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Development of a Sensitivity Analysis method to highlight key parameters of a dry Anaerobic Digestion reactor model

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Abstract

Global sensitivity analysis enables to identify model parameters that have the most significant impact on model outputs and therefore require an estimation effort. This work demonstrates the reliability of a global sensitivity analysis methodology based on Definitive Screening Design and multiple linear regression analysis that requires a low number of runs. The method is applied to a simplified anaerobic digestion model. The model is firstly used to simulate a case study of a thermophilic dry anaerobic digestion of a potential agricultural waste. Then, the influence of the kinetic and mass transfer parameters of the model on the biogas flowrate, the percentage of methane in the biogas and the pH are estimated and discussed. The sensitivity analysis reveals that the slow hydrolysis constant and the upper pH inhibition limit of the hydrolytic biomass are decisive in correctly describing the biogas flowrate. The methane percentage in the biogas slightly varies with kinetic parameters, between 53 % and 55 %. Moreover, the mass transfer coefficient has significant impact on the pH through CO_2 desorption. The method simplicity and reliability make its application easy to any type of model.

Keywords: Dry anaerobic digestion, Modelling, Sensitivity analysis, Definitive screening design method

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1. Introduction

Anaerobic digestion (AD) is known as an alternative way to treat and to recycle organic wastes while producing biogas. AD is a natural process carried out by anaerobic microorganisms and led by biological and physicochemical phenomena. Biogas is mainly composed of CH_4 and CO_2 and is the result of the organic matter breakdown through a cascade of enzymatic reactions namely hydrolysis, acidogenesis, acetogenesis and methanogenesis [1]. Various anaerobic process technologies exist but due to the coupling between the phenomena involved and the high sensitivity of the microbial flora, these processes may present a low robustness [2,3].

The mathematical modelling of AD process enables to understand and to describe biological, as well as mass transfer phenomena. Models are also predictive tools used to design processes and to optimise process control. In order to propose a generic model that would be a common basis, the IWA Task Group for Mathematical Modeling of Anaerobic Digestion Processes developed the Anaerobic Digestion Model No.1 (ADM1) [1]. The ADM1 is a very complete structured biological model that considers the major physical and biochemical mechanisms describing the dynamics of 24 species including 19 bioconversion processes associated to 80 kinetic and mass transfer parameters. These parameters compose the set of input model parameters that have to be defined to correctly describe the dynamic behaviour of a particular digestion medium in a given digester technology. The ADM1 was initially based on the AD of sewage sludge [1]. Since its publication, modified ADM1 and adapted ADM1 models have emerged in order to consider specific processes taking place during the digestion of complex substrates such as organic substrate with high solid content [4–8]. Various works have also discussed the development of simplified ADM1 models [9–14]. Although these models are less generic, they can be sufficient to model particular AD operations, reducing the number of parameters to be calibrated.

Nevertheless, whatever the complexity of the model is, it is interesting to know which parameters have the most influence on model outputs to obtain a reliable model while reducing the estimation effort [15]. In some adapted ADM1 models, parametric identification is typically based on the knowledge of the researcher who selects the set of parameters to be calibrated among the existing parameters in the ADM1 [4,5]. Also, sensitivity analysis consisting in the investigation of the change in model outputs resulting from a change in model parameters can be helpful to select the most relevant parameters to be identified

