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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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1 **A systematic methodology to extend the applicability of a**

2 **bioconversion model for the simulation of various co-digestion**

3 **scenarios**

4

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14

15 **Running title**

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

17

18 **ABSTRACT**

19 Detailed simulation of anaerobic digestion (AD) requires complex mathematical models

20 and the optimization of numerous model parameters. By performing a systematic

21 methodology and identifying parameters with the highest impact on process variables in

22 a well-established AD model, its applicability was extended to various co-digestion

23 scenarios. More specifically, the application of the step-by-step methodology led to the

24 estimation of a general and reduced set of parameters, for the simulation of scenarios

25 where either manure or wastewater were co-digested with different organic substrates.

26 Validation of the general parameter set involved the simulation of laboratory-scale data

27 from three continuous co-digestion experiments, treating mixtures of different organic

28 residues either at thermophilic or mesophilic conditions. Evaluation of the results

29 showed that simulations using the general parameter set fitted experimental data quite

30 well, indicating that it offers a reliable reference point for future simulations of

31 anaerobic co-digestion scenarios.

32 **KEYWORDS**

33 Anaerobic digestion, mathematical modeling, dynamic simulation, organic residue,

34 parameter set.

35 **1 Introduction**

36 Throughout the years, various mathematical models simulating both anaerobic

37 mono- and co-digestion processes have been proposed. From simpler empirical models

38 (Andrews, 1969; Graef and Andrews, 1974; Hill and Barth, 1977; Kleinstreuer and

39 Poweigha, 1982), to more complex ones (Angelidaki et al., 1999, 1993; Batstone et al.,

40   2002b; Costello et al., 1991; Siegrist et al., 1993). All of these models have been used to

41   describe, to a certain extent, the anaerobic digestion of complex substrates.

42   The majority of the complex models are specialized in anaerobic digestion of

43   specific feedstocks such as agricultural energy crops, residues, manures and wastewater

44   sludge. For instance, the Anaerobic Digestion Model No. 1 or ADM1 (Batstone et al.,

45   2002b) has been the most prominent among scientists working in the field of anaerobic

46   wastewater treatment processes and more recently in solid waste bioconversion

47   technologies. Likewise, the model (BioModel) proposed by Angelidaki et al. (1999)

48   gives a good description of manure-based anaerobic digestion systems. The BioModel

49   focuses on ammonia inhibition, which is often relevant in manure-based digestions, and

50   includes a detailed description of pH and temperature, in order to simulate free

51   ammonia concentrations. Compared to the ADM1, which expresses the concentration of

52   solid substrate and product components using the indirect Chemical Oxygen Demand

53   (COD), the BioModel features a more convenient, mass-based unit system. This allows

54   for the characterization of substrates and products using simpler sampling and

55   measurement techniques more appropriate for slurries and solid wastes, than COD.

56   Despite their extensive application, the optimal use of such complex models requires the

57   adjustment or modification of numerous parameters, depending on the type and nature

58   of the simulated case (Donoso-Bravo et al., 2011). General experience shows, however,

59   that the more parameters are contained in a mathematical model, the more difficult it

60   becomes to verify their values for individual cases. Specifically, the large number of

61   reactions and chemical species involved in these models gives a better description of the

62   process, but complicates modeling, and – depending on the system to be "modeled" –

63   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

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The core dynamic model (BioModel) of this work was developed by Angelidaki et

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al. (1999, 1993) and describes the degradation of complex substrates, along with the co-

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digestion of different types of organic wastes. In the BioModel, the substrate is

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described in terms of its basic organic components' composition – carbohydrates, lipids

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and proteins –, the concentration of intermediates such as volatile fatty acids (VFA) and

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long-chain fatty acids (LCFA), and important inorganic components, such as ammonia,

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phosphate, cations and anions. The model was upgraded to include the hydrolysis of

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lipids so that it includes three enzymatic hydrolytic and eight bacterial steps, and

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involves 19 chemical compounds, together with a detailed description of pH and

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temperature characteristics. Free ammonia, VFA and LCFA constitute the primary

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modulating factors. The BioModel was previously calibrated with experimental co-

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digestion scenarios utilizing substrates rich in carbohydrates, proteins and lipids

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(Angelidaki et al., 1999, 1997). For a detailed description of the model, see Table SI in

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the Supplementary material.

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2.2   Computational Methods

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Initially written in Microsoft Pascal, and later translated to the Delphi Pascal

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programming language, the BioModel was recently implemented in MATLAB,

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combined with a Microsoft Excel-based data input and output platform. The MATLAB

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model is able to simulate the AD process in one anaerobic fermenter, considering the

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composition of the inoculum, a primary substrate and up to three optional co-substrates.

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Organization and processing of parameters defining substrates, pump and flow rates,

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metabolic steps and chemical components, as well as the collection of model output

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variables was set up similar to as described by Angelidaki et al. (1999). Integration of

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112   model equations in time and the selection of a suitable time step for calculations also

113   resembled the method outlined in this earlier publication, and for the solution of the

114   model ordinary differential equation system, MATLAB's *ode15s* solver was used.

115   **2.3   Systematic methodology**

116   The four steps describing the systematic methodology are depicted in Figure 1 and

117   are described further in the following subsections. During the analysis, the model

118   structure was kept as taken from the literature (Angelidaki et al., 1999).

119   **2.3.1   Step 1: Parameter selection**

120   In this step, a preliminary selection of the model parameters was performed based

121   on the assessment of available literature (Batstone et al., 2002a; Biernacki et al., 2013;

122   Bułkowska et al., 2015; López and Borzacconi, 2010; Lübken et al., 2007; Nguyen,

123   2014; Ramirez et al., 2009; Rivera-Salvador et al., 2014; Rosén and Jeppsson, 2006).

124   Details of this process are explained in the Supplementary material and the complete list

125   of parameters considered is shown in the Supplementary material, Table SII. As a

126   systematic reduction of the complete model parameter space and based on the

127   comparison of studies, biochemical parameters that showed significant variance and are

128   included in the BioModel were selected for subsequent sensitivity analysis in Step 2.

