rate |
| $r_A$ | acidogenesis rate |
| $r_M$ | methanogenesis rate |
| $Y_{X_1}$ | acidogens yield |
| $Y_{X_2}$ | methanogens yield |
| $f_{\_IC\_S_1} \cdot f_{\_IC\_S_2}$ | stoichiometric coefficients of IC production |
| $k_0$ | hydrolysis coefficient |
| $K_X$ | Contois affinity constant |
| $\mu_{m_2}$ | maximum specific growth rate of the methanogens |
| $K_{S_1}$ | affinity constant of acidogens |
| $K_{S_2}$ | affinity constant of methanogens |
| $K_i$ | inhibition constant of the methanogens |
| $P_T$ | total pressure of the reactor |
| $K_H$ | Henry's constant |
| $K_a$ | affinity constant (acetic acid/acetate) |
| $k_La$ | the volumetric mass transfer coefficient |
| $\xi$ | state variable |
| $\xi_{in}$ | state variable value in the inlet |
| $\xi_{ic}$ | initial condition of the state variable value |
| $D$ | dilution rate |
| fB | fraction of anaerobically biodegradable substrate |
| $\alpha$ | thermophilic biomass inactivation fraction |

## 1. Introduction

Anaerobic digestion is the most frequently used technology for the stabilization and treatment of sewage sludge in the European Union.[1] Therefore, as is always the case of a well-established and consolidated technology, ongoing and future research must focus in maximizing the reactor's performance (i.e. the biogas production) by evaluating, for instance, different reactor configurations and operating conditions. Although the one-stage mesophilic treatment is the most used system, the separation of the treatment in two stages (or phases) and the use of thermophilic conditions have shown interesting results.[2,3]

Mathematical models have demonstrated to be proper tools for different purposes in bioreactor operations such as: developing control strategies, the prediction of the

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system's performance under different conditions, reactor design criteria selection and the optimization of operational conditions, among others.[4] Few studies have been reported on the modelling application of two-phase anaerobic systems. Some models have also been implemented in a two-phase mesophilic system composed by a continuous stirred tank reactor (CSTR) followed by an upflow anaerobic sludge blanket (UASB) reactor.[5,6] A UASB unit allows the separation of the hydraulic retention time (HRT) and the solid retention time (SRT), making the SRT high enough to avoid the washout of low-growth methanogens. This promising configuration alternative may be only applied to wastewaters because UASB reactors cannot cope with high-solid content substrates. Other modelling attempts have been made in a system with two CSTRs connected in series for the treatment of solid waste, such as grass silage.[7] The temperature-phased reactor (TPAD) has been the subject of some attention.[8,9] This configuration is composed by a thermophilic reactor followed by a mesophilic reactor. TPAD systems assure an increase in the hydrolysis rate of the particulate organic material along with the removal of pathogens in the thermophilic reactor and the methanization of the volatile fatty acids (VFAs) in the mesophilic reactor.[10] In all cases, the anaerobic digestion model ADM1, developed by Batstone et al. [11] was used to describe the systems. ADM1 is a quite large and complex model, thus the alternative option of using a more simplified version has been gaining importance.[12,13] The aim of this work is to develop, implement and validate a model for a two-phase anaerobic digester, operating under thermophilic–mesophilic conditions. This model may be subsequently employed as an easier and practical tool for two-stage digester operators.

## 2. Materials and methods

### 2.1. Mathematical model description

#### 2.1.1. Assumptions and considerations

Before going further with the model description, the most important considerations of the proposed model, emphasizing the model's usefulness and limitations, should be mentioned: (1) with regard to the units, all the variables are measured on a COD basis except from inorganic carbon. (2) The main macromolecular compounds: carbohydrates, proteins and lipids are grouped in one macromolecular generic compound. This issue considers the common sewage sludge characterization, which is carried out in terms of particulate COD. (3) Instead of a pool of VFAs, only a generic equivalent acetic acid (mole base) is considered. This is an assumption taken from Bernard et al.,[14] which is quite convenient for reducing the number of parameters. Despite the fact that each VFA has its own degradation rate, a global variable grouping all the VFAs is more commonly reported in real applications. As a consequence, the acetogenesis is suppressed from the global model. (4) Ammonia, a natural compound produced in the acidogenesis of aminoacids, was not taken into account in this model. Despite few measurements of the ammonia concentration were carried out, all the observed values indicated that there was always a very low concentration of ammonia, far from the possible inhibition level. In any case and when working in more extreme conditions, this compound may be easily added into the reaction pathways, thus, in the model equations. (5) Hydrogen is an intermediate gas in the process and normally, under normal conditions, its concentration is negligible. Moreover, hydrogen is not normally measured; therefore, this gas is not considered in the model. (6) The pH will be estimated as an output of the system as described by Bernard et al. [14]. (7) Methane is assumed to have a negligible solubility in the liquid; hence, all the methane generated are released into the gas phase.

#### 2.1.2. General pathway

The model is a three-reaction based process (for both thermophilic and mesophilic populations), in which, the acidogenic population ($X_1$) hydrolyses the particulate organic matter ($S_0$) into soluble compounds (monomers) ($S_1$). Afterwards, these compounds are converted into VFAs ($S_2$) in the acidogenesis process, controlled by the same population ($X_1$), which is finally consumed by methanogenic biomass ($X_2$) and converted into methane ($CH_4$). Carbon dioxide ($CO_2$) is produced in both reactions. The following presents the reactions:

$$\text{Hydrolysis}: \quad S_0 \xrightarrow{r_H} S_1, \tag{1}$$

$$\text{Acidogenesis}: \quad S_1 \xrightarrow{r_A} Y_{X_1} \cdot X_1 + (1 - Y_{X_1})S_2 + f_{\_IC\_S_1} \cdot CO_2, \tag{2}$$

$$\text{Methanogenesis}: \quad S_2 \xrightarrow{r_M} Y_{X_2} \cdot X_2 + (1 - Y_{X_2}) \cdot CH_4 + f_{\_IC\_S_2} \cdot CO_2. \tag{3}$$

#### 2.1.3. Reaction kinetics

Recent studies show that the hydrolysis rate is better represented by the Contois model [12,15] rather than the classic first-order equation.[16,17] Contois kinetic better explains the hydrolysis phenomena since it takes both the substrate and biomass concentrations into account. A Monod and Haldane kinetic for acidogenesis and methanogenesis was considered. The expressions of each equation are presented in Table 1 in a Petersen matrix.

#### 2.1.4. Inorganic compounds

To represent the inorganic compounds present in an anaerobic systems, the approach presented by Bernard et al. [14] was used. The model considers two main inorganic compounds: the inorganic carbon content (IC) as a state

variable and the total alkalinity of the system ($Z$) as a constant value. These two variables do not exert an influence on the other state variables (substrates and microbial populations) instead they have a strong influence on the $CO_2$ flow and the pH of the system.