[6,7,16–18]. Sensitivity analysis can also help to verify the validity of model assumptions and to check the identifiability of the parameters [19]. The most widely used sensitivity analysis technique, especially for adapted ADM1 model, is the local sensitivity method that consists in analysing how a small perturbation near a central parameter value influences a model output [6,7]. The drawbacks of this method are the small range of variation of the parameters and the fact that interaction effects are not considered [10]. Because of the complexity of the phenomena involved during AD, the values of the kinetic and mass transfer parameters strongly depend on a large number of conditions such as inoculum, nature of the substrate [20], temperature [21], water content of the media [12] or mixing efficiency [22]. This is accentuated in the case of simplified models where phenomena are described through fewer parameters. Thus, it can be necessary to conduct sensitivity analysis on large ranges of parameter values. Some authors have sought to measure the effect of large parameter variations by changing the value of each parameter "one at a time" (OAT) while leaving the other fixed and calculating the relative difference in outputs over time [18,23]. This methodology was applied by Fatolahi et al. [24] to identify important parameters of ADM1 to simulate the digestion of an organic fraction of municipal solid wastes. In their work, Shannon entropy was applied as a sensitivity index to interpret the sensitivity analysis screening results. The major flaws of the OAT method are the large number of runs or experiments required and again the fact that the interaction effects are not considered [10]. On the other side, global sensitivity analysis not only provides quantitative approach to assess the significant influences of several kinetic parameters at a time on model outputs but also allows a focus on how the variability of each parameter influences the variance of model outputs [10]. Thus, more and more works underline the usefulness and necessity of applying reliable global sensitivity analysis methods to AD models. For instance, Donoso et al. [16], have developed a two steps model where 12 kinetic and mass transfer parameters are involved. Monte-Carlo method has been used to generate random parameter values and the Sobol analysis has allowed to decompose variances of several model outputs into fractions that can be attributed to parameter variances [16]. In their work, Schroyen et al. [17] performed global sensitivity analysis on an ADM1 simplified model using Monte-Carlo simulations and linear regression to analyse the effects of kinetic parameter variations on biomethane production. In another study, Pastor-Poquet et al. [19] used global sensitivity analysis to highlight the most influential parameter of an adapted ADM1 model to be calibrated with an available set of experimental

data. In this aim, Latin-hypercube sampling technique was used and the individual and global effects of each parameter upon the global model output variance were calculated. Moreover, this work also helped to evaluate the suitability of the ammonia inhibition function used in the model by performing sensibility analysis based on experimental data. Recently, a new approach of global sensitivity analysis has enabled to assess the effect of feedstock variations on parameter sensitivities of two models [15]. This methodology is based on the coupling between the Morris method and the functional principal component analysis and enables the interpretation of time-dependent outputs.

These methods can be time-consuming as they can require a large number of runs. An alternative method is the use of screening design methods to assess the influence of parameter variations on model outputs. Definitive Screening Design (DSD) is particularly adapted for this purpose. Indeed, this is a three-level screening design that enables to estimate the main effects of parameter variations on a given variable. Moreover, compared to classical fractional factorial designs, DSD has the advantage to provide estimates of main effects that are orthogonal to other main effects and that are unbiased by any second-order effect [25,26]. On top of that, this design requires a relatively low number of runs, only one more run than twice the number of parameters. DSD has been mainly used for operating parameter optimisations because of its capacity to also estimate quadratic effects without confounding with two-factor interactions [27–29]. However, the literature lacks information on the application of DSD on numerical modelling.

Therefore, the aim of the present work is to show the relevancy of the application of DSD coupled with multiple linear regression analysis to global sensitivity analysis to assess the key parameters that significantly influence AD model outputs. The methodology is applied to an ADM1 simplified model for thermophilic dry anaerobic digestion of agricultural wastes which is firstly presented. A literature review is carried out to define realistic ranges of the model parameters in relation to the process studied. This choice is essential to ensure the consistency of the results obtained from the sensitivity analysis. The global sensitivity analysis based on DSD is then described and applied to highlight the model parameters that have the most significant impacts on the simulation outputs in the case study considered. The results obtained are compared to trends observed in literature for similar cases.

2. Model description

2.1. Reaction scheme

The model considered in this paper is a dynamic model developed for process control purpose and more precisely to prevent failures of high solid anaerobic digestion, over 15% total solid (TS) of agricultural and livestock wastes. This is a simplified ADM1 model intended to describe major phenomena involved during dry anaerobic digestion of different substrates.

