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On the derivation of a simple dynamic model of anaerobic digestion including the evolution of hydrogen

In memory of Prof. Gonzalo Ruiz-Filippi

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Abstract

Hydrogen has been found to be an important intermediate during anaerobic digestion (AD) and a key variable for process monitoring as it gives valuable information about the stability of the reactor. However, simple dynamic models describing the evolution of hydrogen are not commonplace. In this work, such a dynamic model is derived using a systematic data driven-approach, which consists of a principal component analysis to deduce the dimension of the minimal reaction subspace explaining the data, followed by an identification of the kinetic parameters in the least-squares sense. **The procedure requires the availability of informative data sets. When the available data does not fulfill this condition, the model can still be built from simulated data, obtained using a detailed model such as**

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ADM1. This dynamic model could be exploited in monitoring and control applications after a re-identification of the parameters using actual process data. As an example, the model is used in the framework of a control strategy, and is also fitted to experimental data from raw industrial wine processing wastewater.

Keywords: Mathematical modeling, parameter estimation, principal component analysis, sensitivity analysis

1. Introduction

Despite its numerous advantages, anaerobic digestion (AD) is still not used at its full potential, due to the high complexity of the process and its dependency on many operational variables. Under some circumstances the stability of the AD process can be endangered, which may deteriorate the efficiency of the waste treatment and the associated biogas production (Chen et al., 2008). Therefore, an important step towards an optimal operation and control is a better understanding of the interplay between the process dynamics and the operational conditions, which may be achieved by means of a reliable model.

One of the most detailed and well-accepted description of the process is provided by the Anaerobic Digestion Model 1 (ADM1) (Batstone et al., 2002), which can be customized for a wide variety of wastes and plant configurations. However, from a control and optimization viewpoint, ADM1, with its 32 state variables, is too complex.

The underlying idea behind the present work is to use informative data and to investigate the derivation of low-order dynamic models to predict

the time evolution of the key variables of interest. The methodology is data-driven in essence as it infers a low-dimensional subspace spanned by the columns of the stoichiometric matrix using a principal component analysis. The first step is therefore to select the measurement signals, which are potential candidates for describing the process behaviour. Once a candidate reaction scheme has been identified, the kinetic parameters can be estimated using a weighted least squares method. In this procedure, the use of virtual data (i.e., synthetic data generated by a detailed process model) allows to explore a large range of operating conditions, possibly wider than feasible in actual practice with a real plant, to ascertain the derivation of the low-order model structure. Of course, real-life experimental data has to be used at a later stage to estimate the parameters of the low-order model in the framework of a specific application.

Several mathematical models describing anaerobic digestion processes have been developed in past years in order to achieve specific goals (Yu et al., 2013). The majority of them are identified from experimental data starting from an imposed model structure. A few others are developed using data-driven techniques, which first analyze the available data and then propose a structure of the model to accommodate the features of the data. Most of the dynamic models are developed for monitoring and control purposes, and to a less extent, for simulation purposes. Among the models which were identified based on experimental data, one can note the work of Bernard et al. (2001), who developed the model of an AD process treating winery wastewater (the so-called AM2 model), the work of Simeonov and Karakashev (2012), who built a model of a pilot plant treating acti-

vated sludge from municipal wastewater treatment plants, and the work of Owmondah et al. (2016), who, aside model identification, investigated the most appropriate structure in terms of number of reactions and kinetics for an AD process treating green and food waste. Models were also developed based on data generated by simulation models such as ADM1. Among the latter, one can highlight the work of Beltramo et al. (2016), who developed an artificial neural network model to predict the biogas flow rate for a two-substrate co-digestion system simulated by ADM1, or the model presented by García-Diéguez et al. (2013), who used principal component analysis to determine the number of reactions and built a model based on data generated by an adjusted ADM1 to simulate winery effluents. Another research direction is the extension of models identified from experimental data to reproduce the dynamics of ADM1. Such works are reported by Ficara et al. (2012), who emphasized that nitrogen has to be included in the model structure introduced by Bernard et al. (2001), and by Hassam et al. (2015), who included the hydrolysis step, along with acidogenesis and methanogenesis, in the model development. Finally, the work of Della Bona et al. (2015) uses a linear fractional transformation to first identify the model parameters from data generated by ADM1 and then from data collected from a lab-scale AD process treating ultra-filtered cheese-whey.

Recently, considerable attention has been paid to the role of hydrogen in anaerobic digestion processes. Indeed, it is an intermediary metabolite present in many reactions, and it is considered a fast indicator of destabilization of the process (Giraldo-Gomez et al., 1992; Ryhiner et al., 1993;

68 Bhattacharya et al., 1995; Björnsson et al., 2001; Boe et al., 2010; Hou et al.,
69 2014; Giovannini et al., 2016). However, some authors have nuanced its
70 potential as a monitoring indicator (Voolapalli and Stuckey, 1999, 2001).
71 In fact, the type of substrates and operational conditions during anaerobic
72 digestion can trigger certain metabolic pathways which are more sensitive
73 to hydrogen production and/or consumption. For example, it has been
74 reported that high-strength wastewater composed mainly of well-defined
75 sugars, such as glucose, sucrose or lactate will produce more hydrogen
76 (Pauss and Guiot, 1993; Hawkes et al., 2002; Yu et al., 2002) compared to
77 particulate substrates (Boe, 2006). In the latter case, VFA measurements are
78 suggested as better indicators of stability. In this study, having in mind this
79 restriction, the focus is on developing a dynamic model of the AD process
80 including hydrogen as a state variable, in order to be able to subsequently
81 develop monitoring and control systems based on this variable (provided
82 it is pertinent). On the other hand, online hydrogen sensors are available at
83 competitive cost (Pauss and Guiot, 1993; Cord-Ruwisch et al., 1997), which
84 makes this kind of strategy practically feasible.

85 The resulting mathematical model, built from informative data gener-
86 ated by simulating ADM1, contains two trophic groups, total organic mat-
87 ter (characterized by COD), organic acids, methane, and hydrogen flow
88 rates, which represent the key variables of the process and can be either
89 measured or estimated. This model is envisioned as a good basis for an ad-
90 vanced (model-based) monitoring and control approach of the process. To
91 date most of the control strategies are based on COD, VFA and/or methane.
92 Only a few hydrogen-based control strategies have been proposed so far,

93 some of them based on empirical principles (Cord-Ruwisch et al., 1997;
94 Rodriguez et al., 2006), others based on dynamic models (Dochain et al.,
95 1991; Ryhiner et al., 1993). In this study, the control strategy proposed
96 by Rodriguez et al. (2006) is exploited to test our dynamic model and its
97 consistency with respect to ADM1. Further, experimental data is used to
98 identify the parameters of the proposed model and to prove its predictive
99 capability.