#### *2.1.5. Liquid–gas transfer*

As mentioned above, the methane solubility in the liquid was assumed to be negligible; thus, all the methane generated ($q_M$ in molar flow) goes directly to the gas phase (Equation (4)). By contrast, as the solubility of $CO_2$ in the liquid phase is much higher than the methane, the quantity of $CO_2$ ($q_C$ in molar flow) that goes to the gas phase depends on the mass transfer coefficient and a combination of the effects of $Z$, IC and $S_2$ as it is given in Equation (5). Both $CH_4$ and $CO_2$ are converted into volumetric flow according the ideal law gas:

$$q_M = k_6 r_2, \tag{4}$$

$$q_C = k_L a\,(\mathrm{IC} + S_2 - Z - K_H \times \left(\frac{\varphi - \sqrt{\varphi^2 - 4K_H P_T(\mathrm{IC} + S_2 - Z)}}{2K_H}\right)\Bigg), \tag{5}$$

where $\varphi = \mathrm{IC} + K_H P_T + q_M/k_L a$.

### *2.2. Description of the two-phase system*

#### *2.2.1. General approach*

The only difference and, at the same time, the main characteristic of modelling a two-phase system in comparison to a conventional one-phase reactor is that all the output variables of the first reactor correspond to the input variables of the second reactor. However, in the case of the microbial populations, since the first reactor operates under thermophilic conditions, it is logical to expect that the microbial populations that are transferred to the second reactor are thermophilic microorganisms. Hence, one interesting question arises, how active is this thermophilic biomass under the new mesophilic conditions? It is known that there are three main groups of biomass in terms of optimum temperature conditions: thermophils (50–55 °C), mesophils (35–37 °C) and psichrophils (15–25 °C), each of them presenting an Arrhenius-type activity within their respective working temperature range.[18] This issue has not been addressed so far for any article dealing with modelling of a two-phase system. In this study, to cope with this issue, a new parameter ($\alpha$) is added into the mass balance, which has to lie between 0 and 1. This parameter multiplies the biomass that enters the mesophilic reactor, a value close to zero means that only a small fraction of the microbial population of the thermophilic reactors remain active in the second reactor; in turn, a value close to 1 means that most of the thermophilic biomass is active in the mesophilic reactor.

#### *2.2.2. Differential equations system*

The system is composed of 12 ordinary differential equations (ODE) and 6 state variables ($S_0$, $S_1$, $S_2$, $X_1$, $X_2$ and IC) for each reactor. Some assumptions were made in order to define the mass balances of the systems: (1) the organic particulate matter entering the system possesses a fraction (fB) of anaerobically biodegradable substrate. (2) All the soluble organic matter entering the system is biodegradable. (3) Nonactive anaerobic biomass is present in the sewage sludge that enters the system, and the concentration of VFA present in the sewage sludge entering the digester is negligible.

The mass balance for each sate variable ($\xi$) in the liquid phase is shown in Equation (6). This general equation is valid for both the thermophilic and the mesophilic reactor, and the only differences are the input conditions and the value of the parameters

$$\frac{d\xi_i}{dt} = D \cdot (\xi_{in,i} - \xi_i) + \sum_{j=3} a_j r_{i,j}\,. \tag{6}$$

The right-side term represents the sum of the kinetic rate process $j$, described by multiplication of their stoichiometric coefficient $a$ and the reaction rate $r$ (Table 1).

The equations for both reactors and each state variable are described, in detail, below. All the variables, the reaction rates and the kinetic and stoichiometric parameters are noted with a T or M subscript in case of thermophilic or mesophilic conditions.

Table 1. Petersen matrix.

| | State variable | | | | | | |
|---|---|---|---|---|---|---|---|
| Process | $S_0$ | $S_1$ | $S_2$ | $X_1$ | $X_2$ | IC | Reaction rate |
| Hydrolysis | −1 | 1 | | | | | $r_H = \left(k_o \cdot \frac{S_0}{K_X \cdot X_1 + S_0}\right) \cdot X_1$ |
| Acidogenesis | | −1 | $(1 - Y_{X_1})$ | $Y_{X_1}$ | | $f_{\_IC\_S_1}$ | $r_A = \mu_1 \cdot X_1 = \left(\mu_{m_1} \cdot \frac{S_1}{K_{S_1} + S_1}\right) \cdot X_1$ |
| Methanogenesis | | | −1 | | $Y_{X_2}$ | $f_{\_IC\_S_2}$ | $r_M = \mu_2 \cdot X_2 = \left(\mu_{m_2} \cdot \frac{S_2}{K_{S_2} + S_2 + S_2^2/K_i}\right) \cdot X_2$ |
| Gas transfer | | | | | | −1 | $q_c$ |

*Reactor 1* (*thermophilic*)
For particulate substrates:

$$\dot{S}_{0\_T} = D_T \cdot (S_0\,\text{in} \cdot \text{fB}_T - S_{0\_1}) - r_{0\_T}. \quad (7)$$

For soluble substrates:

$$\dot{S}_{1\_T} = D_T \cdot (S_1\,\text{in} - S_{1\_1}) + r_{H\_T} - r_{A\_T}. \quad (8)$$

For acetic acid equivalent ($S_2$):

$$\dot{S}_{2\_T} = D_T \cdot (-S_{2\_T}) + (1 - Y_{X_1T})r_{A\_T} - r_{M\_T}. \quad (9)$$

For microbial populations (biomass):

$$\dot{X}_{1\_T} = D_T \cdot (-X_{1\_T}) + Y_{X_1T} \cdot r_{A\_T}, \quad (10)$$

$$\dot{X}_{2\_T} = D_T \cdot (-X_{2\_T}) + Y_{X_2T} \cdot r_{M\_T}. \quad (11)$$

Inorganic compounds:

$$\dot{\text{IC}}_{\_}T = D_T \cdot (\text{IC}\,\text{in} - \text{IC}_{\_T}) - q_{C\_T} + f_{\_\text{IC}\_S_1T} \cdot r_{A\_T} + f_{\_\text{IC}\_S_2T} \cdot r_{M\_T}, \quad (12)$$

$$\dot{Z}_{\_T} = D_T \cdot (Z\,\text{in} - Z_{\_T}). \quad (13)$$

*Reactor 2* (*mesophilic*)
For particulate substrates:

$$\dot{S}_{0\_M} = D_M \cdot (S_{0\_T} \cdot \text{fB}_M - S_{0\_M}) - r_{0\_M}. \quad (14)$$

For soluble substrates ($S_1$):

$$\dot{S}_{1\_M} = D_M \cdot (S_{1\_T} - S_{1\_M}) + r_{H\_M} - r_{A\_M}. \quad (15)$$

For acetic acid equivalent ($S_2$):

$$\dot{S}_{2\_M} = D_M \cdot (S_{2\_T} - S_{2\_M}) + (1 - Y_{X_1M}) \cdot r_{A\_M} - r_{M\_M}. \quad (16)$$

