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A systematic methodology to extend the applicability of a bioconversion model for the simulation of various co-digestion scenarios

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Running title

Model simulating manure- and wastewater- based anaerobic co-digestion.

ABSTRACT

Detailed simulation of anaerobic digestion (AD) requires complex mathematical models and the optimization of numerous model parameters. By performing a systematic methodology and identifying parameters with the highest impact on process variables in a well-established AD model, its applicability was extended to various co-digestion scenarios. More specifically, the application of the step-by-step methodology led to the estimation of a general and reduced set of parameters, for the simulation of scenarios where either manure or wastewater were co-digested with different organic substrates. Validation of the general parameter set involved the simulation of laboratory-scale data from three continuous co-digestion experiments, treating mixtures of different organic residues either at thermophilic or mesophilic conditions. Evaluation of the results showed that simulations using the general parameter set fitted experimental data quite well, indicating that it offers a reliable reference point for future simulations of anaerobic co-digestion scenarios.

KEYWORDS

Anaerobic digestion, mathematical modeling, dynamic simulation, organic residue, parameter set.

1 Introduction

Throughout the years, various mathematical models simulating both anaerobic mono- and co-digestion processes have been proposed. From simpler empirical models (Andrews, 1969; Graef and Andrews, 1974; Hill and Barth, 1977; Kleinstreuer and Poweigha, 1982), to more complex ones (Angelidaki et al., 1999, 1993; Batstone et al.,

2002b; Costello et al., 1991; Siegrist et al., 1993). All of these models have been used to describe, to a certain extent, the anaerobic digestion of complex substrates.

The majority of the complex models are specialized in anaerobic digestion of specific feedstocks such as agricultural energy crops, residues, manures and wastewater sludge. For instance, the Anaerobic Digestion Model No. 1 or ADM1 (Batstone et al., 2002b) has been the most prominent among scientists working in the field of anaerobic wastewater treatment processes and more recently in solid waste bioconversion technologies. Likewise, the model (BioModel) proposed by Angelidaki et al. (1999) gives a good description of manure-based anaerobic digestion systems. The BioModel focuses on ammonia inhibition, which is often relevant in manure-based digestions, and includes a detailed description of pH and temperature, in order to simulate free ammonia concentrations. Compared to the ADM1, which expresses the concentration of solid substrate and product components using the indirect Chemical Oxygen Demand (COD), the BioModel features a more convenient, mass-based unit system. This allows for the characterization of substrates and products using simpler sampling and measurement techniques more appropriate for slurries and solid wastes, than COD. Despite their extensive application, the optimal use of such complex models requires the adjustment or modification of numerous parameters, depending on the type and nature of the simulated case (Donoso-Bravo et al., 2011). General experience shows, however, that the more parameters are contained in a mathematical model, the more difficult it becomes to verify their values for individual cases. Specifically, the large number of reactions and chemical species involved in these models gives a better description of the process, but complicates modeling, and – depending on the system to be “modeled” – the selection of the model itself to use. This also implies that existing complex models

64 are currently incapable of simulating dynamic processes describing diverse
65 experimental conditions, without a considerable amount of customization. Criteria to
66 select among models must weigh the trade-off between increased information
67 requirements and potentially better process description. Moreover, the model refinement
68 is an iterative procedure where the experimental and expert guided process of adding,
69 excluding, or modifying assumptions until a model that satisfactorily explains the
70 experimental data is obtained, is in general a difficult and time-consuming task (Sales-
71 Cruz and Gani, 2006).

72 Based on aforementioned premises, the objective of this study was to identify a set
73 of “benchmark” parameters that can be used without previous calibration for specific
74 digestion cases and which can satisfactorily describe different digestion cases such as
75 manure- or wastewater-based digestions. This was achieved through the application of a
76 systematic methodology, which essentially consisted of the following. First, parameter
77 selection was performed to reduce the parameter space for further treatment, based on a
78 detailed assessment of complex bioconversion model parameters, found to be reported
79 in literature with the greatest variations in their values. Second, detailed parameter
80 sensitivity analysis using Latin Hypercube Sampling (LHS) and the Partial Rank
81 Correlation Coefficient (PRCC) methods was performed, so that the less sensitive
82 parameters could be further discriminated/eliminated. Third, numerical optimization
83 using the Simulated Annealing (SA) method was carried out to estimate optimal
84 parameter values and statistical information was obtained to determine the feasibility of
85 the model parameters. Finally, the resulting set of optimized parameters was validated
86 with three selected experimental case studies, in order to demonstrate improved model
87 efficiency when using optimized parameters for simulation.

2 Materials and MethodsModel Description

The core dynamic model (BioModel) of this work was developed by Angelidaki et al. (1999, 1993) and describes the degradation of complex substrates, along with the co-digestion of different types of organic wastes. In the BioModel, the substrate is described in terms of its basic organic components' composition – carbohydrates, lipids and proteins –, the concentration of intermediates such as volatile fatty acids (VFA) and long-chain fatty acids (LCFA), and important inorganic components, such as ammonia, phosphate, cations and anions. The model was upgraded to include the hydrolysis of lipids so that it includes three enzymatic hydrolytic and eight bacterial steps, and involves 19 chemical compounds, together with a detailed description of pH and temperature characteristics. Free ammonia, VFA and LCFA constitute the primary modulating factors. The BioModel was previously calibrated with experimental co-digestion scenarios utilizing substrates rich in carbohydrates, proteins and lipids (Angelidaki et al., 1999, 1997). For a detailed description of the model, see Table SI in the Supplementary material.

2.2 Computational Methods

Initially written in Microsoft Pascal, and later translated to the Delphi Pascal programming language, the BioModel was recently implemented in MATLAB, combined with a Microsoft Excel-based data input and output platform. The MATLAB model is able to simulate the AD process in one anaerobic fermenter, considering the composition of the inoculum, a primary substrate and up to three optional co-substrates. Organization and processing of parameters defining substrates, pump and flow rates, metabolic steps and chemical components, as well as the collection of model output variables was set up similar to as described by Angelidaki et al. (1999). Integration of

model equations in time and the selection of a suitable time step for calculations also resembled the method outlined in this earlier publication, and for the solution of the model ordinary differential equation system, MATLAB's *ode15s* solver was used.

2.3 Systematic methodology

The four steps describing the systematic methodology are depicted in Figure 1 and are described further in the following subsections. During the analysis, the model structure was kept as taken from the literature (Angelidaki et al., 1999).