100 This paper is organized as follows. The next section explains the de-
101 velopment of the dynamic model using informative data sets generated
102 by ADM1. Principal component analysis is used to deduce a macroscopic
103 reaction scheme. Nonlinear least squares is then applied to estimate the
104 kinetic parameters, and parametric sensitivity analysis is carried out to
105 further assess practical parameter identifiability and possibly propose fur-
106 ther simplifications. Measurement noise is also discussed, from the point
107 of view of applications to actual process data, with maximum likelihood
108 principal component analysis and estimation. The numerical results show
109 the predictive capability of the low-dimensional model as compared to the
110 original ADM1. Section 3 exploits the reduced model in the context of a
111 simple hydrogen-based controller initially introduced by Rodriguez et al.
112 (2006). In section 4, the model parameters are estimated based on experi-
113 mental data collected from a $1m^3$ fixed-bed reactor treating industrial wine
114 wastewater, thus demonstrating its predictive capability. Finally, the last
115 section draws some conclusions and perspectives.

2. Model derivation

In this section, synthetic data is generated by simulating ADM1 (Batstone et al., 2002). This data is used to infer a low-dimensional dynamic model involving the main variables of interest, i.e. those with interesting monitoring and control prospects. The next subsection therefore discusses:

- the selection of the model variables and data collection,
- the determination of the minimum number of reactions and pseudo-stoichiometric matrix using principal component analysis,
- kinetic parameter estimation using least-squares identification, and possibly re-estimation of stoichiometric parameters,
- parametric sensitivity analysis for further model simplification, and assessment of the parameter confidence intervals based on the Fisher Information Matrix.

2.1. Model variable selection and data collection

Data has to be informative enough to capture the most important process dynamics. In an actual process study, this step is crucial but can be particularly delicate to conduct as operating a process at optimal conditions is in contradiction with getting information on the several operating ranges where the process operates under abnormal conditions or is even at risk. This is why the use of a reliable, well-accepted, detailed model is appealing. One expects the model to be sufficiently detailed to represent the process in a proper way in several operating ranges, and one is able to generate excitation signals that drive the process in these various ranges.

139 The synthetic database can therefore be made rich enough to draw con-
140 clusion on the significance of a reduced-order model. In contrast, a poor
141 database could lead to oversimplification and models whose predictive
142 capabilities would be drastically limited.

143 2.1.1. Liquid phase variables

144 Microbial populations and substrates described in ADM1 are clustered
145 in a reasonable and congruent manner in order to include tractable infor-
146 mation in the reduced model. Similar clustering has been used by Ficara
147 et al. (2012) and Hassam et al. (2015), who respectively compared the dy-
148 namics of AM2 and ADM1 and built AM2HN, an extension of AM2 which
149 includes also the hydrolysis step, to approximate the ADM1 dynamics:

- 150 • The total organic matter, denoted by S_1 , is the sum of monosaccha-
151 rides, amino acids, long chain fatty acids, composite, carbohydrates,
152 proteins, and lipids:

$$153 \quad S_1 = S_{su} + S_{aa} + S_{fa} + X_c + X_{ch} + X_{pr} + X_{li}$$

- 154 • Organic acids, called S_2 , are the sum of valerate, acetate, butyrate,
155 propionate:

$$156 \quad S_2 = S_{va} + S_{ac} + S_{bu} + S_{pro}$$

- 157 • The seven microbial populations considered in ADM1 are lumped
158 into two main groups, acidogenic microorganisms called X_1 and ace-
159 togens and methanogens called X_2 :

$$160 \quad X_1 = X_{su} + X_{aa} + X_{fa}$$

$$161 \quad X_2 = X_{ac} + X_{H_2} + X_{c4} + X_{pro}$$

For the sake of simplicity endogenous decay of microorganisms is not considered.

2.1.2. Gaseous compounds

Unlike biomass and substrates which are only present in the liquid phase, gaseous compounds, such as methane, hydrogen and carbon dioxide, are produced in the liquid phase and in large part transferred to the gas compartment. It is interesting to have a closer look at the mass balance equations in order to carefully define the transfer terms. As the reduced model is designed for monitoring and control purposes we are interested in following up the variations in hydrogen and methane, while carbon dioxide is not considered.

The mass balance equations of a biochemical system involving M reactions and N components in the liquid phase can be written as:

$$V_L \frac{d\xi_L}{dt} = F_{in}(\xi_{L,in} - \xi_L) + V_L K \varphi(\xi_L) - V_L Q_G(\xi_G) \quad (1)$$

with $\xi_{L,in}$ and $\xi_L \in \mathbb{R}^N$ the inlet concentration and state vector respectively, $K \in \mathbb{R}^{N \times M}$ the stoichiometric matrix, $\varphi(\xi_L) \in \mathbb{R}^M$ the reaction rate vector, F_{in} the inlet flow rate and V_L the liquid volume, $Q_G(\xi_G) \in \mathbb{R}^N$ the gaseous transfer rates.

Mass balance in the gas phase gives:

$$V_G \frac{d\xi_G}{dt} = -q_G \xi_G + V_L Q_G(\xi_G) \quad (2)$$

where q_G is the gas outflow, and V_G the headspace volume.

183 The transfer term between the two phases disappears in the addition
184 of equations (1) and (2) and the following expression is obtained:

$$V_L \frac{d\xi_L}{dt} + V_G \frac{d\xi_G}{dt} = F_{in}(\xi_{L,in} - \xi_L) + V_L K \varphi(\xi_L) - q_G \xi_G \quad (3)$$

185 The left-hand side term corresponds to the variation of total mass of
186 the compounds under consideration:

$$\frac{dm_G}{dt} = V_L \frac{d\xi_L}{dt} + V_G \frac{d\xi_G}{dt} \quad (4)$$

187 Considering that the compounds are only produced in the liquid phase
188 and then transported to the gas phase, equation (3) is divided by the liquid
189 volume to obtain a new auxiliary state variable, which corresponds to the
190 total mass concentration in the liquid phase:

$$\frac{1}{V_L} \frac{dm_G}{dt} = D (\xi_{L,in} - \xi_L - \frac{q_G}{F_{in}} \xi_G) + K \varphi(\xi_L) \quad (5)$$

191 In this expression the term $D (\xi_L + \frac{q_G}{F_{in}} \xi_G)$ corresponds to the total compound
192 outflow either in liquid or gaseous forms. *D denotes the dilution rate,*
193 *defined as the ratio between the inlet flow rate (F_{in}) and the liquid volume*
194 *(V_L).*

195 2.1.3. Synthetic data

196 In this study, informative data is generated *in silico* by simulation of the
197 ADM1 model as a plant emulator. Simulations are performed considering
198 a 1 m³ reactor operating in continuous mode and treating mainly soluble
199 waste matter with 50% biomass retention. *The influent concentrations*
200 *used in the ADM1 model are listed in Table ??.*

Two data sets are built, one for parameter identification, and another one for cross-validation, both run over a period of 120 days and sampling time of 3.6 hours. These time scales are used to capture the slow and fast dynamics. Indeed, analysis of ADM1 shows that the dominant time constant is of the order of a month, whereas fast time constants are in the range of a few hours.