129   **2.3.2   Step 2: Parameter sensitivity analysis**

130   Following the parameter selection (Step 1), a detailed sensitivity analysis was

131   performed on the selected parameters, in order to evaluate the magnitude of the

132   parameters' individual effect on specific simulation output variables. The output

133   variables chosen were biogas and methane production, VFA and total ammonium

134   nitrogen-TAN concentration, pH, commonly reported as good indicators of the AD

135   process performance (Boe et al., 2010; Labatut and Gooch, 2012). Values of the

136   parameters selected in Step 1 were allowed to vary between lower and upper

137   boundaries, defined based on the literature assessment of Step 1, and sampling of the

138   available parameter space was performed with the Latin Hypercube Sampling (LHS)

139   method (McKay, 1992; McKay et al., 1979). LHS was an integral part of the analysis,

140   in order to make sure that the parameter values were selected from the whole range

141   available, avoiding bias and maintaining statistical accuracy. Concerning the

142   distribution of parameter intervals by the LHS method, uniform parameter distribution

143   was assumed (Manache and Melching, 2007), and the number of parameter sample sets

144   generated by the method was ten times the number of parameters selected for analysis.

145   Following the sampling process, simulations were performed with every set of

146   parameter samples generated previously. The length of the simulated periods

147   corresponded to the periods where experimental data were available. Furthermore, to

148   reduce computational demand, four approximately equidistant time points of each case

149   simulation period were selected and only the output variable values of these time points

150   were used thereafter.

151   Sampling-based Partial Rank Correlation Coefficient (PRCC) method (Marino et

152   al., 2008; Pennington, 2015; Wu et al., 2013; Zi, 2011) was used to perform sensitivity

153   analysis. As the PRCC method does not account for time as an independent variable,

154   PRCC analyses for the previously selected, equidistant time points were conducted

155   separately, in order to produce statistically representative results for complete

156   simulation periods. Further to that, for PRCC results to be considered relevant, their

157   probability values (p-values) were required to be smaller than 0.05 (Jackson and

158   Radunskaya, 2015). For each case study, results of the PRCC analyses for individual

159   time points were combined, providing an aggregate PRCC value over the entire

160 simulated period. Parameters were ranked according to their PRCC values to define the

161 most sensitive parameters with respect to each model output variable specified in Step

162 2. Both LHS and the PRCC analyses were carried out using the MATLAB-based

163 Sampling and Sensitivity Analyses Tool (SaSAT) (Hoare et al., 2008).

164 **2.3.3   Step 3: Parameter estimation**

165 After identification of the most sensitive parameters in Step 2, numerical estimation

166 of their values was performed for both case studies. Variation in parameter values was

167 allowed according to lower and upper parameter boundaries specified in Step 2. The

168 parameters were estimated by minimization of the sum of squares of the differences

169 between predicted and experimental data sets (see Table SIII of the Supplementary

170 material). For the optimization task, the Simulated Annealing (SA) method was used

171 (Ingber, 1996; Kirkpatrick et al., 1983). Implementation of the method was done in

172 MATLAB, using the *simulannealbnd* function. Each case study was simulated with 250

173 iterations (a number used also by López and Borzacconi (2010)), in three consecutive

174 parameter estimation cycles to support the results of the stochastic optimization method

175 statistically. At the last step, SA iteration histories, objective function values and

176 estimated parameter values were collected from all simulations, and were used for

177 comparing the different scenarios on a quantitative and qualitative basis.

178 **2.3.4   Step 4: Validation and evaluation of the results**

179 First, performance criteria simulations – benchmark simulations – with the original

180 model parameter values were compared against simulations using the optimized

181 parameter values identified in Step 3, for both case studies used during parameter

182 estimation. Second, following the unification of optimized parameter values used in

183 case study 1 and 2 – by calculating the mathematical average of the respective

184   parameter values – validation of optimized parameters was performed with the data of

185   three lab-scale CSTR experiments. Finally, conclusions were drawn based on the results

186   of validation.

187   **2.4   Case studies**

188   Below a short overview of the two experimental case studies, which were used

189   during parameter estimation is provided. For further details on simulated substrate and

190   process characteristics, see the Supplementary material, Table SIV and SV.

191   **2.4.1   Case study 1 (C1)**

192   Process data was collected from the doctoral dissertation of Schön (2009). In his

193   work, the author investigated the applicability of ADM1 for the simulation of the AD

194   process of a demonstration biogas plant, and lab-scale reactors fed only with manure.

195   The reactor selected for simulation had a volume of 75 L and was operated at

196   mesophilic conditions (37 °C), with a hydraulic retention time (HRT) of 10 days, in four

197   consecutive periods. Period 1 (day 0-8): no influent feed, operated as batch with only

198   inoculum. Period 2 (day 9-15), Period 3 (day 16-22) and Period 4 (day 23-30) fed solely

199   with manure of varying composition (Supplementary material, Table SIV). Due to the

200   simplicity of the experimental setup and the availability of relevant data such as input

201   manure characteristics, biogas production and pH, this case was selected as the initial

202   case study for analysis.

203   **2.4.2   Case study 2 (C2)**

204   A continuous lab-scale experiment, carried out by Wang et al. (2016) using GTO

205   and ammonia as co-substrates, was used as the second case study. The reactor had a

206   working volume of 1.8 L, its inoculum originated from digestion of a mixture of cattle

207   and pig manure, while cattle manure served as the primary substrate for reactor feeding

208 (Supplementary material, Table SV). Reactor temperature was kept at 54 °C throughout

209 the whole experiment. Feeding took place with an HRT of 15 days, throughout the

210 experiment. The experiment was divided into two main phases; in the first phase,

211 manure feed was mixed with rapidly increasing concentrations of GTO, raising the

212 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

213 ended with the collapse of the reactor. Following re-inoculation, the reactor in the

214 second phase was fed with manure and a gradually increasing concentration of GTO,

215 reaching from 3.2 to 4 g-VS $L^{-1}d^{-1}$ added organic material in 91 days, after which OLR

216 was kept stable. Meanwhile, ammonia addition in this last period increased from 2.1 to

217 5 g-N L^{-1}, during the course of 157 days. Thus for the simulation, 9 feeding periods

218 were defined, based on data provided by Wang et al. (not shown).