2.3.1 Step 1: Parameter selection

In this step, a preliminary selection of the model parameters was performed based on the assessment of available literature (Batstone et al., 2002a; Biernacki et al., 2013; Bułkowska et al., 2015; López and Borzacconi, 2010; Lübken et al., 2007; Nguyen, 2014; Ramirez et al., 2009; Rivera-Salvador et al., 2014; Rosén and Jeppsson, 2006). Details of this process are explained in the Supplementary material and the complete list of parameters considered is shown in the Supplementary material, Table SII. As a systematic reduction of the complete model parameter space and based on the comparison of studies, biochemical parameters that showed significant variance and are included in the BioModel were selected for subsequent sensitivity analysis in Step 2.

2.3.2 Step 2: Parameter sensitivity analysis

Following the parameter selection (Step 1), a detailed sensitivity analysis was performed on the selected parameters, in order to evaluate the magnitude of the parameters' individual effect on specific simulation output variables. The output variables chosen were biogas and methane production, VFA and total ammonium nitrogen-TAN concentration, pH, commonly reported as good indicators of the AD process performance (Boe et al., 2010; Labatut and Gooch, 2012). Values of the

parameters selected in Step 1 were allowed to vary between lower and upper boundaries, defined based on the literature assessment of Step 1, and sampling of the available parameter space was performed with the Latin Hypercube Sampling (LHS) method (McKay, 1992; McKay et al., 1979). LHS was an integral part of the analysis, in order to make sure that the parameter values were selected from the whole range available, avoiding bias and maintaining statistical accuracy. Concerning the distribution of parameter intervals by the LHS method, uniform parameter distribution was assumed (Manache and Melching, 2007), and the number of parameter sample sets generated by the method was ten times the number of parameters selected for analysis.

Following the sampling process, simulations were performed with every set of parameter samples generated previously. The length of the simulated periods corresponded to the periods where experimental data were available. Furthermore, to reduce computational demand, four approximately equidistant time points of each case simulation period were selected and only the output variable values of these time points were used thereafter.

Sampling-based Partial Rank Correlation Coefficient (PRCC) method (Marino et al., 2008; Pennington, 2015; Wu et al., 2013; Zi, 2011) was used to perform sensitivity analysis. As the PRCC method does not account for time as an independent variable, PRCC analyses for the previously selected, equidistant time points were conducted separately, in order to produce statistically representative results for complete simulation periods. Further to that, for PRCC results to be considered relevant, their probability values (p-values) were required to be smaller than 0.05 (Jackson and Radunskaya, 2015). For each case study, results of the PRCC analyses for individual time points were combined, providing an aggregate PRCC value over the entire

simulated period. Parameters were ranked according to their PRCC values to define the most sensitive parameters with respect to each model output variable specified in Step 2. Both LHS and the PRCC analyses were carried out using the MATLAB-based Sampling and Sensitivity Analyses Tool (SaSAT) (Hoare et al., 2008).

2.3.3 Step 3: Parameter estimation

After identification of the most sensitive parameters in Step 2, numerical estimation of their values was performed for both case studies. Variation in parameter values was allowed according to lower and upper parameter boundaries specified in Step 2. The parameters were estimated by minimization of the sum of squares of the differences between predicted and experimental data sets (see Table SIII of the Supplementary material). For the optimization task, the Simulated Annealing (SA) method was used (Ingber, 1996; Kirkpatrick et al., 1983). Implementation of the method was done in MATLAB, using the *simulannealbnd* function. Each case study was simulated with 250 iterations (a number used also by López and Borzacconi (2010)), in three consecutive parameter estimation cycles to support the results of the stochastic optimization method statistically. At the last step, SA iteration histories, objective function values and estimated parameter values were collected from all simulations, and were used for comparing the different scenarios on a quantitative and qualitative basis.

2.3.4 Step 4: Validation and evaluation of the results

First, performance criteria simulations – benchmark simulations – with the original model parameter values were compared against simulations using the optimized parameter values identified in Step 3, for both case studies used during parameter estimation. Second, following the unification of optimized parameter values used in case study 1 and 2 – by calculating the mathematical average of the respective

parameter values – validation of optimized parameters was performed with the data of three lab-scale CSTR experiments. Finally, conclusions were drawn based on the results of validation.

2.4 Case studies

Below a short overview of the two experimental case studies, which were used during parameter estimation is provided. For further details on simulated substrate and process characteristics, see the Supplementary material, Table SIV and SV.

2.4.1 Case study 1 (C1)

Process data was collected from the doctoral dissertation of Schön (2009). In his work, the author investigated the applicability of ADM1 for the simulation of the AD process of a demonstration biogas plant, and lab-scale reactors fed only with manure. The reactor selected for simulation had a volume of 75 L and was operated at mesophilic conditions (37 °C), with a hydraulic retention time (HRT) of 10 days, in four consecutive periods. Period 1 (day 0-8): no influent feed, operated as batch with only inoculum. Period 2 (day 9-15), Period 3 (day 16-22) and Period 4 (day 23-30) fed solely with manure of varying composition (Supplementary material, Table SIV). Due to the simplicity of the experimental setup and the availability of relevant data such as input manure characteristics, biogas production and pH, this case was selected as the initial case study for analysis.

2.4.2 Case study 2 (C2)

A continuous lab-scale experiment, carried out by Wang et al. (2016) using GTO and ammonia as co-substrates, was used as the second case study. The reactor had a working volume of 1.8 L, its inoculum originated from digestion of a mixture of cattle and pig manure, while cattle manure served as the primary substrate for reactor feeding

(Supplementary material, Table SV). Reactor temperature was kept at 54 °C throughout the whole experiment. Feeding took place with an HRT of 15 days, throughout the experiment. The experiment was divided into two main phases; in the first phase, manure feed was mixed with rapidly increasing concentrations of GTO, raising the organic loading rate (OLR) from 3.2 g-VS $L^{-1}d^{-1}$ to 5 g-VS $L^{-1}d^{-1}$ in 54 days, which ended with the collapse of the reactor. Following re-inoculation, the reactor in the second phase was fed with manure and a gradually increasing concentration of GTO, reaching from 3.2 to 4 g-VS $L^{-1}d^{-1}$ added organic material in 91 days, after which OLR was kept stable. Meanwhile, ammonia addition in this last period increased from 2.1 to 5 g-N L^{-1}, during the course of 157 days. Thus for the simulation, 9 feeding periods were defined, based on data provided by Wang et al. (not shown).