The six candidate state variables of our reduced model, namely X_1 , X_2 , S_1 , S_2 , CH_4 , H_2 , are sampled from ADM1, and for the sake of realism are corrupted with independent, normally-distributed, additive white noises, with standard deviation of 1% of the error-free values for biogases and 5% for the rest of the variables:

$$\xi_i^m = \xi_i + \eta_i \quad (i = 1, \dots, n_s) \quad (6)$$

where, ξ_i^m is the noisy measurement, ξ_i is the noise-free variable and η_i is the additive noise.

Figure ?? shows the two data sets. Cross-validation will be performed to challenge the identified model with fresh data (data that has not been used for parameter identification purposes). The data for cross-validation differs from the data for identification in the initial condition values and the dilution rate evolution.

2.2. Minimum number of reactions and pseudo-stoichiometric matrix estimation

A challenge in deriving a macroscopic model of a biological process is to determine the structure of the mathematical model, which consists of defining the adequate number of biological reactions while keeping the complexity of the model as low as possible (Rodriguez et al., 2008).

224 In this study the minimum number of reactions and pseudo-stoichiometric
225 matrix are obtained using Maximum Likelihood Principal Component
226 Analysis (MLPCA) as described by Mailier et al. (2013).

227 The reaction number is obtained by successive construction of affine
228 linear subspaces of increasing dimensions p (with p ranging from 1 to
229 $M = 6$) that represent at best the noisy data. To formulate the MLPCA
230 problem, the transport terms of the general mass balance equation are
231 lumped into $v(t)$ as follows:

$$\frac{d\xi}{dt} = K\varphi(\xi) + v(t) \quad (7)$$

232 The solution of this equation is given by:

$$\xi(t) - \xi_0 = K \int_0^t \varphi(\xi) + \int_0^t v(t) \quad (8)$$

233 If we define the transport-free concentration $\xi_f(t)$ by:

$$\xi_f(t) = \xi(t) - \int_0^t v(t) \quad (9)$$

234 the solution can then be expressed as:

$$\xi_f(t) = \xi_0 + K \int_0^t \varphi(\xi) \quad (10)$$

235 The transport-free state ξ_f evolves within a linear affine subspace κ
236 defined by the column-subspace (or range) of the yield matrix K , and
237 translated from the origin by the initial state vector ξ_0 . This affine subspace

is independent of the reaction rates and its dimensionality is equal to the reaction number M .

MLPCA can be used to determine this linear affine subspace by solving a maximum likelihood problem of the form

$$\mathcal{J}_p = \sum_{i=1}^{n_s} (\xi_{f,m_i} - \hat{\xi}_{f_i}^p)^T \Sigma_i^{-1} (\xi_{f,m_i} - \hat{\xi}_{f_i}^p) \quad (11)$$

where n_s denotes the number of measured samples, ξ_{f,m_i} is the noisy measurement, $\hat{\xi}_{f_i}^p$ a p -dimensional maximum-likelihood estimate, Σ_i is the error covariance matrix of the noisy measurements. In general terms, the problem can be formulated to estimate the stoichiometric matrix only, or the stoichiometric matrix together with the initial conditions, and is actually solved using singular value decomposition (see (Mailier et al., 2013) for more details on the method and its solution).

The minimum value of the criterion has a chi-square distribution χ^2 with $N \times (n_s - 1)$ degrees of freedom. The reaction number can be selected by progressively increasing the dimensionality p of the candidate stoichiometric subspace, starting from $p = 1$. A value of J_p larger than $\chi_{N \times (n_s - 1)}^{2, (1-\alpha)}$ leads to the rejection of the hypothesis $M = p$ at the significance level α and the next value of p should then be tested (Mailier et al., 2013).

Besides the selection of the minimum number of reactions, MLPCA also allows to obtain information about the pseudo-stoichiometric matrix K , in the form of an orthonormal basis $\rho \in \mathbb{R}^{N \times M}$ of the affine subspace. To find the columns of matrix K , it is then necessary to determine a transformation matrix $G \in \mathbb{R}^{M \times M}$, such that:

$$\hat{K} = \hat{\rho}G \quad (12)$$

The regular matrix $G \in \mathbb{R}^{M \times M}$ can be estimated independently of the reaction kinetics only if sufficient prior knowledge is available. In general, M constraints should be formulated to guarantee this property, which is equivalent to the concept of C-identifiability introduced in (Chen and Bastin, 1996).

Based on the synthetic data collected from ADM1, MLPCA yields the results of Figure ?? for subspace dimensionalities ranging from 1 to 4. The chi-square test shows that a two-reaction scheme ($p = 2$) would be sufficient to represent the given data set, i.e., leads to a log-likelihood cost smaller than any plausible value of a random variable with distribution $\chi_{4806}^{2,(99.9\%)}$. This result is in agreement with the observations of Bernard et al. (2001), who also proposed a two-reaction model (the AM2 model that has been extensively used in the meantime for analysis, estimation and control of AD processes).

MLPCA also delivers the orthonormal basis:

$$\hat{\rho} = \begin{bmatrix} -0.18 & -0.06 \\ -0.07 & -0.13 \\ 0.92 & 0.28 \\ -0.30 & 0.94 \\ -0.06 & -0.04 \\ -2.1 \cdot 10^{-6} & 6.3 \cdot 10^{-6} \end{bmatrix} \quad (13)$$

In order to find the transformation matrix G , one can invoke that only

one microbial population should be involved in each reaction. Normalizing the reactions with respect to these populations, the first two rows of K can be imposed, and G can be deduced as

$$G = \begin{bmatrix} -6.38 & 2.77 \\ 3.33 & -8.61 \end{bmatrix} \quad (14)$$

The matrix K then results:

$$\hat{K} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \\ -4.95 & 0.09 \\ 5.12 & -8.99 \\ 0.26 & 0.21 \\ 3.4 \cdot 10^{-5} & -6.0 \cdot 10^{-5} \end{bmatrix} \quad (15)$$

Each k_{ij} element in the $\hat{K}$ matrix corresponds to a stoichiometric coefficient that relates the j^{th} reaction with the i^{th} compound. Here, the rows correspond to X_1 , X_2 , S_1 , S_2 , CH_4 , H_2 , respectively. A positive value in the $\hat{K}$ matrix corresponds to a product of the reaction, while negative values refer to substrates.