For microbial populations (biomass):

$$\dot{X}_{1\_M} = D_M \cdot (X_{1\_T} \cdot \alpha - X_{1\_M}) + Y_{X_{1\_M}} \cdot r_{A\_M}, \quad (17)$$

$$\dot{X}_{2\_M} = D_M \cdot (X_{2\_T} \cdot \alpha - X_{2\_M}) + Y_{X_{2\_M}} \cdot r_{M\_M}. \quad (18)$$

Inorganic compounds:

$$\dot{\text{IC}}_{\_M} = D_M \cdot (\text{IC}_{\_T} - \text{IC}_{\_M}) - q_{C\_M} + f_{\_\text{IC}\_S_1M} \cdot r_{A\_M} + f_{\_\text{IC}\_S_2M} \cdot r_{M\_M}, \quad (19)$$

$$\dot{Z}_{\_M} = D_M \cdot (Z_{\_T} - Z_{\_M}). \quad (20)$$

### 2.3. Model parameters: sensitivity analysis and reported values

Sensitivity analysis (SA) attempts to assess the influence of the parameters of a model (kinetic parameters, stoichiometric coefficients, initial conditions, etc.) upon its outputs (the measured variables). In this case, the sum of the mean squared (relative) prediction error (MSRE), as given by Equation (21), was used to compare the results obtained in a nominal or baseline simulation with a parameter-disturbed simulation. The parameters were varied ±2% within a ±50% of range of fluctuation.

$$\text{MSRE} = \frac{1}{N}\sum_{t=1}^{N}\left(\frac{y_{\text{nom},i} - y_{\text{sim},i}}{y_{\text{sim},i}}\right)^2, \quad (21)$$

where $y_{\text{nom}}$ and $y_{\text{sim}}$ are the nominal and the evaluated-disturbed simulation, respectively, $i$ corresponds to the output and $N$ corresponds to the number of data points. The nominal simulation was performed in continuous conditions for a period of 50 days, with simulated sewage sludge influent (pCOD = 20 g $L^{-1}$, sCOD = 4 g $L^{-1}$) at an HRT of 20 days and the parameters are shown in Table 2.

### 2.4. Experimental data

The calibration of the most sensitive parameters of the model as well as its cross-validation was carried out with data collected from a pilot-scale two-phase anaerobic system (TPAD) comprising a thermophilic (CSTR-type, volume of 60 L, 55 ± 1 °C), an intermediate tank and a mesophilic (CSTR-type, volume of 190 L, 35 ± 1 °C) anaerobic digester, which has been operating for nearly 1.5 years. The reactor is fed with thickened mixed sludge (5% TS, composed by 50% of primary and 50% of secondary sludge) coming from the domestic wastewater treatment plant (WWTP) of Valladolid, Spain. This WWTP operates with an inlet flow of 3.05 $m^3$ $d^{-1}$ for 233,000 inhab-eq (PE) and comprises lamellar-type primary settlers, $A^2/O$ biological treatment for simultaneous removal of organic matter and nutrients, and a suction-type secondary settler. Every load of sludge for feeding was conserved at 4 °C and lasted 3 days. The average composition of the raw sludge was as follows: TS 52.2 ± 6.5 g $L^{-1}$, VS 36.2 ± 4.5 g $L^{-1}$, total COD (tCOD) 53.1 ± 2.7 g $L^{-1}$ and soluble COD (sCOD) 2.8 ± 1.3 g $L^{-1}$. Samples of sludge, from the feeding tank and both digester outlets, were taken periodically and characterized in terms of solids and organic matter content (tCOD and sCOD), both determined according to standard UNE 77004:2002 based on dichromate method. The biogas production was measured daily by liquid displacement in an inverted cylinder equipped with an electro-valve. The biogas composition was measured by sampling (100 μL) and subsequent injection in a gas chromatograph (GC). Gas chromatography was carried out in a VARIAN CP 3800 GC with VARIAN capillary columns (TCD). To obtain smoother experimental data profiles, the average of three consecutive output measurements were used for the model's calibration.

Table 2. Parameter values used in the sensitivity analysis.

| Thermophilic | | | | Mesophilic | | | |
|---|---|---|---|---|---|---|---|
| Parameter | Value | Unit | Ref. | Parameter | Value | Unit | Ref. |
| $k_{oT}$ | 0.4 | $d^{-1}$ | [19] | $k_{oM}$ | 0.12 | $d^{-1}$ | [20] |
| $K_{XT}$ | 0.5 | gCODs $gCODx^{-1}$ | [19] | $K_{XM}$ | 1.5 | gCODs $gCODx^{-1}$ | [20] |
| $\mu_{m_1}T$ | 16 | $d^{-1}$ | [19] | $\mu_{m_1}M$ | 4 | $d^{-1}$ | [19] |
| $K_{s_1}T$ | 0.2 | gCOD $L^{-1}$ | [19] | $K_{s_1}T$ | 0.05 | gCOD $L^{-1}$ | [19] |
| $\mu_{m_2}T$ | 1.5 | $d^{-1}$ | [19] | $\mu_{m_2}M$ | 0.4 | $d^{-1}$ | [19] |
| $K_{s_2}T$ | 0.3 | gCOD $L^{-1}$ | [19] | $K_{s_2}M$ | 0.04 | gCOD $L^{-1}$ | [19] |
| $K_iT$ | 16.4 | gCOD $L^{-1}$ | Es | $K_iM$ | 16.4 | gCOD $L^{-1}$ | [14] |
| $Y_{X_1}T$ | 0.1 | gCODx $gCODs^{-1}$ | [19] | $Y_{X_1}M$ | 0.05 | gCODx $gCODs^{-1}$ | [11] |
| $Y_{X_2}T$ | 0.1 | gCODx $gCODs^{-1}$ | [19] | $Y_{X_2}M$ | 0.05 | gCODx $gCODs^{-1}$ | [11] |
| $f_{\_IC\_S_{1T}}$ | 0.005 | molIC $gCODs^{-1}$ | Es | $f_{\_IC\_S_{1M}}$ | 0.03 | molIC $gCODs^{-1}$ | Es |
| $f_{\_IC\_S_{2T}}$ | 0.005 | molIC $gCODs^{-1}$ | Es | $f_{\_IC\_S_{2M}}$ | 0.03 | molIC $gCODs^{-1}$ | Es |
| $K_{bT}$ | 7.7e − 10 | – | [19] | $K_{bM}$ | 6.5e − 7 | – | [14] |
| $K_{HT}$ | 2.31 | – | [4] | $K_{HM}$ | 16 | – | [14] |
| fB | 0.8 | – | Ex | fB | 0.8 | – | Ex |
| $k_La$ | 50 | $d^{-1}$ | Es | $k_La$ | 50 | $d^{-1}$ | Es |
| | | | | $\alpha$ | 0.5 | – | Es |

Note: Es, estimated; Ex, experimental.