3 Results and Discussion

Base case simulations for the two case studies (C1 and C2) were generated with the original BioModel parameters. The response of the model in terms of biogas or methane productivities, and total VFA concentrations (where applicable) is shown in Figure 2a (C1) and Figure 2b (C2), and are discussed in the following sections. pH simulations were included in the Supplementary material (Figure S1 and S2).

Following the steps outlined in the systematic methodology, 44 parameters were initially selected in Step 1 for sensitivity analysis, with lower and upper boundaries defined based on the smallest and largest values reported for anaerobic digestion of complex substrates. The list of initially selected parameters, along with their lower and upper limits, can be found in the Supplementary material, Table SVI. In Step 2, the most sensitive parameters were identified for the individual estimation case studies (average PRCC values shown in Table SVII of the Supplementary material). Out of 44

initial parameters tested, model output variables were found to be sensitive to mainly 13 specific parameters. These 13 parameters included: $Hydr_{carb,in}$, $Hydr_{prot,in}$, Ks_{AA}, Ks_{HPr}, Ks_{HVal}, Ks_{HAc}, $Ki_{NH3,HAc}$, pKh_{Ac}, Kd_{AA}, Kd_{HPr}, Kd_{HBut}, Kd_{HVal} and Kd_{HAc}. These parameters and their quantified effect (PRCC values) on the output variables are shown in Figure 3. As seen from the graphs, parameter effects show significant variations depending on the output variables considered, but the trends in PRCC values, and thus the overall parameter effects on the simulated systems appear similar. Once the most sensitive parameters were identified, Step 3 was then executed, the results of which are discussed in the next sections, for each case study respectively.

3.1 Case study 1 (C1)

In the first benchmark simulation, the response of the model with the original set of parameters is shown in red color in Figure 2a. As observed, model response fitted well the trend exhibited by experimental data, particularly in Periods 1, 2 and 3 at which biogas production increased – due to an increase in the organic loading rate – and then stabilized at a new steady state level. In contrast with the trend exhibited by the experimental data during Period 4, where biogas production is shown to decrease throughout the whole period, the model predicted a slight decrease at the beginning and subsequently reached a new steady state level. This discrepancy is explained by the fact that during this operational period experimental values were not recorded properly as pointed out by the authors. Figure 2a shows in green color the response of the model when the set of optimized parameters (see Table II) was used. Although qualitative improvement is difficult to assess, improvements in the fitting were obtained. This was further confirmed by the value of the objective function, which was reduced from 0.498 to 0.356 representing a 28.5% improvement in the model response (Table I).

Meanwhile, the quality of the pH simulation was unchanged and remained highly accurate (see Figure S1 in Supplementary material). Compared to the ADM1 simulation that is shown in Figure 2a in blue color, both the benchmark and optimized simulations fit experimental data with high accuracy, especially in Period 2, where a rapid increase in biogas productivity is observed. This indicates that the BioModel appeared to produce more accurate simulations for anaerobic manure digestion than the ADM1.

3.2 Case study 2 (C2)

In the second benchmark simulation, the response of the model with the original set of parameters is shown in Figure 2b in red color. First, two operational periods can be observed with a considerable degree of uncertainty. Operational Period 2 between days 50 and 80, where simulated methane productivity increased more rapidly compared to the experimental trend, while the simulated total VFA concentrations only reached about half of the experimental values. Periods 8 and 9 (between day 300 and 420), on the other hand, showed an opposite trend, with a significant delay in the decrease of methane productivity and an overestimation in total VFA concentration simulated. The value of the objective function for the benchmark simulation was found to be 461.289 (see Table I). Figure 2b shows in green the response of the model when the set of optimized parameters (see Table II) were used. As observed, by using the optimized parameters a significant improvement (82.5%) was obtained in the objective function value (see Table I), which is well represented by the satisfactory fit of the total VFA experimental data – particularly between days 300 and 420 (see Figure 2b, bottom in green).

3.3 Parameter set validation

As a result of the parameter optimization process carried out using the two aforementioned case studies, a general set of estimated parameters was compiled (see Table II), with parameter boundaries defined based on the lowest and highest optimized parameter values used by the SA algorithm. For validating the above, generally applicable set of parameters, three case studies are described below. They were selected from a wide range of experiments, and covered manure co-digestion with carbohydrates, manure co-digestion with complex substrates and wastewater co-digestion with complex substrates.

3.3.1 Validation case study 1 (V1)

Experimental material for the first validation case scenario was taken from Søndergaard et al. (2015), who investigated the effect of meadow grass on biogas productivity, when added to manure and co-digested in CSTR-type reactors (Supplementary material, Table SVIII). By gradually increasing the concentration of meadow grass in the reactor, while using the same manure substrate, the experiment had four distinct feeding periods. Period 1 (day 0-12): manure feed without additional meadow grass. Period 2 (day 13-61): manure feed with 12 g L^{-1} meadow grass. Period 3 (day 62-91): manure feed with 23 g L^{-1} meadow grass. Period 4 (day 92-107): manure feed with 34 g L^{-1} meadow grass. Operation temperature was 54 °C and the working volume was 3.5 L.

Benchmark simulations can be seen in Figure 4 in red, covering biogas productivity (top) and total VFA concentrations (bottom). Although the trend in total VFA concentrations is well captured by the BioModel, the total amounts are higher than the experimentally measured values. This is inversely true for the biogas productivity

simulation, where the curve in the second half of Period 2 and in Period 3 and 4 falls below the zone where experimental points are found. A clear improvement is achieved in biogas productivity simulation using the general set of optimized parameters (curves in green), as the curve becomes higher, fitting experimental data quite well in Period 2 and 3 and almost reaching experimental levels in Period 4. This is achieved by increasing the simulated total VFA concentration slightly, which decreases simulation accuracy somewhat further in Period 3 and 4. However, it also provides a better description of the elevated total VFA concentration in the first half of Period 2 and keeps the overall trend marked by experimental points.

3.3.2 Validation case study 2 (V2)

A complex experiment published by Fitamo et al. (2016a, 2016b) served as source material for the second validation case study, where the authors were co-digesting mixed wastewater sludge (MS) with different urban organic wastes (UOW), such as food waste, grass clippings and garden waste (Supplementary material, Table SIX). Although the experiment involved two reactors, only the first one was considered in present study. According to the description of the process, five feeding periods were defined during the experiment, where the first covered only MS digestion and UOW were added from Period 2. Between Period 2 and 5, the volatile solid-based mixture of the four substrates was kept constant, meaning an approximately 10:68:15:7 mixing ratio for mixed sludge, food waste, grass clippings and garden waste, respectively. The distribution of feeding periods is as follows. Period 1 (day 0-75): MS digestion with an HRT of 30 days. Period 2 (day 76-130): MS and UOW, HRT of 30 days. Period 3 (day 131-164): MS and UOW, HRT of 20 days. Period 4 (day 165-203): MS and UOW,

HRT of 15 days. Period 5 (day 204-230): MS and UOW, HRT of 10 days. The reactor working volume was 3 L and operation temperature was 55 °C.