In the present study, the anaerobic biological processes are described through two steps. The disintegration, hydrolysis and acidogenesis stages are gathered in a single solubilisation step named DHA. Hydrogenotrophic methanogenesis is also included in this step to consider the consumption of H_2 and inorganic carbon (IC) resulting from the acidogenesis stage (

Table 1). During DHA, hydrolytic biomass (X_{bha}) degrades the readily (X_r) and the slowly (X_s) biodegradable fractions of the particulate substrate into soluble matter such as acetate (S_A), methane (S_{CH4}), inorganic carbon (S_{IC}), and inorganic nitrogen (S_N). The division of particulate matter into two fractions enables to consider the complexity of various substrates. The acidogenic step of anaerobic digestion produces various volatile fatty acids (VFA) represented by acetate. Inorganic nitrogen production appears in the DHA step because ammonia is a by-product of both hydrolysis and acidogenesis of nitrogen rich compounds such as proteins or urea [1]. The reaction equations of the DHA step are defined as follows:

$$X_r \rightarrow \alpha_{1,A}S_A + \left(1 - \alpha_{1,A} - \alpha_{1,CH4}\right)X_{bha} + \alpha_{1,IC}S_{IC} + \alpha_{1,N}S_N + \alpha_{1,CH4}S_{CH4} \quad (1)$$

$$X_s \rightarrow \alpha_{2,A}S_A + \left(1 - \alpha_{2,A} - \alpha_{2,CH4}\right)X_{bha} + \alpha_{2,IC}S_{IC} + \alpha_{2,N}S_N + \alpha_{2,CH4}S_{CH4} \quad (2)$$

where $\alpha_{j,i}$ are the stoichiometric coefficients of the component i in the reaction j.

The methanogenic pathway of the conversion of acetate (S_A) into dissolved CH_4 (S_{CH4}) and inorganic carbon (S_{IC}) by methanogens (X_{bm}) is described by the following equation:

$$S_A \rightarrow \alpha_{3,CH4}S_{CH4} + \alpha_{3,IC}S_{IC} + (1 - \alpha_{3,CH4})X_{bm} \quad (3)$$

The biomass decay is also accounted for. According to the ADM1, death of biomass (X_{bha} and X_{bm}) leads to the formation of slowly degradable particulate matter, particulate inert (X_I) and soluble inert (S_I):

$$X_{bha} \rightarrow \alpha_{4,Xi}X_I + \left(1 - \alpha_{4,Xi} - \alpha_{4,Si}\right)X_s + \alpha_{4,Si}S_I \quad (4)$$

$$X_{bm} \rightarrow \alpha_{5,Xi}X_I + (1 - \alpha_{5,Xi} - \alpha_{5,Si})X_s + \alpha_{5,Si}S_I \quad (5)$$

Thus, the simplifications made on degradation pathways lead to 5 stoichiometric reactions in which 10 variables are involved.

2.2. Model units and notations

As suggested in the ADM1, chemical component base unit is the chemical oxygen demand (COD). Molar basis is used for components with no COD such as inorganic carbon (CO_2 and HCO_3^-) or inorganic nitrogen (NH_3 and NH_4^+). Concentrations are expressed according to the wet medium mass unit: $g_{COD}.kg^{-1}$ (or $mol.kg^{-1}$).

2.3. Stoichiometric coefficients

The stoichiometric coefficients are estimated based on assumptions made on biochemical reaction schemes and experimental data.

In DHA step, the solubilisation of carbohydrate and fats contained in the particulate matter mainly leads to monomers like monosaccharides [1]. Glucose is used as the model monomer to calculate the stoichiometric parameters of the DHA reactions, for both readily and slowly degradable particulate matters. According to the acidogenesis equation of glucose (Step 1,

Table 1), a part of the glucose is transformed into hydrogen. Hypothesis of an implicit hydrogen-utilising methanogenesis (Step 2,

Table 1) leads to the global balance equation of the DHA step (Step 3,

Table 1).

Table 1: Reaction schemes of the bioconversion processes.