3   Results and Discussion

220   Base case simulations for the two case studies (C1 and C2) were generated with the

221 original BioModel parameters. The response of the model in terms of biogas or methane

222 productivities, and total VFA concentrations (where applicable) is shown in Figure 2a

223 (C1) and Figure 2b (C2), and are discussed in the following sections. pH simulations

224 were included in the Supplementary material (Figure S1 and S2).

225   Following the steps outlined in the systematic methodology, 44 parameters were

226 initially selected in Step 1 for sensitivity analysis, with lower and upper boundaries

227 defined based on the smallest and largest values reported for anaerobic digestion of

228 complex substrates. The list of initially selected parameters, along with their lower and

229 upper limits, can be found in the Supplementary material, Table SVI. In Step 2, the

230 most sensitive parameters were identified for the individual estimation case studies

231 (average PRCC values shown in Table SVII of the Supplementary material). Out of 44

232   initial parameters tested, model output variables were found to be sensitive to mainly 13

233   specific parameters. These 13 parameters included: $Hydr_{carb,in}$, $Hydr_{prot,in}$, Ks_{AA}, Ks_{HPr},

234   Ks_{HVal}, Ks_{HAc}, $Ki_{NH3,HAc}$, pKh_{Ac}, Kd_{AA}, Kd_{HPr}, Kd_{HBut}, Kd_{HVal} and Kd_{HAc}. These

235   parameters and their quantified effect (PRCC values) on the output variables are shown

236   in Figure 3. As seen from the graphs, parameter effects show significant variations

237   depending on the output variables considered, but the trends in PRCC values, and thus

238   the overall parameter effects on the simulated systems appear similar. Once the most

239   sensitive parameters were identified, Step 3 was then executed, the results of which are

240   discussed in the next sections, for each case study respectively.

241   **3.1   Case study 1 (C1)**

242   In the first benchmark simulation, the response of the model with the original set of

243   parameters is shown in red color in Figure 2a. As observed, model response fitted well

244   the trend exhibited by experimental data, particularly in Periods 1, 2 and 3 at which

245   biogas production increased – due to an increase in the organic loading rate – and then

246   stabilized at a new steady state level. In contrast with the trend exhibited by the

247   experimental data during Period 4, where biogas production is shown to decrease

248   throughout the whole period, the model predicted a slight decrease at the beginning and

249   subsequently reached a new steady state level. This discrepancy is explained by the fact

250   that during this operational period experimental values were not recorded properly as

251   pointed out by the authors. Figure 2a shows in green color the response of the model

252   when the set of optimized parameters (see Table II) was used. Although qualitative

253   improvement is difficult to assess, improvements in the fitting were obtained. This was

254   further confirmed by the value of the objective function, which was reduced from 0.498

255   to 0.356 representing a 28.5% improvement in the model response (Table I).

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256   Meanwhile, the quality of the pH simulation was unchanged and remained highly

257   accurate (see Figure S1 in Supplementary material). Compared to the ADM1 simulation

258   that is shown in Figure 2a in blue color, both the benchmark and optimized simulations

259   fit experimental data with high accuracy, especially in Period 2, where a rapid increase

260   in biogas productivity is observed. This indicates that the BioModel appeared to

261   produce more accurate simulations for anaerobic manure digestion than the ADM1.

262   **3.2   Case study 2 (C2)**

263   In the second benchmark simulation, the response of the model with the original set of

264   parameters is shown in Figure 2b in red color. First, two operational periods can be

265   observed with a considerable degree of uncertainty. Operational Period 2 between days

266   50 and 80, where simulated methane productivity increased more rapidly compared to

267   the experimental trend, while the simulated total VFA concentrations only reached

268   about half of the experimental values. Periods 8 and 9 (between day 300 and 420), on

269   the other hand, showed an opposite trend, with a significant delay in the decrease of

270   methane productivity and an overestimation in total VFA concentration simulated. The

271   value of the objective function for the benchmark simulation was found to be 461.289

272   (see Table I). Figure 2b shows in green the response of the model when the set of

273   optimized parameters (see Table II) were used. As observed, by using the optimized

274   parameters a significant improvement (82.5%) was obtained in the objective function

275   value (see Table I), which is well represented by the satisfactory fit of the total VFA

276   experimental data – particularly between days 300 and 420 (see Figure 2b, bottom in

277   green).

278 **3.3 Parameter set validation**

279   As a result of the parameter optimization process carried out using the two

280 aforementioned case studies, a general set of estimated parameters was compiled (see

281 Table II), with parameter boundaries defined based on the lowest and highest optimized

282 parameter values used by the SA algorithm. For validating the above, generally

283 applicable set of parameters, three case studies are described below. They were selected

284 from a wide range of experiments, and covered manure co-digestion with

285 carbohydrates, manure co-digestion with complex substrates and wastewater co-

286 digestion with complex substrates.

287 **3.3.1 Validation case study 1 (V1)**

288   Experimental material for the first validation case scenario was taken from

289 Søndergaard et al. (2015), who investigated the effect of meadow grass on biogas

290 productivity, when added to manure and co-digested in CSTR-type reactors

291 (Supplementary material, Table SVIII). By gradually increasing the concentration of

292 meadow grass in the reactor, while using the same manure substrate, the experiment had

293 four distinct feeding periods. Period 1 (day 0-12): manure feed without additional

294 meadow grass. Period 2 (day 13-61): manure feed with 12 g L^{-1} meadow grass. Period 3

295 (day 62-91): manure feed with 23 g L^{-1} meadow grass. Period 4 (day 92-107): manure

296 feed with 34 g L^{-1} meadow grass. Operation temperature was 54 °C and the working

297 volume was 3.5 L.