Results of the simulation carried out by Fitamo et al., with default parameters (Figure 5, curves in blue) indicate that biogas productivity (top) was captured very well, along with total ammonia concentrations (bottom) outside Period 2. The total VFA simulation (middle), however, showed higher levels than seen during the experiment. By running simulations with the general set of optimized parameters (Figure 5, curves in green), significant improvements were achieved in fitting experimental data. Moreover, the simulation of total ammonia concentrations was now highly accurate, including that of Period 2, while the biogas productivity did not change considerably. Interestingly, simulated total VFA concentrations were lowered, to about half of what was simulated by Fitamo et al., providing a more accurate fit of experimental data. The simulated peak in Period 2 is most probably the result of starting the addition of UOW, where food waste contained high amounts of soluble lipids and carbohydrates. In contrast, low experimental values might indicate a microorganic community already well adapted to such concentrations.

3.3.3 Validation case study 3 (V3)

For the simulation of the third validation case study, lipid hydrolysis with first-order kinetics was included as a structural part of the BioModel and it was set up assuming inert and soluble fractions as described in Miron et al. (2000). Information about substrates and process decisions used during the case study were collected from Fezzani and Cheikh (2008, 2007), who described the co-digestion of olive mill wastewater and olive mill solid waste at different HRTs and influent concentrations (Supplementary material, Table SX). The selected experiment used an influent total Chemical Oxygen

Demand (TCOD) of 80 g-COD L^{-1} and was divided into three periods. Period 1 (day 0-70): mixed feed with an HRT of 36 days. Period 2 (day 71-120): mixed feed with an HRT of 24 days. Period 3 (day 121-150): mixed feed with an HRT of 12 days. The reactor, despite being a tubular type, was completely mixed and had a working volume of 18 L. Operation temperature was 37 °C.

The response of the model with the original set of parameters is shown in Figure 6 in red. For operation Period 1 and 2, qualitatively the model prediction was good. However, the model was not able to forecast the third period at which a rapid decrease in biogas productivity and accumulation of VFA were observed. Another important aspect to point out is the sharp maximum in biogas productivity that the model predicts in Period 1 (between days 1-5), which happens early, yet is well in line with the experimental trend. Using the general set of optimized parameters and together with a slight increase in biogas productivity in Period 1 and 2 (Figure 6, top), a favorable increase in total VFA concentrations was experienced, visible principally in Period 3 (Figure 6, bottom).

When compared to the performance of ADM1 as seen in Figure 6, the BioModel performed better for the simulation of the initial increase in biogas production, however, it was not able to simulate the rapid decline in biogas productivity (Figure 6, top) and the proportional increase in total VFA concentrations (Figure 6, bottom) seen in the last feeding period. This is most likely because the BioModel does not include a VFA inhibition term effective on the growth of methanogenic microorganic groups, while these inhibitory kinetics were added to the ADM1 by Fezzani and Cheikh. Another way to decrease biogas productivity forecasted by the BioModel would have been the reduction of the ammonia inhibition term K_{i,NH_3} (whose value was 0.259 before and

373 became 0.275 after optimization), which takes effect on acetoclastic methanogens.
374 Being the overall most sensitive parameter among the 13 parameters identified in Step 2
375 of the methodology, this would have improved the fit in Period 3. Nevertheless, this
376 adjustment would not be feasible, as the authors have stated that ammonia concentration
377 was kept constant, at a low concentration of around 1.3 g-N L^{-1}, throughout the whole
378 experiment (Fezzani and Cheikh, 2008). Assuming, however, that the rapid decline in
379 biogas productivity was due to the inhibition of acetoclastic methanogenic groups by
380 the accumulation of phenolic compounds (Borja et al., 1997) justifies the performance
381 of the BioModel, as this factor is not accounted for in the model and thus could not
382 decrease the productivity in Period 3.

383 **3.4 Evaluation**

384 The evaluation of above three validation case studies showed that by restricting
385 future parameter estimations to the 13 sensitive parameters shown, significant
386 improvements can be expected in simulation results. Further to the above, results of the
387 present study indicate that in order to improve BioModel simulations, especially for
388 wastewater-based co-digestion, process inhibition dynamics should be redesigned,
389 considering certain effects that are currently missing in the microorganic growth
390 equations. This will form part of subsequent studies carried out by the authors.

391 As a general comment and regarding the data accuracy of the three case studies,
392 findings of present study and earlier work of Zielesny (2016) indicate that the inclusion
393 of experimental measurement errors in objective function calculations might be
394 favorable. Using such information, weighing the importance of experimental data points
395 would become possible, in order to discount for the effect of outliers and improve the
396 optimization system to be solved.

4 Conclusions

The aim of present work was to develop a parameter estimation methodology, for the improvement of anaerobic digestion modelling. By identifying the sensitive parameters of a complex bioconversion model (BioModel) and estimating their optimal values, it was found that the model was able to simulate the most relevant process variables with improved accuracy. Although the microbial growth expressions in the BioModel need further improvement for accurately describing certain inhibition phenomena, using the optimized parameter set was proven to expand its applicability for simulating both manure- and wastewater-based co-digestion cases, at either mesophilic or thermophilic conditions.

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Conflict of Interest

The authors claim no conflict of interest concerning any part of the work presented here.