To avoid the use of the indexes (i, j) and simplify the notation, the correspondence given in Table ?? is proposed. Hence, the reaction scheme becomes:

288 where the first microbial population X_1 transforms the organic matter S_1
289 into organic acids S_2 , methane CH_4 , and hydrogen H_2 at a reaction rate r_1 .
290 Products of the first reactions would then be used by the second population
291 X_2 to produce methane at reaction rate r_2 .

292 The values of the stoichiometric coefficients in [matrix \(15\)](#) will be used
293 as a starting point for the development of a reduced model, the next identi-
294 fication step being dedicated to the kinetic parameters. Of course, one can
295 question the precision of this first estimation of the stoichiometric matrix as
296 it leads to somewhat unexpected results, such as the production of organic
297 matter in the second reaction. These results have to be considered [as an](#)
298 [abstract mathematical representation and as a starting point](#), which is then
299 subject to refinement in the following sections.

300 It is also interesting to consider the influence of the data set on the
301 MLPCA results. The results of several tests are summarized in Table ??,
302 where the duration (43 and 120 days) and the level of noise corrupting the
303 gaseous compounds (1% and 5% relative errors), as well as the level of
304 excitation are varied into three types of signals (step function, ramp, and
305 ramp-sinusoidal). The ramp-sinusoidal is chosen as the identification set
306 as it gives the most informative response of the system.

307 It can be seen that the most affected stoichiometric coefficient is the
308 one associated to S_1 in the second reaction. Longer experiments with
309 relatively rich excitation signals are necessary to extract the information
310 about this coefficient. These observations are in agreement with results
311 obtained after re-estimation of stoichiometric parameters and the relatively
312 large uncertainty on this parameter (see Table ??), which will lead to its

elimination from the model.

2.3. Kinetic parameter identification and re-estimation of stoichiometric parameters

Finding the stoichiometric coefficients independently of the kinetics allows to divide the parameter estimation problem into subproblems which are easier to solve. The kinetic parameters can now be estimated by solving a weighted least squares problem where the deviation between the experimental data $y_{i,meas}(t)$ and the model prediction $y(\theta, t)$ can be quantified by:

$$J(\theta) = \sum_{i=1}^{n_s} \left[(y_i(\theta) - y_{i,meas})^T W_i^{-1} (y_i(\theta) - y_{i,meas}) \right] \quad (18)$$

where n_s denotes the number of samples, θ is the kinetic parameter vector, and W is a weighting matrix, which in the absence of more information on the measurement noise, is usually chosen so as to compensate for different scales and units between the variables (if more information is available, W could be taken as the covariance matrix of the measurement error, thus expressing the criterion (18) in the ML sense).

In a last step, the nonlinear identification problem can also be extended to the stoichiometric parameters. The idea is to subdivide the identification in as many steps as necessary, initializing one problem with the results of the previous subproblems. Here the stoichiometric parameters found by MLPCA could possibly be re-estimated together with the kinetic parameters in a final nonlinear identification problem.

The Nelder-Mead algorithm implemented in the Matlab routine *fminsearch*

is used to find the optimal parameter set. Moreover, positivity constraints for the parameters can be imposed using a logarithmic transformation.

Initialization of the first nonlinear optimization problem is also important since parameter identification can be subject to local minima. Reasonable initial guesses are taken from literature. In addition, a multistart strategy (30 runs) using the Latin Hypercube Sampling (LHS) is used to explore the parameter space in a neighbourhood of this starting point (McKay et al., 1979).

In the application under consideration, Monod laws are considered for both reactions:

$$\mu_{1,2}(S_{1,2}) = \mu_{max1,2} \frac{S_{1,2}}{S_{1,2} + K_{S1,2}} \quad (19)$$

$\mu_{1,2}$ is the specific growth rate of the microorganisms, $\mu_{max1,2}$ is the specific maximum bacterial growth rate, $K_{S1,2}$ is the half-saturation constant associated to the substrate $S_{1,2}$.

The estimated kinetic parameters together with their respective 95% confidence intervals are listed in Table ?? while results for stoichiometric parameters are shown in Table ??.

Decoupling the identification problem can help the identification process to proceed faster, reducing the number of iterations. An example of such statistics is given in Table ??.

It is worth noting that kinetic parameters are of the same order of magnitude as values reported in other relevant studies (Bernard et al., 2001; García-Diéguez et al., 2013) and re-estimated stoichiometric values are comparable to those obtained with MLPCA.

Figures ?? and ?? show the comparison between the model prediction, with the best set of parameters, and the noisy data simulated with ADM1 in direct and cross-validation, respectively. The noisy data is represented with red dots, while the model prediction is depicted by solid blue lines. The model fit is satisfactory with sum of squared errors of 7.24 and 12.24, for direct and cross-validation, respectively).

2.4. Sensitivity analysis

As a result of the previous analysis, the following dynamic model equations can be written:

$$\frac{dX_1}{dt} = \mu_1 X_1 - \alpha D X_1 \quad (20)$$

$$\frac{dX_2}{dt} = \mu_2 X_2 - \alpha D X_2 \quad (21)$$

$$\frac{dS_1}{dt} = D (S_{1in} - S_1) - k_1 \mu_1 X_1 + k_2 \mu_2 X_2 \quad (22)$$

$$\frac{dS_2}{dt} = D (S_{2in} - S_2) + k_3 \mu_1 X_1 - k_4 \mu_2 X_2 \quad (23)$$

$$q_{CH_4} = \beta_1 \mu_1 X_1 + \beta_2 \mu_2 X_2 \quad (24)$$

$$q_{H_2} = \beta_3 \mu_1 X_1 - \beta_4 \mu_2 X_2 \quad (25)$$

where the factor α accounts for biomass retention ($\alpha = 0$ for an ideal fixed bed reactor and $\alpha = 1$ for an ideal CSTR - here $\alpha = 0.5$ is considered). Knowing that methane and hydrogen have a relatively low solubility they are assumed to go directly to the gas compartment and leave the reactor at a volumetric flow rate proportional to the reaction rates given by equations (24) and (25), respectively.

373 Sensitivity analysis can be used to assess the influence of each parame-
 374 ter on the measured outputs, as well as the possible interaction (correlation)
 375 between these effects. In this study, local sensitivity analysis is carried out
 376 using a modification of the Matlab toolbox IDEAS (acronym for IDenti-
 377 fication and Analysis of Sensitivity) (Muñoz-Tamayo et al., 2009), which
 378 allows the construction of the dynamic sensitivity equations through sym-
 379 bolic computation, and the numerical simulation of these latter equations.