298   Benchmark simulations can be seen in Figure 4 in red, covering biogas productivity

299 (top) and total VFA concentrations (bottom). Although the trend in total VFA

300 concentrations is well captured by the BioModel, the total amounts are higher than the

301 experimentally measured values. This is inversely true for the biogas productivity

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302   simulation, where the curve in the second half of Period 2 and in Period 3 and 4 falls

303   below the zone where experimental points are found. A clear improvement is achieved

304   in biogas productivity simulation using the general set of optimized parameters (curves

305   in green), as the curve becomes higher, fitting experimental data quite well in Period 2

306   and 3 and almost reaching experimental levels in Period 4. This is achieved by

307   increasing the simulated total VFA concentration slightly, which decreases simulation

308   accuracy somewhat further in Period 3 and 4. However, it also provides a better

309   description of the elevated total VFA concentration in the first half of Period 2 and

310   keeps the overall trend marked by experimental points.

311   **3.3.2   Validation case study 2 (V2)**

312   A complex experiment published by Fitamo et al. (2016a, 2016b) served as source

313   material for the second validation case study, where the authors were co-digesting

314   mixed wastewater sludge (MS) with different urban organic wastes (UOW), such as

315   food waste, grass clippings and garden waste (Supplementary material, Table SIX).

316   Although the experiment involved two reactors, only the first one was considered in

317   present study. According to the description of the process, five feeding periods were

318   defined during the experiment, where the first covered only MS digestion and UOW

319   were added from Period 2. Between Period 2 and 5, the volatile solid-based mixture of

320   the four substrates was kept constant, meaning an approximately 10:68:15:7 mixing

321   ratio for mixed sludge, food waste, grass clippings and garden waste, respectively. The

322   distribution of feeding periods is as follows. Period 1 (day 0-75): MS digestion with an

323   HRT of 30 days. Period 2 (day 76-130): MS and UOW, HRT of 30 days. Period 3 (day

324   131-164): MS and UOW, HRT of 20 days. Period 4 (day 165-203): MS and UOW,

325 HRT of 15 days. Period 5 (day 204-230): MS and UOW, HRT of 10 days. The reactor

326 working volume was 3 L and operation temperature was 55 °C.

327   Results of the simulation carried out by Fitamo et al., with default parameters

328 (Figure 5, curves in blue) indicate that biogas productivity (top) was captured very well,

329 along with total ammonia concentrations (bottom) outside Period 2. The total VFA

330 simulation (middle), however, showed higher levels than seen during the experiment.

331 By running simulations with the general set of optimized parameters (Figure 5, curves

332 in green), significant improvements were achieved in fitting experimental data.

333 Moreover, the simulation of total ammonia concentrations was now highly accurate,

334 including that of Period 2, while the biogas productivity did not change considerably.

335 Interestingly, simulated total VFA concentrations were lowered, to about half of what

336 was simulated by Fitamo et al., providing a more accurate fit of experimental data. The

337 simulated peak in Period 2 is most probably the result of starting the addition of UOW,

338 where food waste contained high amounts of soluble lipids and carbohydrates. In

339 contrast, low experimental values might indicate a microorganic community already

340 well adapted to such concentrations.

341 **3.3.3   Validation case study 3 (V3)**

342   For the simulation of the third validation case study, lipid hydrolysis with first-order

343 kinetics was included as a structural part of the BioModel and it was set up assuming

344 inert and soluble fractions as described in Miron et al. (2000). Information about

345 substrates and process decisions used during the case study were collected from Fezzani

346 and Cheikh (2008, 2007), who described the co-digestion of olive mill wastewater and

347 olive mill solid waste at different HRTs and influent concentrations (Supplementary

348 material, Table SX). The selected experiment used an influent total Chemical Oxygen

349 Demand (TCOD) of 80 g-COD L^{-1} and was divided into three periods. Period 1 (day 0-

350 70): mixed feed with an HRT of 36 days. Period 2 (day 71-120): mixed feed with an

351 HRT of 24 days. Period 3 (day 121-150): mixed feed with an HRT of 12 days. The

352 reactor, despite being a tubular type, was completely mixed and had a working volume

353 of 18 L. Operation temperature was 37 °C.

354   The response of the model with the original set of parameters is shown in Figure 6

355 in red. For operation Period 1 and 2, qualitatively the model prediction was good.

356 However, the model was not able to forecast the third period at which a rapid decrease

357 in biogas productivity and accumulation of VFA were observed. Another important

358 aspect to point out is the sharp maximum in biogas productivity that the model predicts

359 in Period 1 (between days 1-5), which happens early, yet is well in line with the

360 experimental trend. Using the general set of optimized parameters and together with a

361 slight increase in biogas productivity in Period 1 and 2 (Figure 6, top), a favorable

362 increase in total VFA concentrations was experienced, visible principally in Period 3

363 (Figure 6, bottom).

364   When compared to the performance of ADM1 as seen in Figure 6, the BioModel

365 performed better for the simulation of the initial increase in biogas production, however,

366 it was not able to simulate the rapid decline in biogas productivity (Figure 6, top) and

367 the proportional increase in total VFA concentrations (Figure 6, bottom) seen in the last

368 feeding period. This is most likely because the BioModel does not include a VFA

369 inhibition term effective on the growth of methanogenic microorganic groups, while

370 these inhibitory kinetics were added to the ADM1 by Fezzani and Cheikh. Another way

371 to decrease biogas productivity forecasted by the BioModel would have been the

372 reduction of the ammonia inhibition term K_{i,NH_3} (whose value was 0.259 before and

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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.

Conflict of Interest

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

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533   **Tables**

534   **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 %

535

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**

538

539 [a] Where *Hydr* are the hydrolysis constants; *carb,in* and *prot,in* indicate inert carbohydrate and protein substrates; Ks_{sub} are the half-

540 saturation constants of substrates; *AA* indicates soluble proteins; *HPr*, *HBut*, *HVal* and *HAc* are propionic, butyric, valeric and acetic acid,

541 respectively; $Ki_{NH3.HAc}$ is the ammonia inhibition constant effective on methanogenic microorganisms; pKh_{Ac} is the upper pH limit where

542 the microorganic growth rates are approximately 50% of the uninhibited rate; Kd_{sub} are the death rates of substrate degrading microorganic

543 cells. Default and suggested parameter values are shown in bold.