	Step	Balance equation
1	Acidogenesis from monosaccharides	$C_6H_{12}O_6 + 2\,H_2O \rightarrow 2\,CH_3COOH + 2\,CO_2 + 4\,H_2$
2	Hydrogen-utilising methanogenesis	$4\,H_2 + CO_2 \rightarrow CH_4 + 2\,H_2O$
3	DHA of glucose	$C_6H_{12}O_6 \rightarrow 2\,CH_3COOH + CO_2 + CH_4$
4	Methanogenesis	$CH_3COOH \rightarrow CO_2 + CH_4$

The stoichiometric coefficients are estimated from Step 3 in

Table 1. As in the ADM1, it is suggested that 10% of the transformed COD is turned into biomass [1]. Stoichiometric coefficients of the DHA step are calculated from the following equations:

$$\alpha_{1,CH4} = \alpha_{2,CH4} = (1 - Y_{Xbha})\, \nu_{3,CH4} \frac{COD_{CH4}}{COD_{Glucose}} = 0.3\ g_{COD\ CH4} \cdot g_{COD\ Glucose}{}^{-1} \quad (6)$$

$$\alpha_{1,A} = \alpha_{2,A} = (1 - Y_{Xbha})\, \nu_{3,A} \frac{COD_{Acetate}}{COD_{Glucose}} = 0.6\ g_{COD\ A} \cdot g_{COD\ Glucose}{}^{-1} \quad (7)$$

$$\alpha_{1,IC} = \alpha_{2,IC} = (1 - Y_{Xbha})\, \nu_{3,IC} \frac{mol_{CO2}}{COD_{Glucose}} = 0.00468\ mol_{IC} \cdot g_{COD\ Glucose}{}^{-1} \quad (8)$$

where Y_{Xbha} is the percentage of COD consumed for hydrolytic biomass growth (0.1 $g_{COD_Xbha}.g_{COD_Glucose}^{-1}$), $\nu_{3,i}$ is the stoichiometric coefficient of component i from Step 3 in

Table 1, $COD_{Glucose}$ is the COD of one mole of glucose (192 $g_{COD}.mol^{-1}$), COD_{CH4} is the COD of one mole of methane (64 $g_{COD}.mol^{-1}$), $COD_{Acetate}$ is the COD of one mole of acetate (64 $g_{COD}.mol^{-1}$), mol_{CO2} corresponds to a mole of inorganic carbon.

In this study, organic nitrogen biodegradability is assumed equal to the organic carbon biodegradability of the particulate substrate. Hence, stoichiometric coefficients of inorganic nitrogen, $\alpha_{1,N}$ and $\alpha_{2,N}$ (Eq. (1) and Eq. (2)) are estimated from biochemical methanogenic potential (BMP) tests carried out on the influent. The total nitrogen content (TKN) of the raw substrate considered in this work is about 0.50 $mol_N.kg^{-1}$ and the total ammonia concentration (TAN) is 0.18 $mol.kg^{-1}$. The organic carbon biodegradability of the substrate is estimated at 62.7% (see 2.6.1) which leads to stoichiometric coefficients of inorganic nitrogen ($\alpha_{1,N}$ and $\alpha_{2,N}$) of 0.0009 $mol.g_{COD_X}^{-1}$.

$$\alpha_{1,N} = \alpha_{2,N} = \frac{\%BD,N\ (TKN - TAN)}{(X_r + X_s)} \quad (9)$$

where %BD,N is the biodegradability of the organic nitrogen.

Stoichiometric coefficients of the methanogenic step are calculated from the methanogenesis balance equation (Eq. (4),

Table 1). As in ADM1, it is proposed that 5% of the acetate is turned into methanogenic biomass [1].

$$\alpha_{3,CH4} = (1 - Y_{Xbm})\, \nu_{4,CH4} \frac{COD_{CH4}}{COD_{Acetate}} = 0.95\ g_{COD\ CH4} \cdot g_{COD\ A}{}^{-1} \quad (10)$$

$$\alpha_{3,IC} = (1 - Y_{Xbm})\, \nu_{4,IC} \frac{mol_{CO2}}{COD_{Acetate}} = 0.0148\ mol_{IC} \cdot g_{COD\ A}{}^{-1} \quad (11)$$

where Y_{Xbm} is the percentage of COD consumed for methanogenic biomass growth (0.05 $g_{COD_Xbm}.g_{COD_A}{}^{-1}$) and $\nu_{4,i}$ is the stoichiometric coefficient of component i from the Step 4 in Table 1.