380 The first-order sensitivity $s_j = \frac{\partial x}{\partial \theta_j}$ is the solution of:

$$\dot{s}_j = \left[\frac{\partial f}{\partial x} \right]_{(x,\theta,t)} s_j + \left[\frac{\partial f}{\partial \theta_j} \right]_{(x,\theta,t)} \quad (26)$$

381 where $\dot{x}(t) = f(x(t), \theta, t)$ is the state equation. The parametric sensitivity of
 382 the measured outputs is then evaluated as:

$$\left[\frac{\partial y_m}{\partial \theta_j} \right] = \left[\frac{\partial h}{\partial x} \right]_{(x,\theta,t)} s_j + \left[\frac{\partial h}{\partial \theta_j} \right]_{(x,\theta,t)} \quad (27)$$

383 where $y_m(t) = h(x(t), \theta, t)$ is the measurement equation.

384 The sensitivity functions are evaluated at the identified parameter val-
 385 ues $\hat{\theta}$ and used to compute the Fisher Information Matrix (FIM), whose
 386 inverse is a (Cramer-Rao) lower bound of the variance-covariance matrix
 387 P of the parameter errors:

$$\hat{P} > F^{-1}(\hat{\theta}) \quad (28)$$

388 The FIM is computed as:

$$F(\hat{\theta}) = \sum_{i=1}^N \left[\frac{\partial y_m}{\partial \theta} \right]_{(t_i, \hat{\theta})}^T \Sigma^{-1} \left[\frac{\partial y_m}{\partial \theta} \right]_{(t_i, \hat{\theta})} \quad (29)$$

where Σ is the covariance matrix of the measurement noise. When the latter is unknown it can be replaced by its ML estimate $\hat{\Sigma}$.

The variance of $\tilde{\theta}_j = \theta^* - \hat{\theta}$ can be approximated by $\sigma_j^2 = \hat{P}_{jj}$ and used to evaluate a 95% confidence interval for θ_j , i.e., $[\hat{\theta}_j \pm 2\sigma_j]$.

Figure ?? gives a graphical representation of the local normalized sensitivities of each variable with respect to each parameter. Highly sensitive variables with respect to the parameters correspond to colors close to red while less sensitive variables are indicated in blue. The element (k, j) is computed as:

$$\sum_{i=1}^{n_t} \left| \frac{\hat{\theta}_j}{y_{m_k}(t_i, \hat{\theta})} \left[\frac{\partial y_{m_k}}{\partial \theta_j} \right]_{(t_i, \hat{\theta})} \right| \quad (30)$$

The corresponding correlation matrix of the estimated parameters is shown in Figure ?. Trajectories of the output sensitivities at each point in time are shown in Figures ? and ?.

Figure ? reveals low sensitivity with respect to parameter k_2 , while Table ? shows its relatively high uncertainty. Hence, the cancellation of k_2 is investigated. Values of the newly identified parameters do not present significant differences, but the cost function decreases from 8.31 to 7.24. This fully justifies the model simplification.

3. Hydrogen-based control

In this section the control developed by Rodriguez et al. (2006) is implemented and tested on respectively the reduced model and ADM1. Intrinsically, the controller is based on experimental observation, and does

not require a model for its design. However a comparative test allows to assess the consistency of the reduced model.

It has been demonstrated in (Pauss and Guiot, 1993) that a functional relation exists in steady state between hydrogen in the biogas and the organic loading rate (OLR). This relation can be computed using ADM1 and the reduced-order model. Both results are represented in Figure ??.

The controller, described by equation (31) and represented in Figure ??, includes an integral action with variable gain. In its original form, it uses the hydrogen concentration in the gas phase ($ppmH_2$) and the methane flow rate (q_{CH_4}) to determine the appropriate change in the dilution rate D in order to drive the process to the desired set-point.

$$\frac{dD}{dt} = D K f_{CH_4} f_{H_2} \quad (31)$$

In this expression, f_{H_2} and f_{CH_4} are a hydrogen factor and methane factor described by equations (32) and (33), respectively,

$$f_{H_2} = \begin{cases} \left(1 - \frac{ppmH_2}{ppmH_2^*}\right)^{1/m} & \text{if } ppmH_2 \leq ppmH_2^* \\ \left(\frac{ppmH_2}{ppmH_2^*}\right)^n - 1 & \text{if } ppmH_2 > ppmH_2^* \end{cases} \quad (32)$$

$$f_{CH_4} = \frac{\alpha q_{CH_4}^*}{q_{CH_4} + \alpha q_{CH_4}^*} \quad (33)$$

If the level of hydrogen is below the set-point ($ppmH_2^*$), f_{H_2} is positive, otherwise it is negative. This way, the hydrogen concentration in the gas phase determines the direction of change of the dilution rate, i.e. a positive

or negative time derivative (increase or decrease of the dilution rate). As shown in Figure ??, f_{H_2} is a smooth function taking values between 1 and -1.

On the other hand, f_{CH_4} is a positive factor decreasing for increasing value of the methane flow rate (see Figure ??), which will modulate the effect of f_{H_2} .

As a linear relationship exists between the hydrogen concentration (gas and liquid) and the hydrogen gas flow rate (see Figure ??), equations (32) can be adapted accordingly

$$\begin{aligned} f_{H_2} &= \left(1 - \frac{q_{H_2}}{q_{H_2}^*}\right)^{1/m} & \text{if } q_{H_2} \leq q_{H_2}^* \\ f_{H_2} &= \left(\frac{q_{H_2}}{q_{H_2}^*}\right)^n - 1 & \text{if } q_{H_2} > q_{H_2}^* \end{aligned} \quad (34)$$

The performance of the controller is studied in the framework of the process start-up and shown in Figure ?. In this figure the set-point is indicated in ppm H_2 using the conversion given in Figure ?. However, it is not necessary to know this relation to apply the controller. Parameter values used for the controller are shown in Table ?. The controller performance is satisfactory as it allows to start the process in a safe way. The application to both models is comparable, reinforcing the validation of the reduced-order model.

4. Experimental validation

In this section the proposed model structure is identified with experimental data from raw industrial wine processing wastewater. The wastew-

448 ater is treated in a $1m^3$ fully instrumented up-flow fixed bed digester. More
449 details of the AD plant and its online instrumentation can be found in
450 (Steyer et al., 2002).

451 All measurements are recorded with online sensors every 2 minutes,
452 while the H_2 sensor performs a series of measurements every half hour.
453 In order to improve simulation time, sampling of experimental data is
454 decreased using the downsampling function from Matlab. Similarly, data
455 is smoothed using a moving average filter with a span of 35 data points.
456 The full non-smoothed set of data is used at the end of the identification
457 when all parameters are identified together. The results of direct and
458 cross-validation are presented in Figure ?? and Figure ??, respectively.