544   **Figure legends**

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

546   **Figure 2.** C1 and C2: Comparison of experimental and simulated biogas productivity,

547   where *BM_ben* indicates the BioModel benchmark simulation and *BM_opt*

548   indicates the BioModel simulation after the parameter estimation with the

549   best objective function. *ADM1* indicates the ADM1 simulation carried out by

550   Schön. Dashed vertical lines represent the boundaries between feeding

551   periods.

552   **Figure 3.** PRCC values of the most sensitive parameters in the two calibration case

553   scenarios. Each indicator output variable is represented by a different

554   polygon, and the peaks indicate the effects of respective parameters on the

555   variable, on a scale of -1 to 1. Abbreviations are as in Table II.

556   **Figure 4**. V1: Comparison of experimental and simulated biogas productivity (top) and

557   total VFA concentrations (bottom), where *BM_ben* indicates the BioModel

558   benchmark simulation and *BM_opt* indicates the BioModel simulation with

559   optimized parameters. Dashed vertical lines represent the boundaries between

560   feeding periods.

561   **Figure 5**. V2: Comparison of experimental and simulated methane productivity (top),

562   total VFA concentrations (middle) and total ammonia concentrations

563   (bottom), where *BM_Fit* indicates the BioModel simulation with default

564   parameters (carried out by Fitamo et al.) and *BM_opt* indicates the BioModel

565   simulation with optimized parameters. Dashed vertical lines represent the

566   boundaries between feeding periods.

567   **Figure 6.** V3: Comparison of experimental and simulated biogas productivity (top) and

568   total VFA concentrations (bottom), where *BM_ben* indicates the BioModel

569   benchmark simulation, *BM_opt* indicates the BioModel simulation with

570   optimized parameters and *ADM1* indicates the ADM1 simulation carried out

571   by Fezzani & Cheikh. Dashed vertical lines represent the boundaries between
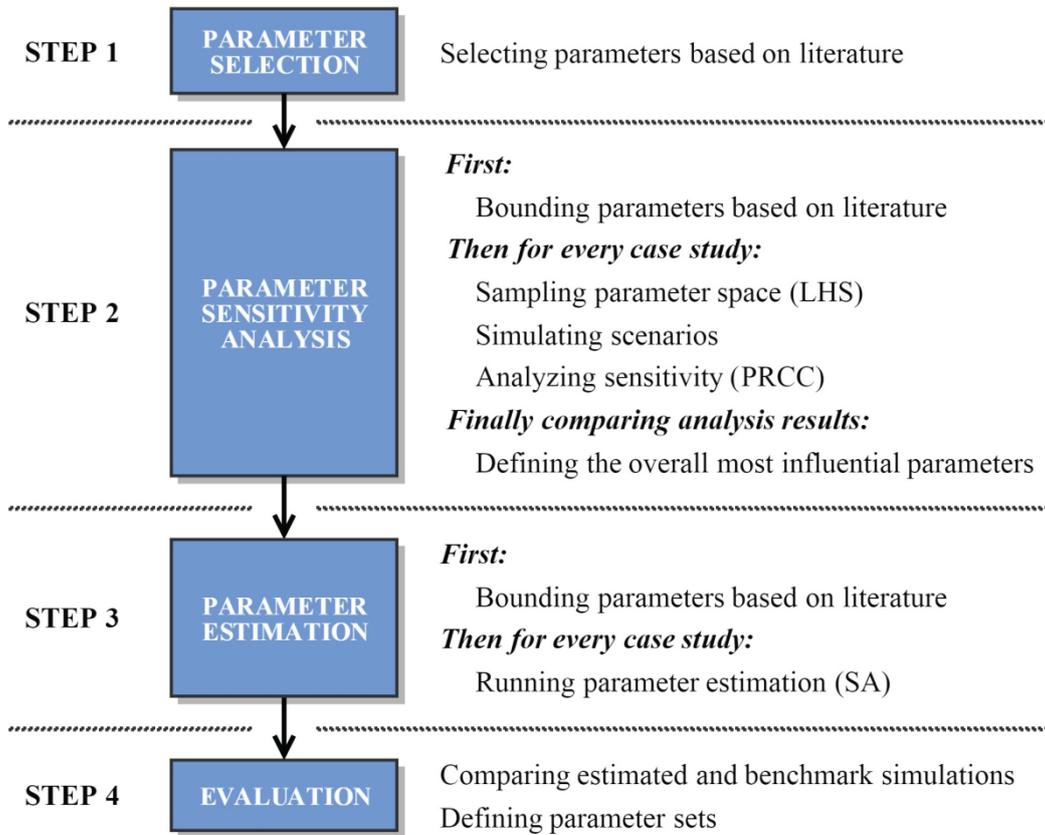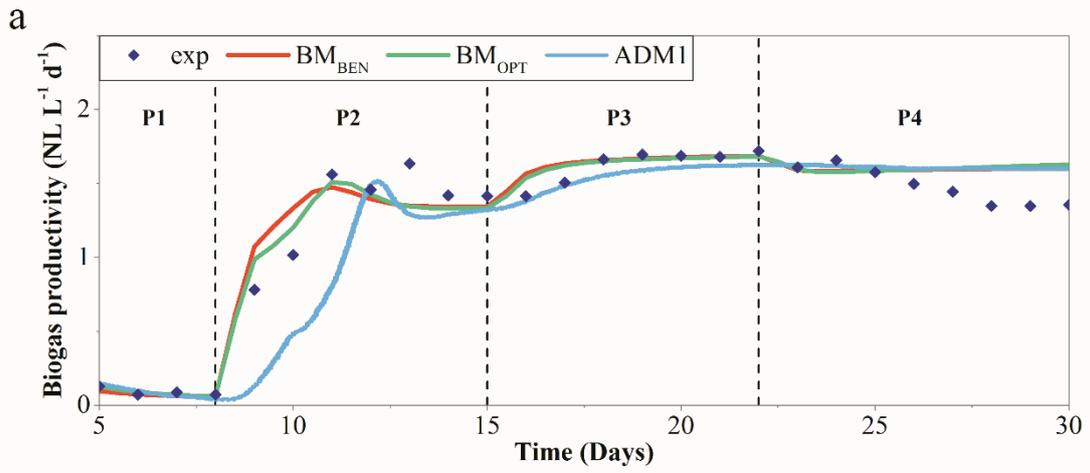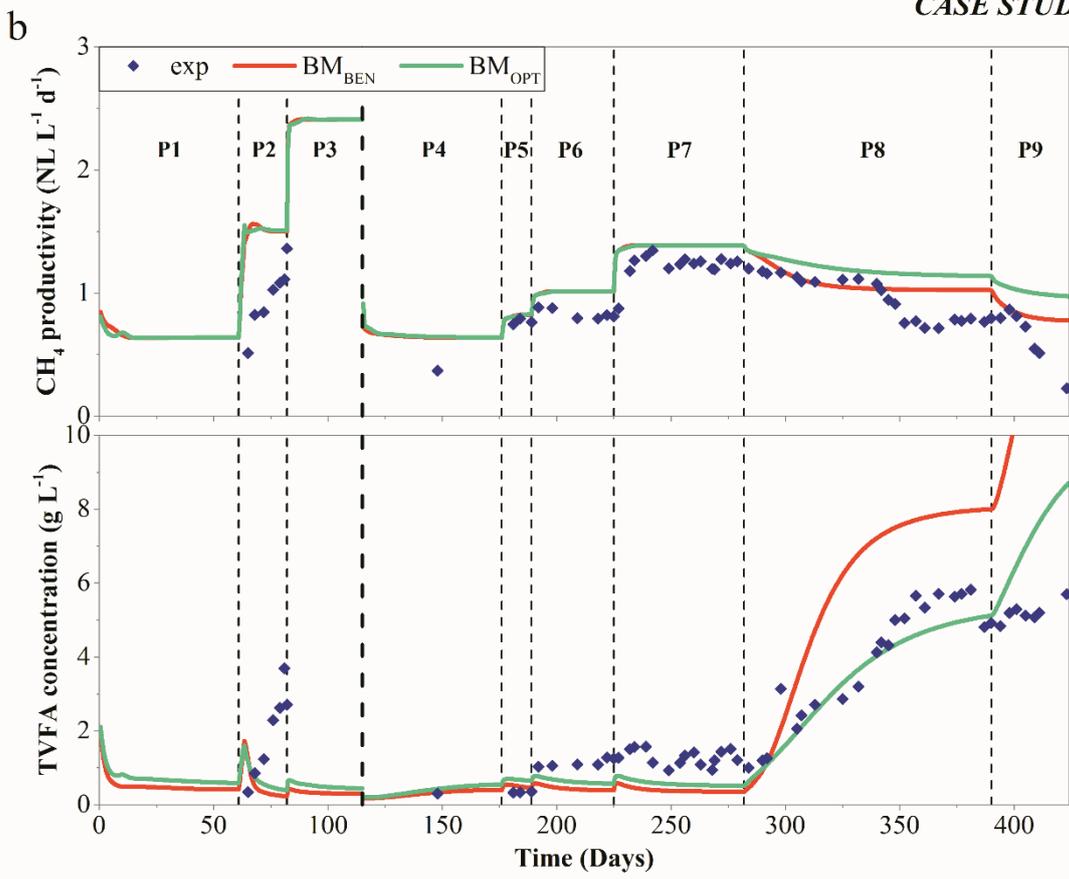
572   feeding periods.