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Tables

Table I. A comparison of objective function values throughout the two estimation case studies

Experimental case	**Objective function value using**		**Improvement**
	reference parameters	estimated parameters	
C1	0.498	0.356	28.5 %
C2	461.289	80.950	82.5 %

536 **Table II**. Parameter sets defined for the two estimation case scenarios and the generally applicable case, considering the minimum and

537 maximum values taken by the SA method and the calculated average values [a]

Parameter category	Parameter	Initial value	Values taken in C1			Values taken in C2			General case (C*)		
			Min	Max	Avg	Min	Max	Avg	Min	Max	Avg
Hydrolysis yield coefficients	$Hydr_{carb,in}$	**0.500**	0.128	0.328	0.213	0.303	0.432	0.382	0.128	0.432	**0.298**
	$Hydr_{prot,in}$	**0.200**	0.202	0.295	0.256	0.152	0.309	0.228	0.152	0.309	**0.242**
Half-saturation constants [g L^{-1}]	Ks_{AA}	**3.500**	1.988	2.968	2.481	0.711	3.373	2.175	0.711	3.373	**2.328**
	Ks_{HPr}	**0.259**	0.035	0.179	0.113	0.074	0.204	0.137	0.035	0.204	**0.125**
	Ks_{HVal}	**0.176**	0.015	0.111	0.068	0.110	0.193	0.143	0.015	0.193	**0.106**
	Ks_{HAc}	**0.120**	0.419	0.599	0.527	0.437	0.604	0.546	0.419	0.604	**0.537**
Inhibition constant [g L^{-1}]	$Ki_{NH3,HAc}$	**0.259**	0.224	0.310	0.264	0.233	0.330	0.285	0.224	0.330	**0.275**
Higher pH	pKh_{Ac}	**8.5**	8.345	9.643	8.893	8.450	9.248	8.759	8.345	9.643	**8.826**

boundary											
Cell death rates [d^{-1}]	Kd_{AA}	**0.050**	0.089	0.117	0.103	0.025	0.154	0.095	0.025	0.154	**0.099**
	Kd_{HPr}	**0.050**	0.109	0.134	0.119	0.114	0.174	0.144	0.109	0.174	**0.132**
	Kd_{HBut}	**0.050**	0.040	0.069	0.053	0.019	0.111	0.076	0.019	0.111	**0.065**
	Kd_{HVal}	**0.050**	0.027	0.115	0.067	0.057	0.170	0.100	0.027	0.170	**0.084**
	Kd_{HAc}	**0.050**	0.026	0.050	0.041	0.010	0.018	0.013	0.010	0.050	**0.027**

[a] Where *Hydr* are the hydrolysis constants; *carb,in* and *prot,in* indicate inert carbohydrate and protein substrates; Ks_{sub} are the half-saturation constants of substrates; *AA* indicates soluble proteins; *HPr*, *HBut*, *HVal* and *HAc* are propionic, butyric, valeric and acetic acid, respectively; $Ki_{NH3.HAc}$ is the ammonia inhibition constant effective on methanogenic microorganisms; pKh_{Ac} is the upper pH limit where the microorganic growth rates are approximately 50% of the uninhibited rate; Kd_{sub} are the death rates of substrate degrading microorganic cells. Default and suggested parameter values are shown in bold.

Figure legends

Figure 1. Flowsheet representation of the systematic methodology used for analysis.

Figure 2. C1 and C2: Comparison of experimental and simulated biogas productivity, where *BM_ben* indicates the BioModel benchmark simulation and *BM_opt* indicates the BioModel simulation after the parameter estimation with the best objective function. *ADM1* indicates the ADM1 simulation carried out by Schön. Dashed vertical lines represent the boundaries between feeding periods.

Figure 3. PRCC values of the most sensitive parameters in the two calibration case scenarios. Each indicator output variable is represented by a different polygon, and the peaks indicate the effects of respective parameters on the variable, on a scale of -1 to 1. Abbreviations are as in Table II.

Figure 4. V1: Comparison of experimental and simulated biogas productivity (top) and total VFA concentrations (bottom), where *BM_ben* indicates the BioModel benchmark simulation and *BM_opt* indicates the BioModel simulation with optimized parameters. Dashed vertical lines represent the boundaries between feeding periods.

Figure 5. V2: Comparison of experimental and simulated methane productivity (top), total VFA concentrations (middle) and total ammonia concentrations (bottom), where *BM_Fit* indicates the BioModel simulation with default parameters (carried out by Fitamo et al.) and *BM_opt* indicates the BioModel simulation with optimized parameters. Dashed vertical lines represent the boundaries between feeding periods.

Figure 6. V3: Comparison of experimental and simulated biogas productivity (top) and total VFA concentrations (bottom), where *BM_ben* indicates the BioModel benchmark simulation, *BM_opt* indicates the BioModel simulation with optimized parameters and *ADM1* indicates the ADM1 simulation carried out by Fezzani & Cheikh. Dashed vertical lines represent the boundaries between feeding periods.