### 2.5. *Model calibration and validation*

#### 2.5.1. *Model implementation*

The model's resolution, SA, calibration and validation were all performed in Matlab®. The ODE system was solved by using the *ode15s* toolbox. The programming starts by loading all the experimental inputs characterization and its specific operation time. The optimization procedure for the parameter calibration was done by using the *fminsearchbnd* toolbox, which uses a direct-search procedure based on the Nelder–Mead algorithm.

#### 2.5.2. *Optimization procedure*

The whole operation period was divided into three subperiods such that the population changes in terms of adaptation and/or enrichment may be identified. In each of them, the parameter estimation and the cross-validation were performed with two different sets of data. The model selected and developed as well as the calibration procedure must be validated with new experimental data, hopefully, at different input conditions than those used for the calibration. This issue has been pointed out as the most important step in a global modelling application procedure.[4] For parameter estimation and calibration, four experimental variables were used: $CH_4$ flow, $CO_2$ flow, sCOD (Equation (22)) and pCOD (Equation (23))

$$\text{sCOD} = S_1 + S_2, \tag{22}$$

$$\text{pCOD} = \text{tCOD} - \text{sCOD} = S_0 + X_1 + X_2. \tag{23}$$

The parameters were estimated by using a minimization algorithm. In this case, the least-squares criterion presented in Equation (24) was used

$$J(\theta) = \sum_{i=1}^{m} \frac{1}{n_i} \sum_{t=1}^{N} \left( \frac{y_{\text{exp}}(t) - y_{\text{sim}}(t,\theta)}{y_{\text{exp}}(t)} \right)^2 \Bigg|_{\theta_0=\theta_L}, \tag{24}$$

where $J$ is the objective function, $y_{\text{exp}}$ is the obtained value from measurements, $y_{\text{sim}}$ is the corresponding simulated value, $\theta$ represents the parameters to be determined and $N$ is the number of measurements.

## 3. Results and discussion

### 3.1. *Sensitivity analysis*

Figures 1 and 2 show the results of the parameter sensitivities for all the outputs of the thermophilic and the mesophilic reactor, respectively. The parameters related to the thermophilic reactor are evaluated on the outputs of both reactors since it is an operation in series. With regard to the thermophilic system, the most influential parameter is the hydrolytic coefficient ($k_{oT}$), which presents the highest sensitivity on three of the outputs. This confirms the fact that the hydrolysis reaction is considered the limiting reaction of the anaerobic degradation of sewage sludge.[16] In fact, this parameter represents almost 50% of the total sensitivity of these three outputs. Furthermore, the maximum growth rate of the methanogenesis biomass shows a high sensitivity especially to the sCOD and the $CH_4$. Methanogenic biomass converts the VFA (part of the sCOD) into biogas, and thus, influences these outputs significantly. Both growth yields ($Y_{X_1T}$ and $Y_{X_2T}$) also exert a certain influence on the outputs as well as the stoichiometric coefficients related to the inorganic carbon production,

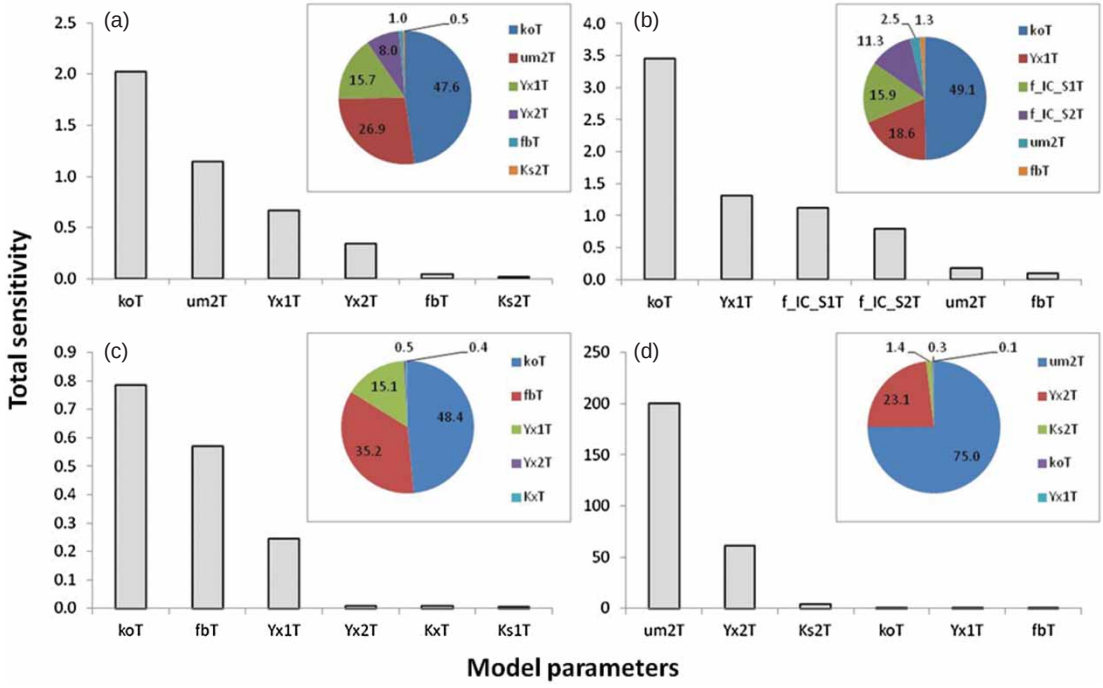


Figure 1. Model parameters' sensitivities on the measured outputs in the thermophilic reactor: (a) $CH_4$ flow, (b) $CO_2$ flow, (c) pCOD and (d) sCOD.