459 The identification is performed as explained in Section 2.3. Table ??
460 shows the estimated parameter values with their respective uncertainties.

461

462 While the direct validation results are quite satisfactory, the cross-
463 validation results are perfectible. Several causes can be observed:

- 464 • the number of available data sets is limited. More data sets would
465 help consolidate the identification and validation;
- 466 • the experiments were not performed with monitoring of hydrogen
467 in mind. Hence hydrogen is measured at a lower frequency, and the
468 sensor was not calibrated accurately. The measurements of hydrogen
469 are therefore more qualitative than quantitative.

5. Conclusions

Using a dynamic simulator based on ADM1, an informative data base is built, which is used to infer a low-order model mimicking the time evolution of the state variables of interest. In the framework of this study, attention is focused on the evolution of hydrogen, which has been identified as an important indicator of the process stability. The resulting model, with 4 states only, captures well the dynamics of ADM1, and is a good basis to develop control strategies. To fit a particular application, the model parameters can be estimated from experimental data, using conventional tools, as exemplified with real experimental data collected from a pilot plant at the Laboratoire de Biotechnologie de l'Environnement, Narbonne, France.

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7. References

- Batstone, D. J., Keller, J., Angelidaki, I., Kalyuzhnyi, S. V., Pavlostathis, S. G., Rozzi, A., Vavilin, V. A., 2002. The IWA Anaerobic Digestion Model No 1 (ADM1). *Water Science and Technology* 45 (10), 65–73.
- Beltramo, T., Ranzan, C., Hinrichs, J., Hitzmann, B., 2016. Artificial neural network prediction of the biogas flow rate optimised with an ant colony algorithm. *Biosystems Engineering* 143, 68–78.
- Bernard, O., Hadj-Sadok, Z., Dochain, D., Genovesi, A., Steyer, J.-P., 2001. Dynamical model development and parameter identification for an anaerobic wastewater treatment process. *Biotechnology and Bioengineering* 75 (4), 424–438.
- Bhattacharya, S., Sluder, J., Uberoi, V., 1995. Effects of 4-nitrophenol on H₂ and CO levels in anaerobic propionate systems. *Water Research* 29 (5), 1249–1258.
- Björnsson, L., Murto, M., Jantsch, T. G., Mattiasson, B., 2001. Evaluation of new methods for the monitoring of alkalinity, dissolved hydrogen and the microbial community in anaerobic digestion. *Water Research* 35 (12), 2833–2840.
- Boe, K., 2006. Online monitoring and control of the biogas process. Ph.D. thesis, Institute of Environment and Resources, Technical University of Denmark.
- Boe, K., Batstone, D. J., Steyer, J. P., Angelidaki, I., 2010. State indicators

- 513 for monitoring the anaerobic digestion process. *Water Research* 44 (20),
514 5973–5980.
- 515 Chen, L., Bastin, G., 1996. Structural identifiability of the yield coefficients
516 in bioprocess models when the reaction rates are unknown. *Mathemati-*
517 *cal Biosciences* 132 (1), 35–67.
- 518 Chen, Y., Cheng, J. J., Creamer, K. S., 2008. Inhibition of anaerobic digestion
519 process: a review. *Bioresource Technology* 99 (10), 4044–4064.
- 520 Cord-Ruwisch, R., Mercz, T. I., Hoh, C.-Y., Strong, G. E., 1997. Dissolved hy-
521 drogen concentration as an on-line control parameter for the automated
522 operation and optimization of anaerobic digesters. *Biotechnology and*
523 *Bioengineering* 56 (6), 626–634.
- 524 Della Bona, A., Ferretti, G., Ficara, E., Malpei, F., 2015. Lft modelling
525 and identification of anaerobic digestion. *Control Engineering Practice*
526 36, 1–11.
- 527 Dochain, D., Perrier, M., Pauss, A., 1991. Adaptive control of the hydrogen
528 concentration in anaerobic digestion. *Industrial & Engineering Chem-*
529 *istry Research* 30 (1), 129–136.
- 530 Ficara, E., Hassam, S., Allegrini, A., Leva, A., Malpei, F., Ferretti, G., 2012.
531 Anaerobic digestion models: a comparative study. *Proceedings of the*
532 *MATHMOD* 2012 45 (2), 1052–1057.
- 533 García-Diéguez, C., Bernard, O., Roca, E., 2013. Reducing the Anaerobic
534 Digestion Model No. 1 for its application to an industrial wastewater

- 535 treatment plant treating winery effluent wastewater. *Bioresource Tech-*
 536 *nology* 132, 244–253.
- 537 Giovannini, G., Donoso-Bravo, A., Jeison, D., Chamy, R., Ruíz-Filippi, G.,
 538 Wouwer, A. V., 2016. A review of the role of hydrogen in past and current
 539 modelling approaches to anaerobic digestion processes. *International*
 540 *Journal of Hydrogen Energy* 41 (39), 17713–17722.
- 541 Giraldo-Gomez, E., Goodwin, S., Switzenbaum, M. S., 1992. Influence of
 542 mass transfer limitations on determination of the half saturation constant
 543 for hydrogen uptake in a mixed-culture CH₄-producing enrichment.
 544 *Biotechnology and Bioengineering* 40 (7), 768–776.
- 545 Hassam, S., Ficara, E., Leva, A., Harmand, J., 2015. A generic and system-
 546 atic procedure to derive a simplified model from the Anaerobic Digestion
 547 Model No. 1 (ADM1). *Biochemical Engineering Journal* 99, 193–203.
- 548 Hawkes, F., Dinsdale, R., Hawkes, D., Hussy, I., 2002. Sustainable fer-
 549 mentative hydrogen production: Challenges for process optimisation.
 550 *International Journal of Hydrogen Energy* 27 (11), 1339–1347.
- 551 Hou, Y.-p., Peng, D.-c., Xue, X.-d., Wang, H.-y., Pei, L.-y., 2014. Hydrogen
 552 utilization rate: A crucial indicator for anaerobic digestion process eval-
 553 uation and monitoring. *Journal of Bioscience and Bioengineering* 117 (4),
 554 519–523.
- 555 Mailier, J., Remy, M., Wouwer, A. V., 2013. Stoichiometric identification
 556 with maximum likelihood principal component analysis. *Journal of*
 557 *Mathematical Biology* 67 (4), 739–765.