Finally, stoichiometric coefficients of the biomass decay balance equations (Eq. (4) and Eq. (5)) are taken from the suggested values of ADM1 where $\alpha_{4,Xi} = \alpha_{5,Xi} = 0.25\ g_{COD\ Xi}.g_{COD\ Xbiomass}{}^{-1}$ and $\alpha_{4,Si} = \alpha_{5,Si} = 0.1\ g_{COD\ Si}.g_{COD\ Xbiomass}{}^{-1}$.

2.4. Kinetics and mass transfer

In dry anaerobic digestion, the rate-limiting step is usually considered to be the hydrolysis [12,30], modelled by first order kinetics in ADM1. Therefore, in this work DHA step is modelled by first order kinetics and characterised by two kinetic parameters, k_1, k_2, respectively for the degradation of the readily (X_r) and the slowly (X_s) degradable fractions of the particulate substrates. As in the ADM1, a Monod kinetic law describes the methanogenic step and the decay rates of the biomass are modelled by first order kinetics. All these bioconversion rates r_j are shown in the Petersen matrix given in Table 2.

According to the ADM1, pH inhibition on both DHA step and methanogenesis are accounted for in this model as well as ammonia inhibition on the methanogenic step. pH and ammonia inhibitions are described by the following equations [1]:

$$I_{pH,i} = \frac{1+2\cdot 10^{0.5(pH_{LL,i}-pH_{UL,i})}}{1+10^{(pH-pH_{UL,i})}+10^{(pH_{LL,i}-pH)}} \quad (12)$$

$$I_{NH_3} = \frac{1}{1+\frac{S_{NH_3}}{MC\ K_i}} \quad (13)$$

where $I_{pH,i}$ is the pH inhibition factor affecting biomass i, $pH_{LL,i}$ and $pH_{UL,i}$ are respectively the lower and upper limits of pH for 50% inhibitory effect on biomass i. I_{NH3} is the free ammonia inhibition factor affecting methanogens activity, S_{NH3} is the molar concentration of free ammonia in the media (mol.kg^{-1}) and MC is the moisture content, which is equal to 1-TS (L_{liquid}.kg^{-1}).

Table 2: Peterson matrix of the model state variables.

		Component i										Rate r_j ($g_{COD}.kg^{-1}.d^{-1}$ or $mol.kg^{-1}.d^{-1}$ for S_{IC} and S_N)
	Process	X_I	X_r	X_s	X_{bha}	X_{bm}	S_A	S_{CH4}	S_{IC}	S_N	S_I	
1	**Fast hydrolysis**		-1		$1-\alpha_{1,A}-\alpha_{1,CH4}$		$\alpha_{1,A}$	$\alpha_{1,CH4}$	$\alpha_{1,IC}$	$\alpha_{1,N}$		$k_1 X_f I_{pH,Xbha}$
2	**Slow hydrolysis**			-1	$1-\alpha_{2,A}-\alpha_{2,CH4}$		$\alpha_{2,A}$	$\alpha_{2,CH4}$	$\alpha_{2,IC}$	$\alpha_{2,N}$		$k_2 X_d I_{pH,Xbha}$
3	**Methanogenesis**					$1-\alpha_{3,CH4}$	-1	$\alpha_{3,CH4}$	$\alpha_{3,IC}$			$\frac{\mu_{max}}{1-\alpha_{3,CH4}} X_{bm} \frac{S_A}{K_s\ MC+S_A} I_{pH,Xbm} I_{NH3}$
4	**Decay X_{bha}**	$\alpha_{4,Xi}$		$1-\alpha_{4,Xi}-\alpha_{4,Si}$	-1						$\alpha_{4,Si}$	$k_4 X_{bha}$
5	**Decay X_{bm}**	$\alpha_{5,Xi}$		$1-\alpha_{5,Xi}-\alpha_{5,Si}$		-1					$\alpha_{5,Si}$	$k_5 X_{bm}$
		Particulate inert ($g_{COD}.kg^{-1}$)	Readily degradable particulate ($g_{COD}.kg^{-1}$)	Slowly degradable particulate ($g_{COD}.kg^{-1}$)	Hydrolytic biomass ($g_{COD}.kg^{-1}$)	Methanogenic biomass ($g_{COD}.kg^{-1}$)	Total acetate ($g_{COD}.kg^{-1}$)	Dissolved methane ($g_{COD}.kg^{-1}$)	Inorganic carbon ($mol.kg^{-1}$)	Inorganic nitrogen ($mol.kg^{-1}$)	Soluble inert ($g_{COD}.kg^{-1}$)	