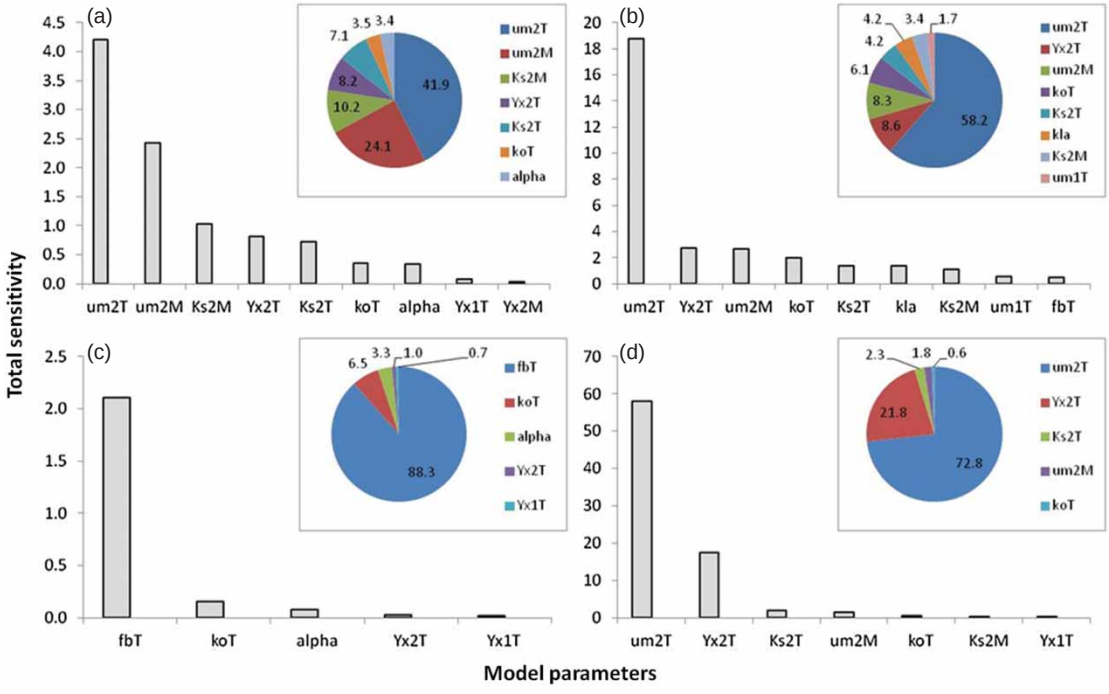


Figure 2. Model parameters' sensitivities on the measured outputs in the mesophilic reactor: (a) $CH_4$ flow, (b) $CO_2$ flow, (c) pCOD and (d) sCOD.

on the $CO_2$ flow. As expected, the fraction of biodegradable organic matter influences the pCOD behaviour significantly. Neither the affinity nor the inhibition constants present a noticeable sensitivity. These parameters, in general, are quite difficult to determine and their influence can only be observed under very specific experimental conditions.[21,22] It is expected to observe that the most sensitive parameters are the ones more directly related to the process where the measured output is consumed or produced [23]; however, the SA helps to distinguish the influence of each parameter related to a specific process (e.g. $\mu_m$ and $K_S$).

Table 3. Calibrated parameter values.

| Parameter | Unit | Calibrated values | | |
|---|---|---|---|---|
| | | Period 1 | Period 2 | Period 3 |
| $k_{0T}$ | $d^{-1}$ | 2.46 | 2.70 | 4.16 |
| $\mu_{m_2T}$ | $d^{-1}$ | 10.31 | 55.86 | 32.11 |
| $Y_{X_1T}$ | g $g^{-1}$ | 0.12 | 0.35 | 0.11 |
| $Y_{X_2T}$ | g $g^{-1}$ | 0.48 | 0.13 | 0.17 |
| $\mu_{m_2M}$ | $d^{-1}$ | 0.20 | 0.28 | 0.27 |
| $f\_IC\_S_{1T}$ | mmol $g^{-1}$ | 0.001 | 0.002 | 0.002 |
| $f\_IC\_S_{2T}$ | mmol $g^{-1}$ | 0.004 | 0.001 | 0.007 |
| $f\_IC\_S_{1M}$ | mmol $g^{-1}$ | 0.1 | 0.1 | 0.08 |
| $f\_IC\_S_{2M}$ | mmol $g^{-1}$ | 0.1 | 0.03 | 0.02 |
| fB | – | 0.57 | 0.50 | 0.44 |
| $A$ | – | 0.18 | 0.89 | 0.73 |

With regard to the parameters of the mesophilic reactor, overall, they are quite less influential than the thermophilic ones, which is due to the fact that the concentration of the main components is already buffered by the first reactor; hence, there is a lower input excitation. Indeed, the most sensitive parameters of, practically, all the outputs of this reactor are the ones of the thermophilic methanogenic biomass ($\mu_{m_2T}$ and $Y_{X_2T}$). In any case, the activity of the methanogenic mesophilic biomass ($\mu_{m_2M}$) presents certain influence on the biogas flow ($CH_4$ and $CO_2$). Unfortunately, the newly proposed parameter ($\alpha$) shows a low sensitivity on all the outputs. In fact, only around 3% of the sensitivity of the $CH_4$ flow and the pCOD is explained by this parameter. In any case, since it is a new parameter (to our knowledge not previously proposed), it is, regardless, included in the calibration process, keeping in mind that the accurate identification of this parameter requires further research.

The set of parameters that was calibrated and their respective values are presented in Table 3. Despite some of the selected parameters showing low sensitivity on the measured outputs, they were included, anyways, in the calibration to improve the model's performance. However, it is worth pointing out that this procedure does not correspond to an identification study, it is just a calibration and preliminary estimation of the parameter's values. As far as we know, performing a SA in a two-phase system has not been done before; hence, the approach presented here may be useful for future applications especially concerning model calibration and parameter identification.

Despite the fact that SA provides valuable information concerning the influence of the parameters on the system's behaviour, it is important to take into account the limitations of this classical procedure. Apart from the influence of each parameter, the outputs are also usually strongly influenced by interactions among themselves. The latter may lead to some identification problems during optimization procedures, consequently to some misleading parameter values. Therefore, the SA results should be carefully considered, since it cannot be distinguished whether this sensitivity corresponds to the direct influence of the parameter (also called first-order effect) or the interactions among them. For instance, both $\mu_{m_2T}$ and $Y_{X_2T}$ possess a significant sensitivity; however, it is possible that the correlation between them is significant as well.

### 3.2. Model calibration and cross-validation

#### 3.2.1. Experimental input conditions

Figure 3 shows the input conditions to which the system was subjected to during 530 days, in terms of OLR and HRT. The whole operation trial was divided into three periods (op1, op2 and op3); in which both calibration and cross-validation were carried out. Throughout the reactor operation, the HRT, in the thermophilic reactor, was decreased from values of around 4 days up to 1.5 days, whereas the OLR was increased from values of around 10 up to values around of 40 gCOD $L^{-1}$ $d^{-1}$. With regard to the mesophilic digester, the HRT applied was around 10 days except for some overload spikes and two more prolonged periods where the HRT was between 20 and 30 days. By contrast, the OLR fluctuated considerably all along, between 0.5 and 3.0 gCOD $L^{-1}$ $d^{-1}$. It is worth pointing out that the thermophilic reactor kept producing biogas, i.e. there was a constant population of methanogens, during the whole operation period, despite the extreme conditions that were applied.[24] The latter will be discussed afterwards. For both reactors, but especially in the thermophilic one, several disturbances in terms of HRT and OLR occurred due to regular variations of the organic matter concentration of the influent and some problems with the sludge pumping. These variable conditions, with continuous perturbations of organic load, represent a proper platform for parameter determination due to the experimental solicitation while helping to test whether the model is able to respond to more extreme conditions.