Figures

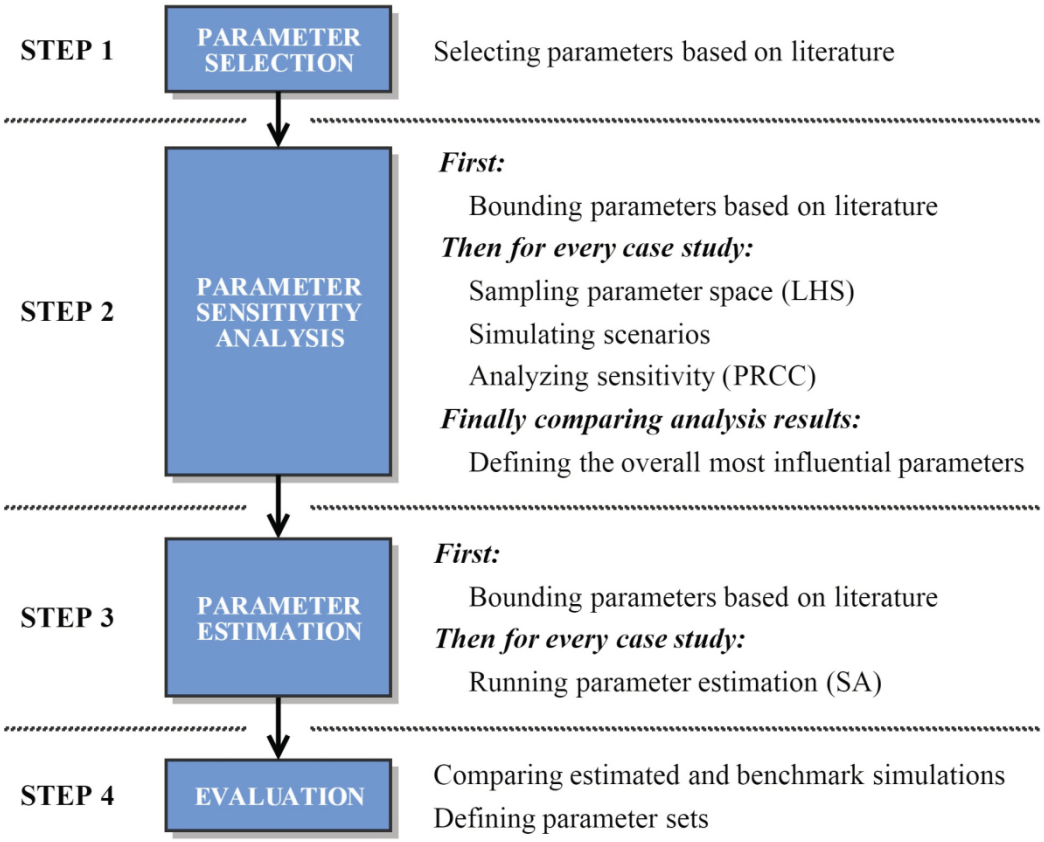
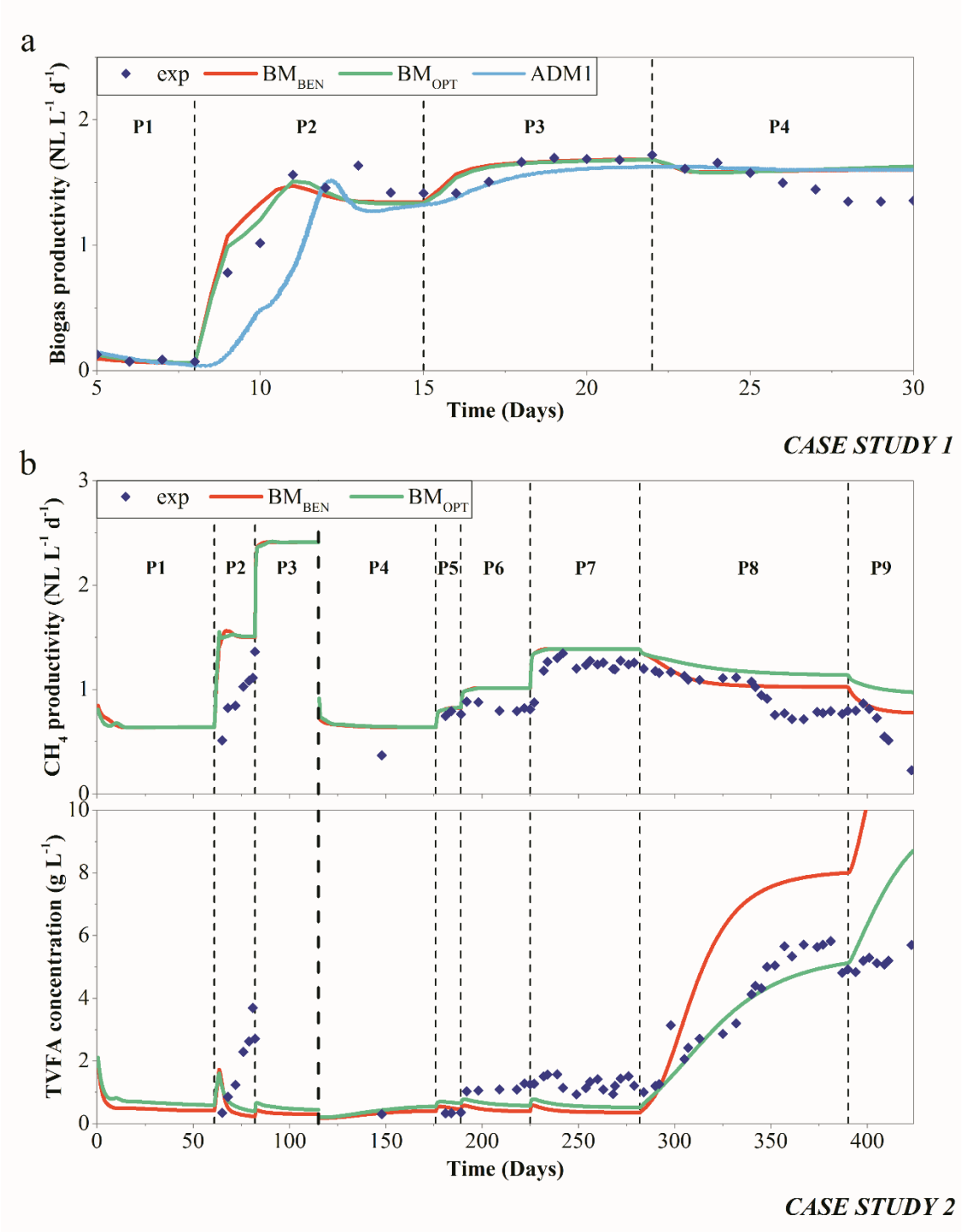