- 558 McKay, M. D., Beckman, R. J., Conover, W. J., 1979. Comparison of three
559 methods for selecting values of input variables in the analysis of output
560 from a computer code. *Technometrics* 21 (2), 239–245.
- 561 Muñoz-Tamayo, R., Laroche, B., Leclerc, M., Walter, E., 2009. Ideas: a
562 parameter identification toolbox with symbolic analysis of uncertainty
563 and its application to biological modelling. 15th IFAC Symposium on
564 System Identification, July 6-8, Saint-Malo, France 42 (10), 1271–1276.
- 565 Owmondah, R. O., Walker, M., Ma, L., Bill, N., B., I. D., Poggio,
566 D., Pourkashanian, M., 2016. Assessment and parameter identifica-
567 tion of simplified models to describe the kinetics of semi-continuous
568 biomethane production from anaerobic digestion of green and food
569 waste. *Bioprocess and Biosystems Engineering* 39, 977992.
- 570 Paus, A., Guiot, S. R., 1993. Hydrogen monitoring in anaerobic sludge bed
571 reactors at various hydraulic regimes and loading rates. *Water Environ-
572 ment Research* 65 (3), 276–280.
- 573 Rodriguez, J., Roca, E., Lema, J. M., Bernard, O., 2008. Determination of
574 the adequate minimum model complexity required in anaerobic bio-
575 processes using experimental data. *Journal of Chemical Technology and
576 Biotechnology* 83 (12), 1694–1702.
- 577 Rodriguez, J., Ruiz, G., Molina, F., Roca, E., Lema, J., 2006. A hydrogen-
578 based variable-gain controller for anaerobic digestion processes. *Water
579 Science and Technology* 54 (2), 57–62.

- 580 Ryhiner, G. B., Heinzle, E., Dunn, I. J., 1993. Modeling and simulation of
581 anaerobic wastewater treatment and its application to control design:
582 case whey. *Biotechnology Progress* 9 (3), 332–343.
- 583 Simeonov, I., Karakashev, D., 2012. Mathematical modelling of the anaero-
584 bic digestion including the syntrophic acetate oxidation. *IFAC Proceed-
585 ings Volumes* 45 (2), 309–314.
- 586 Steyer, J.-P., Bouvier, J., Conte, T., Gras, P., Sousbie, P., 2002. Evaluation
587 of a four year experience with a fully instrumented anaerobic digestion
588 process. *Water Science and Technology* 45 (4-5), 495–502.
- 589 Voolapalli, R. K., Stuckey, D. C., 1999. Relative importance of trophic group
590 concentrations during anaerobic degradation of volatile fatty acids. *Ap-
591 plied and Environmental Microbiology* 65 (11), 5009–5016.
- 592 Voolapalli, R. K., Stuckey, D. C., 2001. Hydrogen production in anaerobic
593 reactors during shock loads-influence of formate production and H₂
594 kinetics. *Water Research* 35 (7), 1831–1841.
- 595 Yu, H., Zhu, Z., Hu, W., Zhang, H., 2002. Hydrogen production from
596 rice winery wastewater in an upflow anaerobic reactor by using mixed
597 anaerobic cultures. *International journal of hydrogen energy* 27 (11),
598 1359–1365.
- 599 Yu, L., Wensel, P. C., Ma, J., Chen, S., 2013. Mathematical modeling in anaer-
600 obic digestion (ad). *Journal of Bioremediation & Biodegradation* (S4:
601 003).

Figures caption:

Fig 1: Noise-free data generated with ADM1 model. Upper left graph: evolution of the dilution rate $D(t)$. Continuous lines: identification set - dashed lines: cross-validation set. Variables concentration units are $kgCOD/m^3$. Flow rates units are m^3/d .

Fig 2: Log-likelihood costs related to the MLPCA-estimated subspaces. A plausible range is delimited by two chi-square quantiles (dashed lines). N is the number of state variables (component concentrations), n_s is the number of samples per variable.

Fig 3: Direct validation. Red dots: ADM1 noisy data - Blue lines model prediction. Variables concentration units are $kgCOD/m^3$. Flow rates units are m^3/d .

Fig 4: Cross validation. Red dots: ADM1 noisy data - Blue lines: model prediction. Variables concentration units are $kgCOD/m^3$. Flow rates units are m^3/d .

Fig 5: L1 norm of the normalized sensitivities.

Fig 6: Parameter correlation matrix.

Fig 7 and 8: Parametric sensitivity trajectories.

Fig 9: Steady-state simulation of H_2 gas at different OLR for ADM1 (red dots) and reduced model (blue stars).

Fig 10: Schematic view of the control.

Fig 11: Control functions for a) Hydrogen and b) Methane flow rate.

Fig 12: Linear relationship between hydrogen concentration and hydrogen gas flow rate.

627 **Fig 13:** Controller and system responses for ADM1 (red dashed lines)
628 and reduced model (blue continuous lines).

629 **Fig 14:** Linear regression relation between hydrogen flow rate and
630 dissolved hydrogen.

631 **Fig 15:** Direct validation. Red dots: experimental data - Blue lines
632 model prediction.

633 **Fig 16:** Cross validation. Red dots: experimental data - Blue lines
634 model prediction.

635

Fig 1:

Figure 1:

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Fig 2:

Figure 2:

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Fig 3:

Figure 3:

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Fig 4:

Figure 4:

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Fig 5:

Figure 5:

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Fig 6:

	μ_{max}^1	k_{s1}	μ_{max}^2	k_{s2}	k_1	k_2	k_3	k_4	β_1	β_2	β_3	β_4
μ_{max}^1	1	0.99	-0.12	-0.11	$7 \cdot 10^{-3}$	$2 \cdot 10^{-2}$	$-7 \cdot 10^{-2}$	$-7 \cdot 10^{-2}$	$-3 \cdot 10^{-2}$	$2 \cdot 10^{-2}$	$-1 \cdot 10^{-5}$	$-8 \cdot 10^{-6}$
k_{s1}		1	-0.11	-0.10	$4 \cdot 10^{-3}$	$2 \cdot 10^{-2}$	$-7 \cdot 10^{-2}$	$-7 \cdot 10^{-2}$	$-2 \cdot 10^{-2}$	$2 \cdot 10^{-2}$	$-1 \cdot 10^{-5}$	$-8 \cdot 10^{-6}$
μ_{max}^2			1	0.98	$-3 \cdot 10^{-2}$	$-2 \cdot 10^{-2}$	$-3 \cdot 10^{-3}$	$8 \cdot 10^{-3}$	$6 \cdot 10^{-2}$	$-5 \cdot 10^{-2}$	$-8 \cdot 10^{-7}$	$-4 \cdot 10^{-7}$
k_{s2}				1	$-2 \cdot 10^{-2}$	$-2 \cdot 10^{-2}$	$-5 \cdot 10^{-3}$	$3 \cdot 10^{-3}$	$6 \cdot 10^{-2}$	$-4 \cdot 10^{-2}$	$-7 \cdot 10^{-7}$	$-2 \cdot 10^{-7}$
k_1					1	0.95	0.94	0.85	$4 \cdot 10^{-2}$	$-1 \cdot 10^{-2}$	$3 \cdot 10^{-5}$	$1 \cdot 10^{-5}$
k_2						1	0.90	0.89	$3 \cdot 10^{-2}$	$-1 \cdot 10^{-2}$	$2 \cdot 10^{-5}$	$1 \cdot 10^{-5}$
k_3							1	0.89	$5 \cdot 10^{-2}$	$-3 \cdot 10^{-2}$	$3 \cdot 10^{-5}$	$1 \cdot 10^{-5}$
k_4								1	$5 \cdot 10^{-2}$	$4 \cdot 10^{-2}$	$2 \cdot 10^{-5}$	$1 \cdot 10^{-5}$
β_1									1	-0.92	$2 \cdot 10^{-6}$	$9 \cdot 10^{-7}$
β_2										1	$-7 \cdot 10^{-7}$	$1 \cdot 10^{-6}$
β_3											1	0.94
β_4												1