#### 3.2.2. Calibrated parameters

The calibrated parameter values from the minimization procedure are presented in Table 3. A more in-depth discussion about the parameter values cannot be done since the calibration of parameters does not correspond to an identification procedure itself, which is normally performed under more controlled conditions and use a more specific experimental design. In addition, the results of an identification procedure must be presented along with a statistical analysis (e.g. confidence intervals, standard deviation). In any case, the calibrated values provide a certain idea about the real values of the parameters. The most remarkable result is the high value of the maximum specific growth rate of thermophilic methanogens ($\mu_{m_2T}$), which is, to our knowledge, greater than any other values ever reported. The obtained values also show a sharp increase of this parameter between periods 1 and 2, which

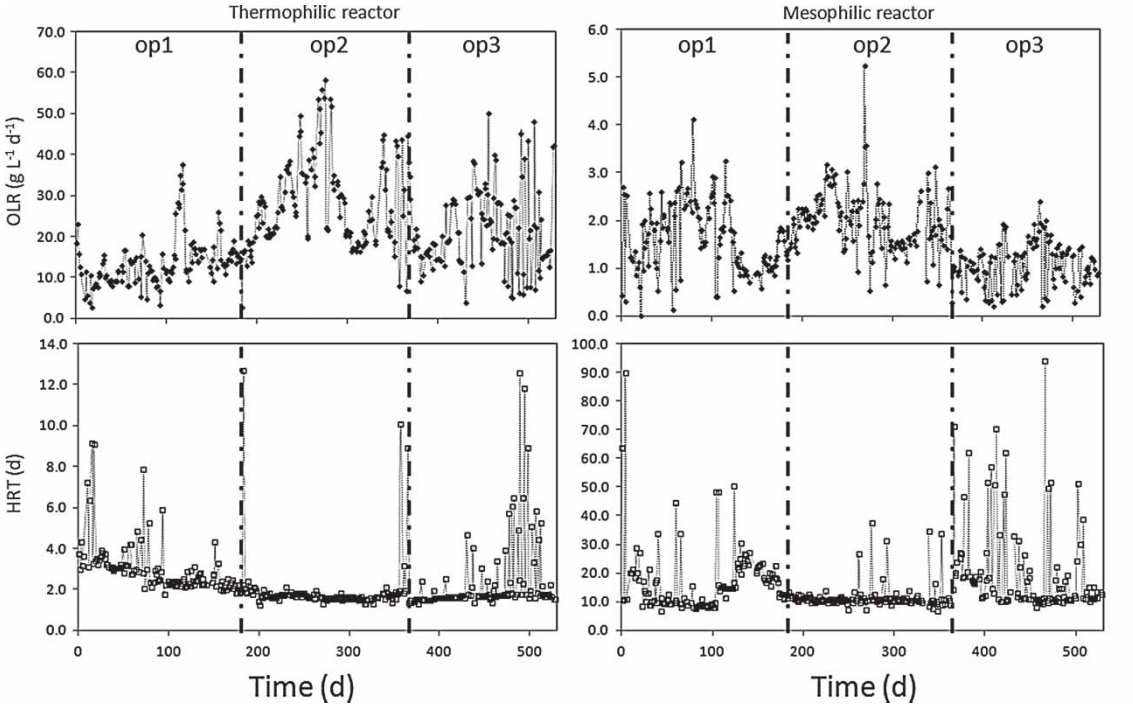


Figure 3. Input conditions of the pilot two-stage (TPAD) anaerobic system in terms of organic load rate (OLR) and hydraulic retention time (HRT).

may have been the result of selection or adaptation of a specific thermophilic biomass. This may in part explain the stability of the thermophilic at these operational conditions. Similarly, the hydrolytic capacity of the acidogenic population of the themophilic is quite high during the evaluation period, showing an important rise when lowest HRT was applied. Overall, the rest of the parameters are around the reported values.

With regard to the biomass transfer parameter ($\alpha$), there is no clear trend concerning the estimated values and, as was mentioned before, it would be a little thoughtless to make any definitive conclusion. Nevertheless, it seems that at least there is some loss of the biomass activity when transferred to mesophilic conditions since all the calibrated values are less than 1. A proper identification of this parameter requires other output measurements since its influence on the measured current outputs is lame.

### *3.2.3. Model fit*

The model fit during the calibration parameter and cross-validation is shown in Figures 4–6 for operation periods op1, op2 and op3, respectively. In general terms, as a global evaluation, the model is able to represent the system's behaviour for both the thermophilic and mesophilic reactor. Making a deeper analysis by the operation period, it can be observed that in op1, the calibration properly described the outputs profile in both reactors; however, some discrepancies are observed during the validation. The biogas in the thermophilic reactor, above all the $CO_2$ flow, is underestimated by the model, although the trend rise of the profiles is represented by the simulated outputs. This may be attributed to the sludge characterization, which is not performed daily, thus, for model purposes; it is assumed that the measured value is constant for the next 3 days until the next characterization. Nevertheless, it is worth to point out the satisfactory performance of the model with regard to the mesophilic reactor even though the important fluctuations in terms of OLR were attained. During op2, the model responds properly to the system's behaviour, especially in the validation period. The most important disagreement is observed in the prediction of the $CH_4$ flow in the thermophilic reactor during the first half the validation period. In this period, the model is not able to cope with the variability of the OLR (Figure 3); hence, it is not totally capable of adequately describing short-term (daily) dynamics. In the last evaluated period (op3), the model, once again, performs well, mimicking practically all the measured outputs properly, especially in the calibration period. The main deviations between the simulation and the experimental measurements are observed in the validation for gas flows in the thermophilic reactor between the day 475 and 525, as well as the $CH_4$ flow in the mesophilic reactor for the same period.

### *3.2.4. Model's overall performance: strengths and weaknesses*

In general terms, the model developed is able to describe the behaviour of the pilot TPAD system in terms of $CH_4$,