573

Figures

STEP 1	**PARAMETER SELECTION**	Selecting parameters based on literature

STEP 2	**PARAMETER SENSITIVITY ANALYSIS**	*First:*
		  Bounding parameters based on literature
		Then for every case study:
		  Sampling parameter space (LHS)
		  Simulating scenarios
		  Analyzing sensitivity (PRCC)
		Finally comparing analysis results:
		  Defining the overall most influential parameters

STEP 3	**PARAMETER ESTIMATION**	*First:*
		  Bounding parameters based on literature
		Then for every case study:
		  Running parameter estimation (SA)

STEP 4	**EVALUATION**	Comparing estimated and benchmark simulations Defining parameter sets

575

576   Figure 1

CASE STUDY 1
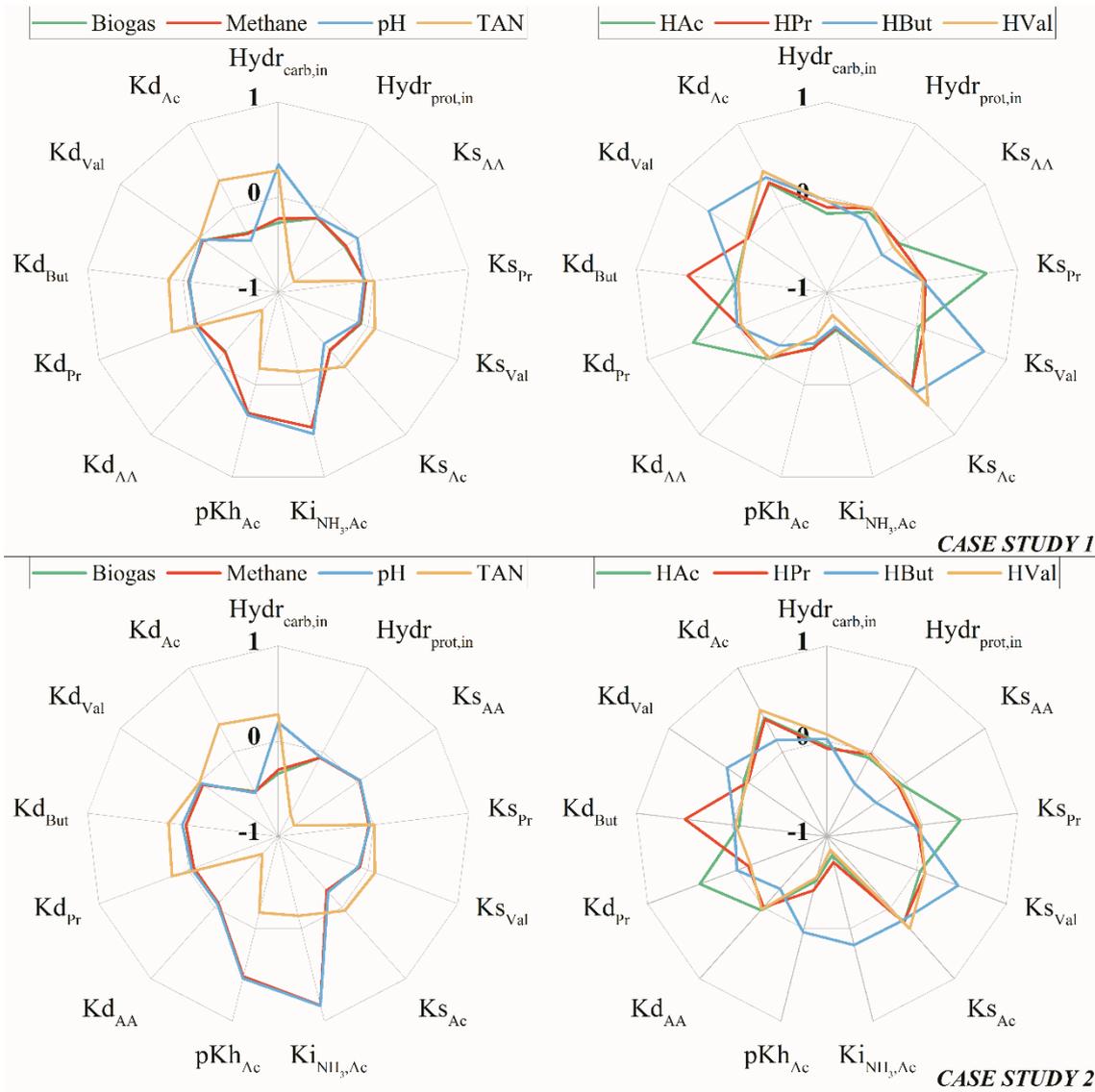
CASE STUDY 2

577

578   Figure 2

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580

581   Figure 3

582

Figure 4

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586   *VALIDATION 2*
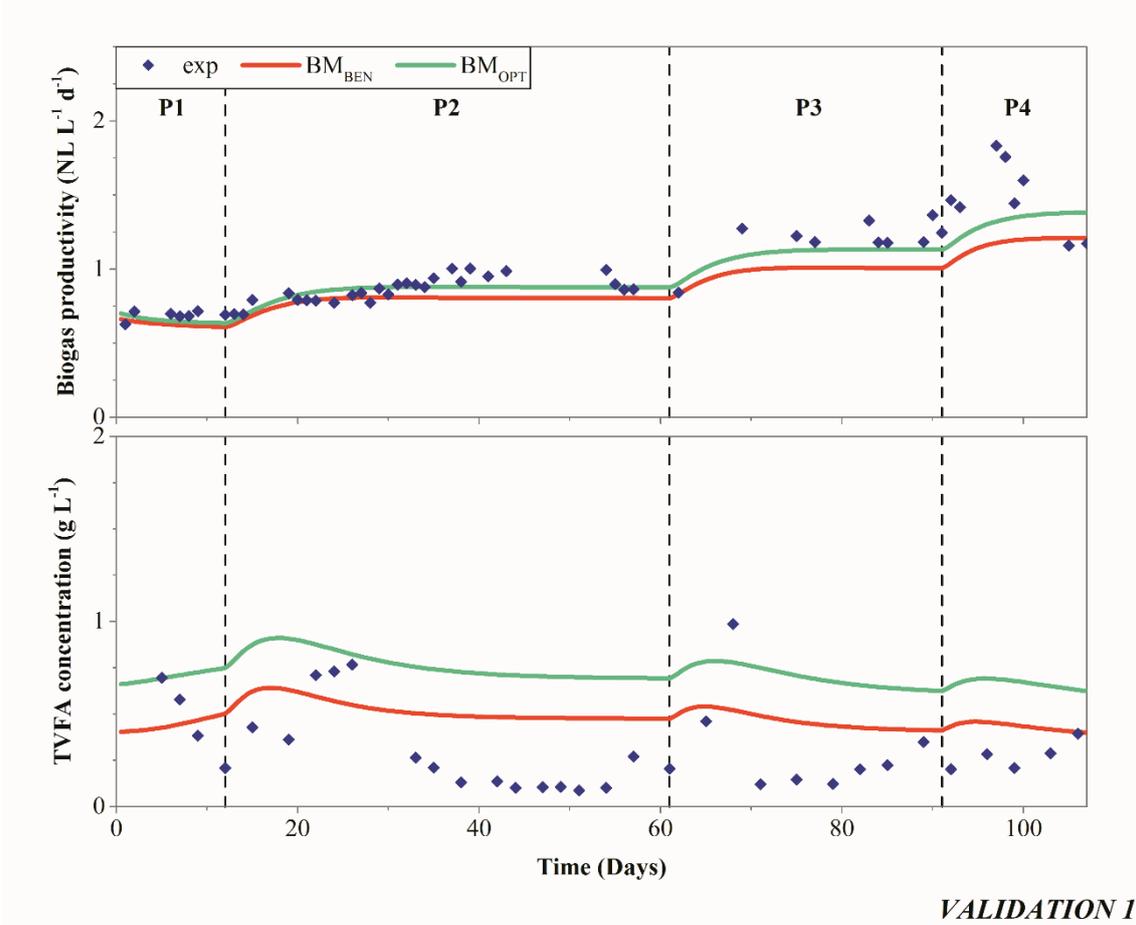
587   Figure 5