Figure 6:

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Fig 7: **Figure 7:**

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Fig 8:

Figure 8:

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Fig 9:

Figure 9:

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Fig 10:

Figure 10:

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Fig 11:

Figure 11:

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Fig 12:

Figure 12:

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Fig 13:

Figure 13:

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Fig 14:

Figure 14:

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Fig 15:

Figure 15:

	ADM1 influent concentrations		ADM1 influent concentrations
$S_{su,in}$	$1.87 \text{ kgCOD}/\text{m}^3$	$S_{IC,in}$	$0.065 \text{ kmol}/\text{m}^3$
$S_{aa,in}$	$0.01 \text{ kgCOD}/\text{m}^3$	$S_{cat,in}$	$0.089 \text{ kmol}/\text{m}^3$
$S_{fu,in}$	$0.01 \text{ kgCOD}/\text{m}^3$	$S_{an,in}$	$0.018 \text{ kmol}/\text{m}^3$
$S_{ac,in}$	$0.01 \text{ kgCOD}/\text{m}^3$	$S_{va,in}$	$0.01 \text{ kgCOD}/\text{m}^3$
$S_{bu,in}$	$0.01 \text{ kgCOD}/\text{m}^3$	$S_{pro,in}$	$0.01 \text{ kgCOD}/\text{m}^3$

Table 1: ADM1 input values used in the model reduction procedure

Parameter	Description	Obtain with MLPCA	Estimated	Units
k_1	S_1 consumption yield	4.95	9.99 ± 0.42	$\text{kg } S_1/\text{kg } X_1$
k_2	S_1 production yield	0.09	$1\text{e-}12 \pm 0.99$	$\text{kg } S_1/\text{kg } X_2$
k_3	S_2 production yield	5.12	7.72 ± 0.34	$\text{kg } S_2/\text{kg } X_1$
k_4	S_2 consumption yield	8.99	11.25 ± 0.86	$\text{kg } S_2/\text{kg } X_2$
β_1	CH_4 proportional constant	-	0.41 ± 0.05	$\text{m}^3 \text{ m}^3/\text{kg } X_1$
β_2	CH_4 proportional constant	-	3.81 ± 0.06	$\text{m}^3 \text{ m}^3/\text{kg } X_2$
β_3	H_2 proportional constant	-	$3\text{e-}4 \pm 0.05$	$\text{m}^3 \text{ m}^3/\text{kg } X_1$
β_4	H_2 proportional constant	-	$1\text{e-}4 \pm 0.06$	$\text{m}^3 \text{ m}^3/\text{kg } X_2$

Table 2: Stoichiometric parameters initially estimated using MLPCA, and identified values together with their 95% confidence intervals

Signals	Step		Step		Step		Ramp		Identification set	
Duration	43 days		120 days		120 days		120 days		120 days	
Noise	1%		5%		1%		1%		1%	
X_1	1	0	1	0	1	0	1	0	1	0
X_2	0	1	0	1	0	1	0	1	0	1
S_1	-6.9	4.8	-3.8	-2.0	-3.6	-2.5	-4.6	-0.6	-4.6	0.09
S_2	8.5	-16.6	3.6	-5.6	3.3	-2.5	4.5	-7.5	5.1	-8.9
CH_4	0.39	-9e-2	0.24	0.24	0.22	0.27	0.26	0.21	0.27	0.21
H_2	5e-5	-1e-4	2e-5	-3e-5	2e-5	-2e-5	3e-5	-4e-5	3e-5	-6e-5

Table 3: Influence of data on the stoichiometric coefficients deduced by MLPCA

Parameter	Description	Estimated	Units
μ_{max1}	Maximum growth rate first reaction	$3.62 \pm 9e-5$	$1/d$
μ_{max2}	Maximum growth rate second reaction	$0.48 \pm 4e-5$	$1/d$
K_{S1}	Half-saturation constant first reaction	$0.61 \pm 1e-2$	Kg/m^3
K_{S2}	Half-saturation constant second reaction	$0.46 \pm 4e-3$	Kg/m^3

Table 4: Estimated kinetic parameters together with their 95% confidence intervals

Identification	Cost Function	Set of parameters	Number of iterations
0	509.66		
1	132.45	Kinetics	116
2	90.84	Stoichiometry	1422
3	14.64	Kinetics + stoichiometry	2063

Table 5: Cost function values obtained after each identification step with their respective number of iterations

Parameter	Value	Units
K	0.4	kg/m^3
$q_{CH_4}^*$	0.18	m^3/d
m	2	-
n	10	-
α	0.1	-

Table 6: Controller parameters used during start-up experiments

Parameter	Description	Estimated	Units
μ_{max1}	Maximum growth rate first reaction	0.60 ± 0.02	$1/d$
μ_{max2}	Maximum growth rate second reaction	0.27 ± 0.15	$1/d$
K_{S1}	Half-saturation constant first reaction	5.10 ± 1.32	g/L
K_{S2}	Half-saturation constant second reaction	0.70 ± 0.13	g/L
K_1	S_1 consumption yield	21.3 ± 5.23	$g S_1/g X_1$
K_4	S_2 consumption yield	10.0 ± 2.39	$g S_2/g X_2$
β_1	Proportional constant first reaction	5.0 ± 1.82	L^2/g
β_2	Proportional constant second reaction	3.9 ± 1.23	L^2/g
β_3	Proportional constant first reaction	$1e-4 \pm 4e-3$	L^2/g
β_4	Proportional constant second reaction	$1e-5 \pm 2e-5$	L^2/g

Table 7: Estimated parameters together with their 95% confidence intervals

Highlights:

- A 2-step dynamic model of anaerobic digestion is derived from ADM1.
- The model involves the concentration of hydrogen, which might be used to monitor the process.
- Maximum likelihood principal component analysis is used to infer the reaction number and stoichiometry.
- A hydrogen control strategy is tested based on the 2-step model and ADM1.