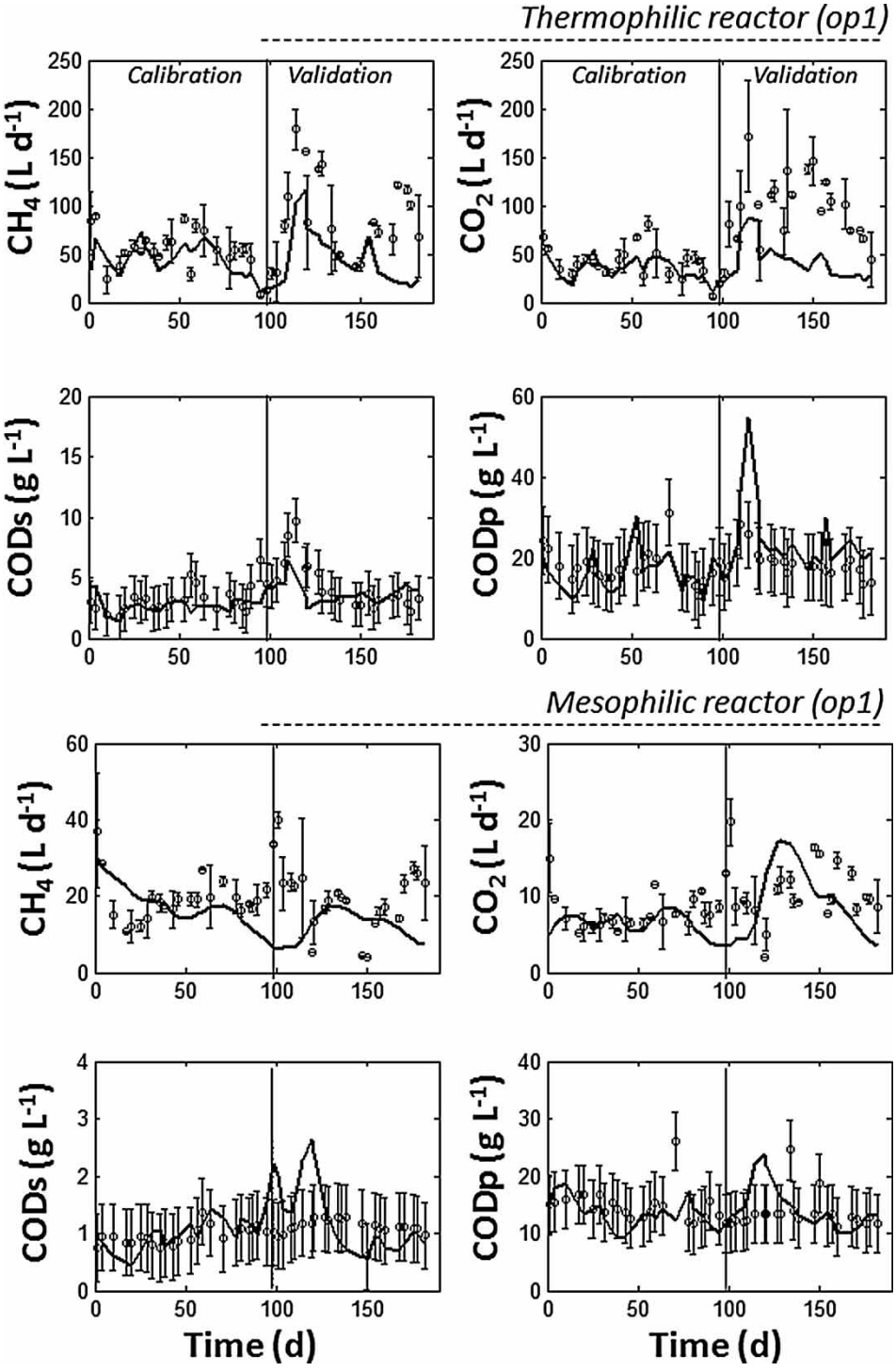


Figure 4. Calibration and validation of the mathematical model with the TPAD system during the first operational period (op1).

$CO_2$ and organic matter. An outstanding model performance outcome is the good prediction of both sCOD and pCOD. The latter represents a practical and desirable outcome, since the substrate concentration values will follow, either downstream pos-treatment or physical treatment before disposal. In addition, it has to be kept in mind that pCOD removal is one of the major aims of anaerobic digesters.

The most significant disagreements are observed in the prediction of the $CH_4$, and $CO_2$ especially in the thermophilic reactor. This contrast with the mesophilic reactor can be explained by the lesser experimental solicitation

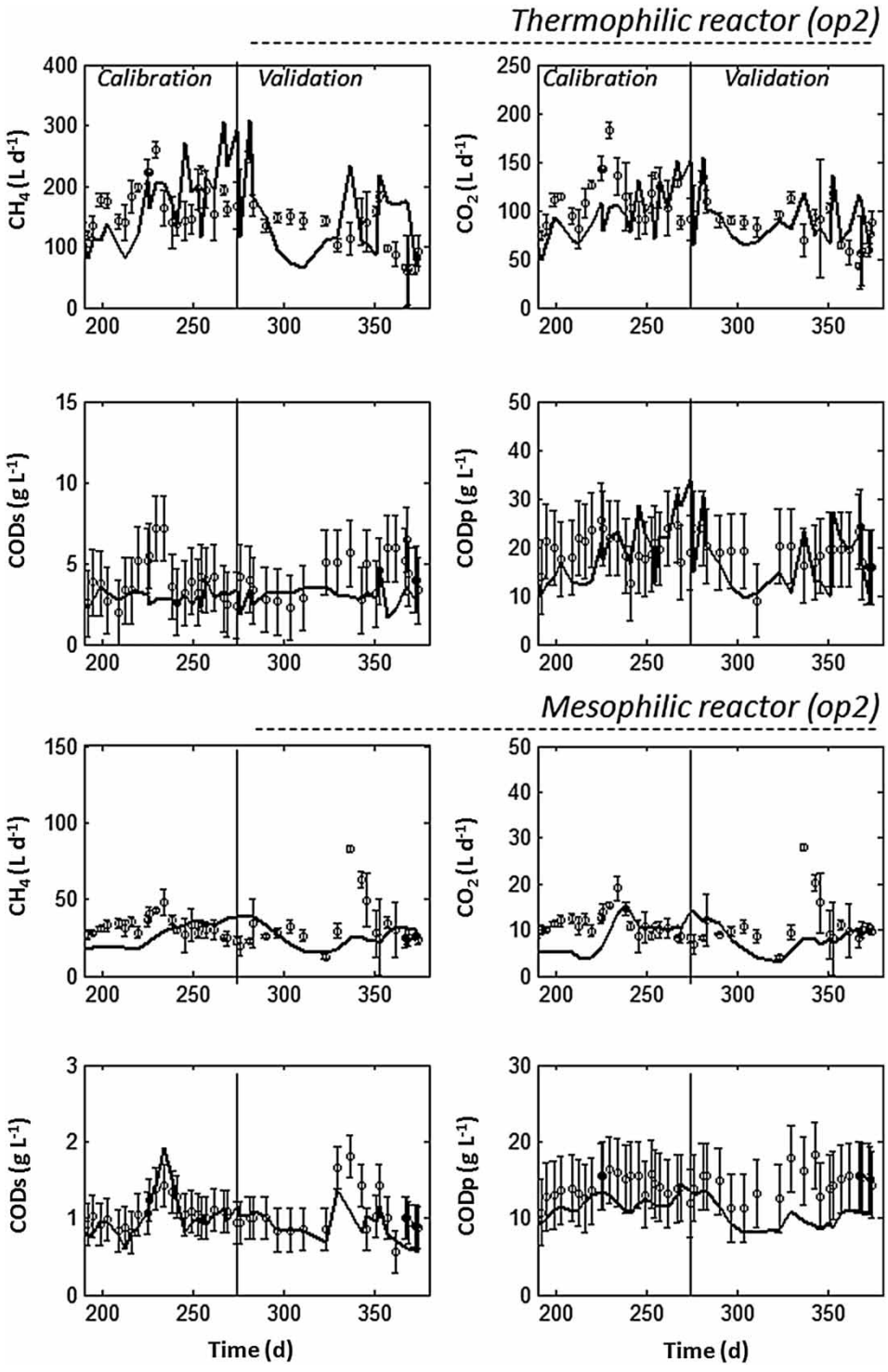


Figure 5. Calibration and validation of the mathematical model with the TPAD system during the second operational period (op2).