Figure 1



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578 Figure 2

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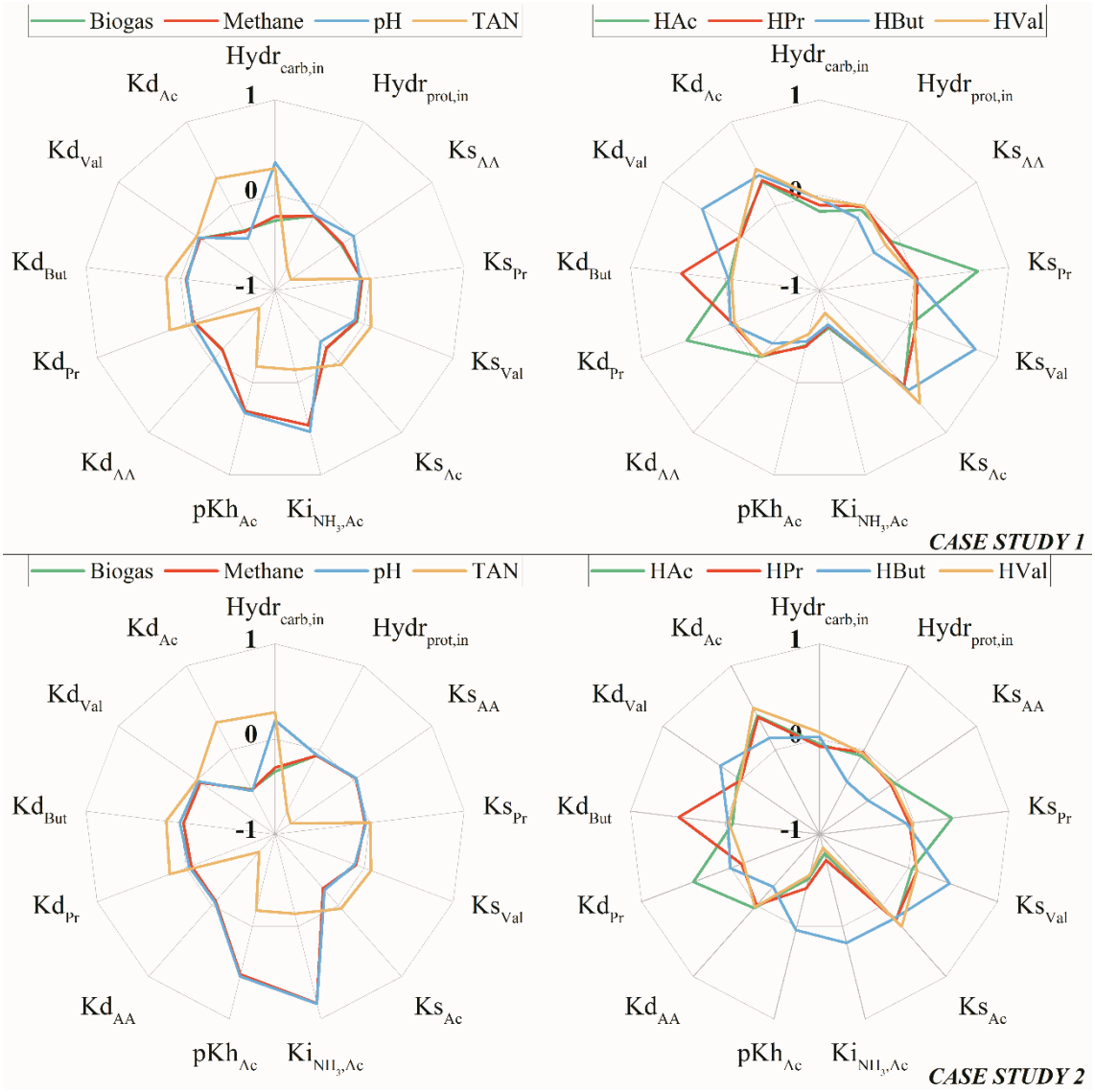

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581 Figure 3

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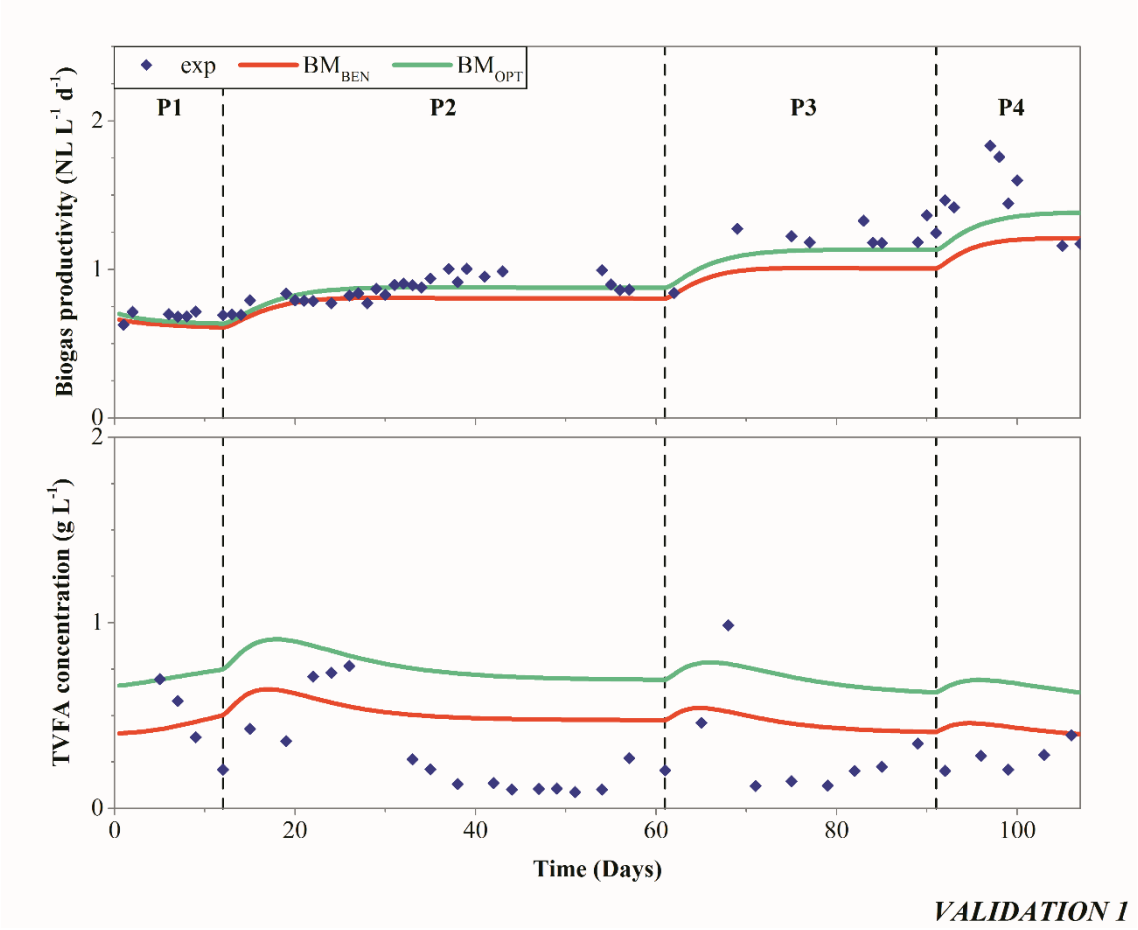