Besides kinetics, the model includes mass transfer of components from the liquid to the gaseous phase for CH_4, CO_2 and NH_3. Resistance to liquid-gas mass transfer is characterised by the two-film theory of Whitman [31]. Since resistance to transfer is mainly in the liquid phase and because diffusivity of CH_4, CO_2 and NH_3 are similar, liquid–gas mass transfer coefficients ($k_{L,i}a$) are supposed to have the same value k_La. Thus, biogas production (CH_4, CO_2 and NH_3) is calculated from soluble concentrations through dynamic liquid-gas transfer equations as follows:

$$r_{liq-g\ \ ,i} = k_L a(S_i - MC \cdot H_i \cdot P_i) \tag{14}$$

where $r_{liq-gas,I}$ is the liquid to gas rate transfer of the gaseous component i ($g_{COD}.kg^{-1}.d^{-1}$ for CH_4 and $mol.kg^{-1}.d^{-1}$ for CO_2 and NH_3). It is necessary to correct H_i by the moisture content (MC) to account for the substrate wet mass unit basis of S_i. Furthermore, to change H_{CH4} from $M.atm^{-1}$ to $g_{COD}.L^{-1}.atm^{-1}$, the methane Henry constant is multiplied by a factor of 64.

Gathered in Table 2, 12 kinetic and mass transfer parameters are required to use the biochemical model considered in the present study. The reliability of the anaerobic digestion process modelling depends obviously on the consistency of these parameters.

2.5. Model implementation

The biological model is integrated in a continuous stirred tank reactor (CSTR) model as CSTR are the more commonly used reactors in the industrial treatment of livestock wastes [3]. Modelling of CSTR implies the hypothesis of a homogeneous media. Concentrations in the output flowrate (W_{out}) are equal to the concentrations in the reactor. Reactor feeding is assumed continuous and constant. The global volume of the CSTR is separated into a working volume (V_d) and a gas volume (V_{Gas}) as illustrated in Figure 1. The working volume is the medium (digestate) where all the bioconversion processes take place. The gas volume is supposed to be at atmospheric pressure and the global outlet biogas flowrate of the reactor is equal to the inlet biogas flowrate in V_{Gas}. This biogas production is therefore depending on the dynamical mass transfer equations Eq. (14).

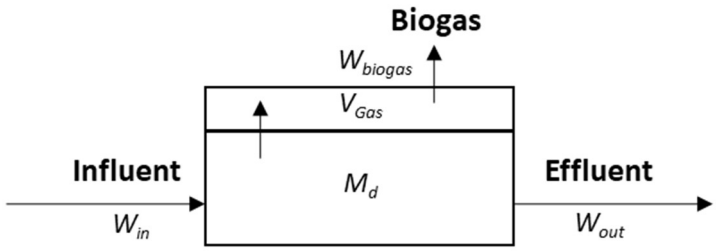

Figure 1: Representation of the continuous stirred tank reactor, influent mass flowrate (W_{in}), biogas mass flowrate (W_{biogas}), digestate mass flowrate (W_{out}), mass of media in the reactor (M_d) and volume of the gas phase of the reactor (V_{Gas}).