of the mesophilic reactor since the thermophilic digester works as a buffer system receiving all the systems input disturbances. With regard to the biogas prediction results themselves, the discrepancies must be attributed, first of all, to some operational hurdles, for instance, the common sludge pumping problems, where the accumulation of organic matter occurs in the digesters is not described by the model that assumes ideal mixing in the reactor. On the other hand, and despite the organic matter behaviour is well represented, it cannot be forgotten that the measurement of COD is a rough approximation of the organic matter content, which is not able to distinguish the different types

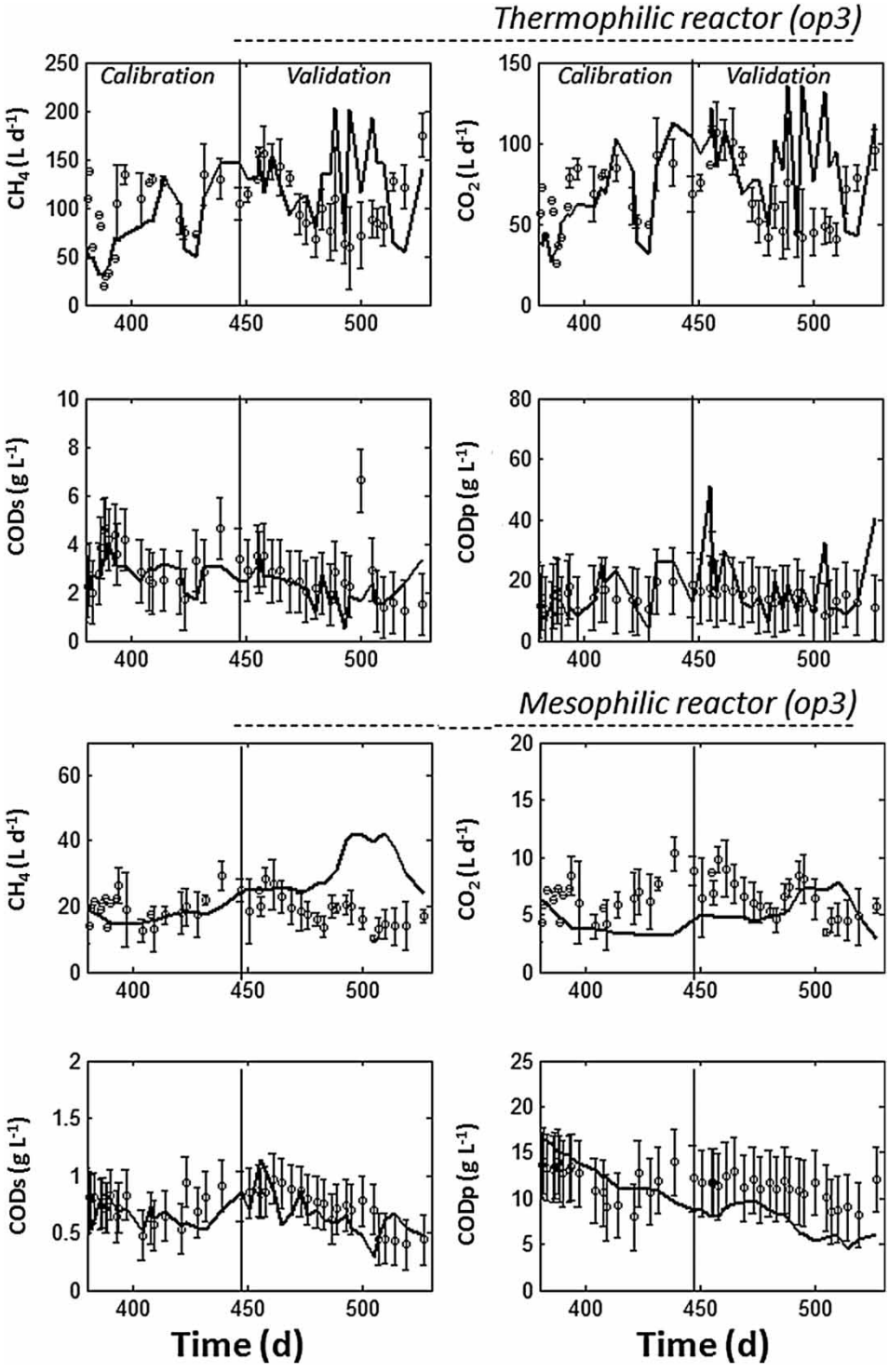


Figure 6. Calibration and validation of the mathematical model with the TPAD system during the third operational period (op3).

of soluble substrates, which can eventually present different biodegradabilities. Another cause of biogas prediction disagreement can be one of the model's assumptions of lumping up the several VFAs. The VFAs also present a variety of biodegradabilites; however, in real plants, only a rough approximation of the total presence of VFAs is usually measured.[25]

In any case, the deviations in predicting the biogas profiles requires further research mainly in terms of parameters sensitivity; for instance, the application of global SA, which allows the detection of the interactions (correlations) between parameters, or in the evaluation of different cost functions during the optimization procedure, rather than making the model more complex. On the other hand,

the developed and implemented model does not require a complex characterization (only conventional COD measurements) of the substrate entering the system, so does the case of using more complex models, so that, in that sense, it can be more easily employed and understood for plant operators.

## 4. Conclusion

A simplified mechanistic mathematical model of the anaerobic digestion of sewage sludge was developed and implemented in a thermophilic–mesophilic (TPAD) two-stage anaerobic system. A procedure consisting of model implementation and testing, SA, model calibration and cross-validation was performed to obtain a well-analysed model by using a thorough modelling procedure. A long-term system operation was used for both calibration and cross-validation; thus, a large set of data points at different input conditions were used, which make the results of the whole modelling application procedure more trustworthy. This simplified mechanistic model presents some important new properties: (1) it requires a conventional and simple sewage sludge characterization, (2) it distinguishes between the biodegradable fraction that enters the thermophilic reactor and the mesophilic one, and (3) it takes into account that only part of the thermophilic biomass remains active under mesophilic conditions.

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## Disclosure statement

No potential conflict of interest was reported by the author(s).

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