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584 Figure 4

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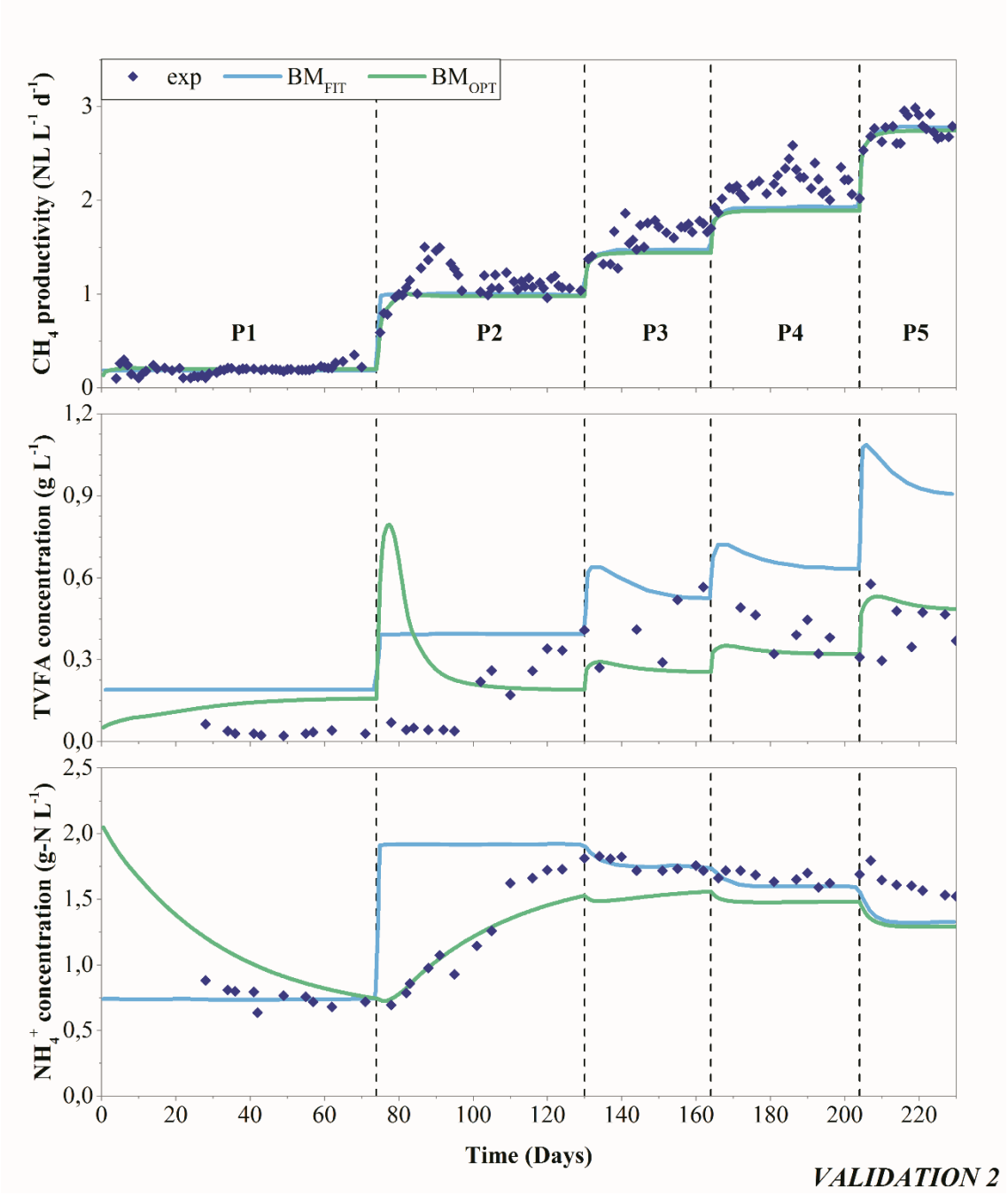

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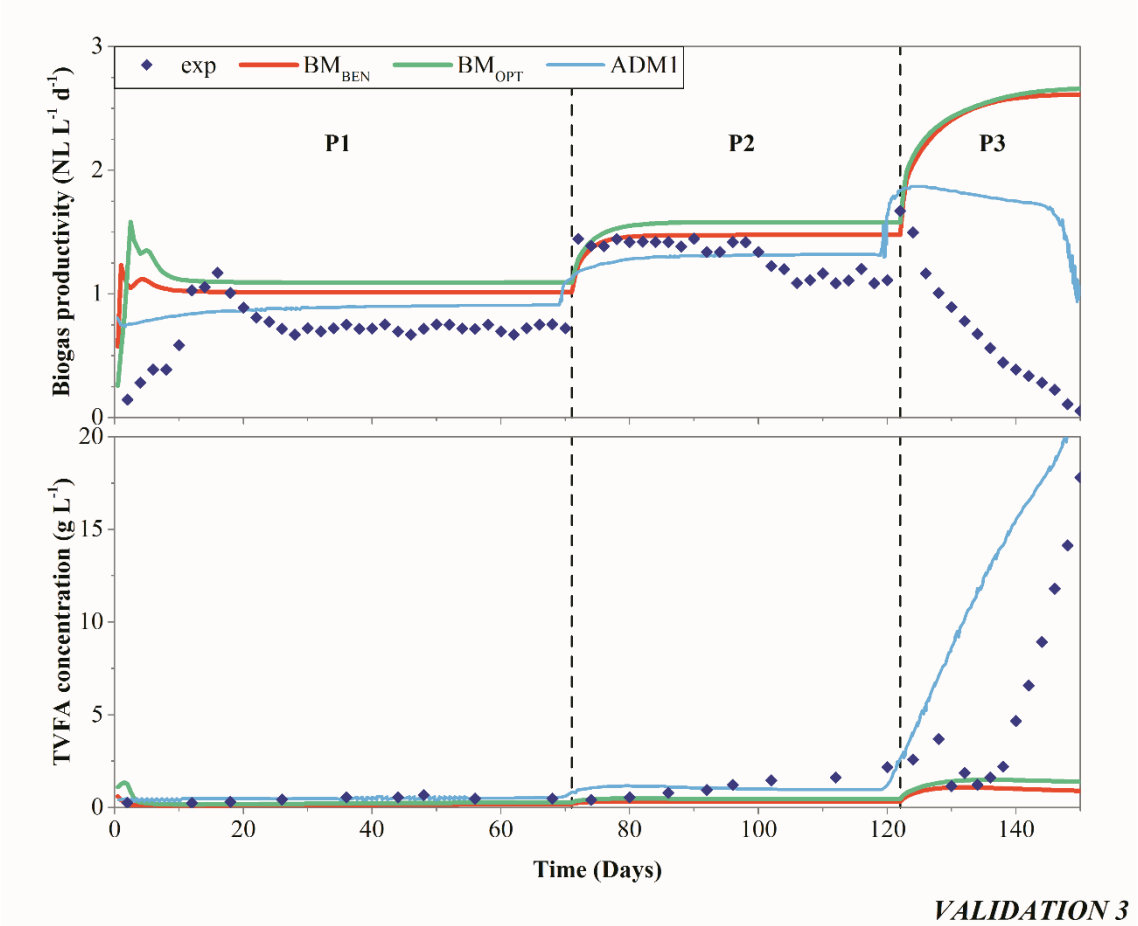
587 Figure 5



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589 Figure 6