34

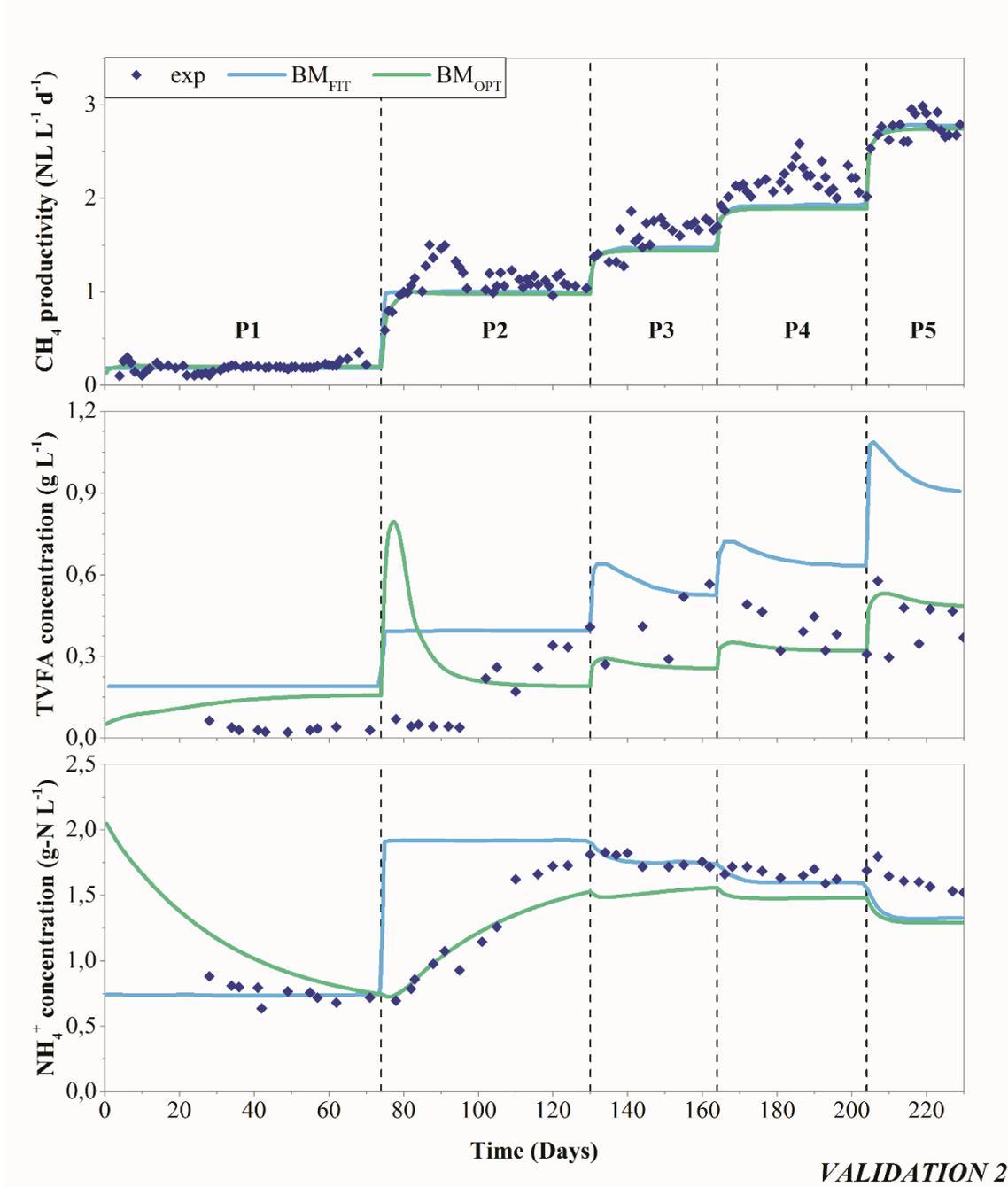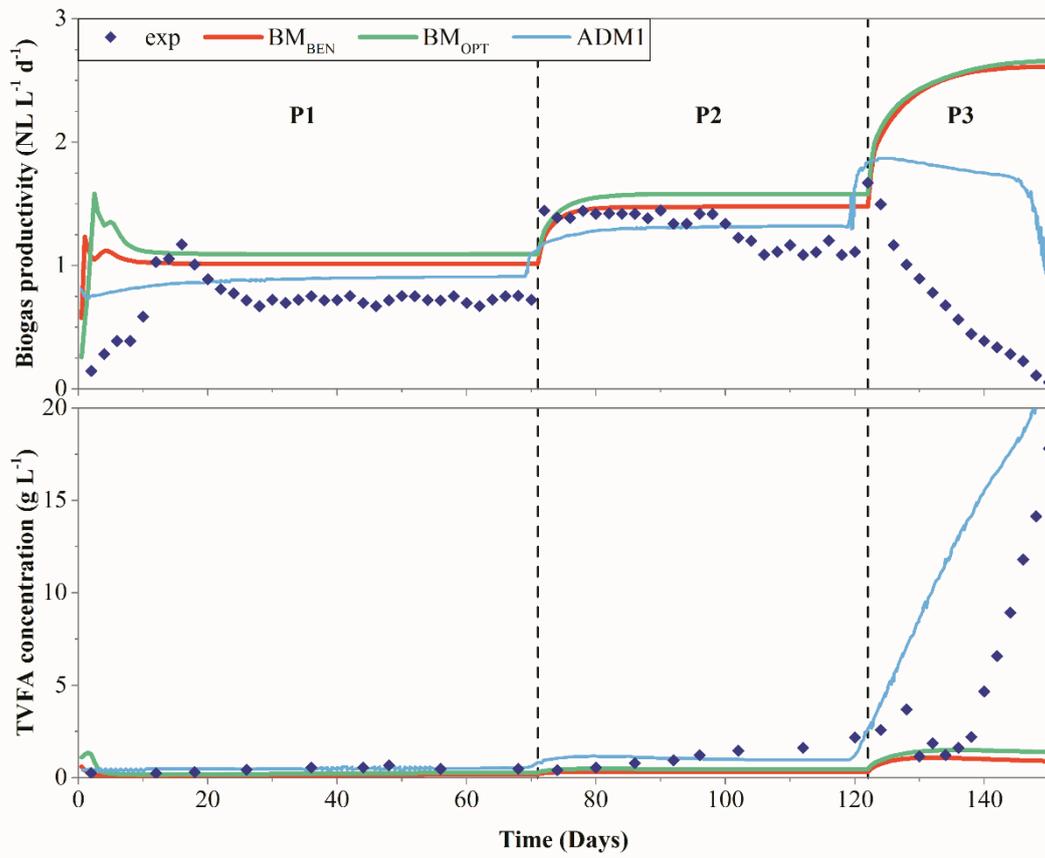*VALIDATION 3*

588

589   Figure 6