The partial pressures of CH_4, CO_2 and NH_3 in the reactor gas volume are expressed as follows:

$$P_i = G_i \cdot R \cdot T \tag{15}$$

where P_i is the partial pressure of the gaseous species i (CH_4, CO_2 or NH_3) (atm), G_i is the molar concentration of the gaseous specie (mol.L^{-1}), R is the ideal gas constant (L.atm.K^{-1}.mol^{-1}) and T is the digester temperature (K). Finally, the biogas production is expressed as follows:

$$q_G = \frac{RT}{P_{atm}} 10^{-3} M_d \left(\frac{r_{liq-gas,CH4}}{64} + r_{liq-gas,CO2} + r_{liq-gas,NH3} \right) \tag{16}$$

where q_G is the total biogas production (m^3.d^{-1}), and M_d is the mass of digestate in the reactor (kg). No mass balance on water is accounted for in this model because a preliminary study has shown that with a mass balance on water considering a saturated gas phase, the water steam represents less than 4% of the total biogas production. The total biogas mass flow is calculated as follows:

$$W_{biogas} = \frac{q_G}{RT} \sum_i P_i M_i \tag{17}$$

where W_{biogas} is the outlet mass flow of biogas (kg.d^{-1}), and M_i is the molar mass of the gaseous component i (g.mol^{-1}). The output mass flowrate (W_{out}) of digestate is then obtained from the global mass balance on the CSTR:

$$W_{out} = W_{in} - W_{biogas} \tag{18}$$

In the working volume, partial mass balances lead to a set of 10 differential equations:

$$\frac{dX_r}{dt} = \left(W_{in} X_{r_in} - W_{out} X_r \right) / M_d - r_1 \tag{19}$$

$$\frac{dX_s}{dt} = \left(W_{in}X_{s_in} - W_{out}X_s\right)/M_d - r_2 + \left(1 - \alpha_{4,Xi} - \alpha_{4,Si}\right)r_4 + (1 - \alpha_{5,Xi} - \alpha_{5,Si})r_5 \quad (20)$$

$$\frac{dX_I}{dt} = \left(W_{in}X_{I_in} - W_{out}X_I\right)/M_d + \alpha_{4,Xi}r_4 + \alpha_{5,Xi}r_5 \quad (21)$$

$$\frac{dX_{bha}}{dt} = \left(W_{in}X_{bha_in} - W_{out}X_{bha}\right)/M_d + (1 - \alpha_{1,A} - \alpha_{1,CH4})r_1 + \left(1 - \alpha_{2,A} - \alpha_{2,CH4}\right)r_2 - r_4 \quad (22)$$

$$\frac{dX_{bm}}{dt} = \left(W_{in}X_{bm_in} - W_{out}X_{bm}\right)/M_d + (1 - \alpha_{3,CH4})r_3 - r_5 \quad (23)$$

$$\frac{dS_A}{dt} = \left(W_{in}S_{A_in} - W_{out}S_A\right)/M_d + \alpha_{1,A}r_1 + \alpha_{2,A}r_2 - r_3 \quad (24)$$

$$\frac{dS_{CH4}}{dt} = \left(W_{in}S_{CH4_in} - W_{out}S_{CH4}\right)/M_d + \alpha_{1,CH4}r_1 + \alpha_{2,CH4}r_2 + \alpha_{3,CH4}r_3 - r_{liq-gas,CH4} \quad (25)$$

$$\frac{dS_{IC}}{dt} = \left(W_{in}S_{IC_in} - W_{out}S_{IC}\right)/M_d + \alpha_{1,IC}r_1 + \alpha_{2,IC}r_2 + \alpha_{3,IC}r_3 - r_{liq-gas,CO2} \quad (26)$$

$$\frac{dS_N}{dt} = \left(W_{in}S_{N_in} - W_{out}S_N\right)/M_d + \alpha_{1,N}r_1 + \alpha_{2,N}r_2 - r_{liq-gas,NH3} \quad (27)$$

$$\frac{dS_I}{dt} = \left(W_{in}S_{I_in} - W_{out}S_I\right)/M_d + \alpha_{4,Si}r_4 + \alpha_{5,Si}r_5 \quad (28)$$

In the gas phase, partial mass balances lead to the 3 following differential equations:

$$\frac{dG_{CH4}}{dt} = r_{liq-gas,CH4}\frac{M_d}{V_{Gas}10^3} - G_{CH4}\frac{q_G}{V_{Gas}} \quad (29)$$

$$\frac{dG_{CO2}}{dt} = r_{liq-gas,CO2}\frac{M_d}{V_{Gas}10^3} - G_{CO2}\frac{q_G}{V_{Gas}} \quad (30)$$

$$\frac{dG_{NH3}}{dt} = r_{liq-gas,NH3}\frac{M_d}{V_{Gas}10^3} - G_{NH3}\frac{q_G}{V_{Gas}} \quad (31)$$

A set of 4 algebraic equations corresponding to the acid-base equilibria (H^+/OH^-, CO_2/HCO_3^-, NH_3/NH_4^+, acetic acid/acetate) are used to calculate the concentrations of the dissociated species. These equations are gathered in the electroneutrality equation to calculate S_{H+} and subsequently pH.

$$\frac{S_N \cdot S_{H^+}}{(MC \cdot K_{a,\,NH_4^+} + S_{H^+})} + S_{H^+} + S_{cations} - \frac{MC \cdot K_{a,\,CO_2} \cdot S_{IC}}{(MC \cdot K_{a,\,CO_2} + S_{H^+})} - \frac{MC \cdot K_{a,S_A} \cdot \frac{S_A}{64}}{(MC \cdot K_{a,S_A} + S_{H^+})} - \frac{K_{a,\,H_2O} \cdot MC^2}{S_{H^+}} - S_{anions} = 0 \quad (32)$$

Acid-base constants ($K_{a,i}$) are determined from volumetric molar concentrations. The use of moisture content (MC) enables to change the base unit of $K_{a,i}$, from volumetric concentrations to mole per kilogram of wet substrate. Also, the moisture content is introduced to express the pH related to the liquid phase concentration.

S_{ions} is defined as the difference between the concentration of cations and anions ($S_{cations}$ - S_{anions}) that are not individually calculated in this model but that are necessary for pH resolution. It implies that S_{ions} can be positive or negative. The dynamical modelling approach leads to a last differential equation for S_{ions}:

$$\frac{dS_{ions}}{dt} = \left(W_{in}S_{ions_in} - W_{out}S_{ions}\right)/M_d \quad (33)$$

This model is implemented in Matlab R2019a and solved using the ode15s solver.

3. Simulation of a case study

3.1. From feedstock characterisation to model input variables

Composition and flowrate of raw substrate in the digester are taken from a potential running condition of digester treating agricultural wastes in Occitanie region in France, mainly composed of grass silage, straw and cattle manure (Table 3). The influent is diluted with water to reach a TS of 30%. This leads to a total influent mass flow (W_{in}) of 62.4 $t.d^{-1}$.

Table 3: Influent characteristics.

Substrate	Particulate + Soluble						Soluble fraction			
	Flow ($t.d^{-1}$)	TS[1] (%)	VS[2] (%)	BMP[3] ($NL.kg_{VS}^{-1}$)	COD ($g.kg^{-1}$)	TKN ($mol.kg^{-1}$)	COD ($g.kg^{-1}$)	VFA ($g_{COD}.kg^{-1}$)	N-NH_4 ($mol.kg^{-1}$)	pH
Cattle manure	6.3	25%	81%	203	310	0.4	30	5	0.00	8.0
Cattle slurry	0.6	9%	80%	222	108	0.3	19	2	0.06	8.0
Pig slurry	2.2	5%	69%	261	51	0.4	10	1	0.21	8.0
Poultry manure	4.4	58%	73%	286	680	2.5	61	11	1.24	8.0
Straw	8.2	89%	91%	248	1070	0.6	33	0	0.00	7.5
Grass silage	28.5	25%	87%	303	260	0.4	119	40	0.18	4.5
Influent	50.2	37%	86%	270	424	0.6	83	24	0.22	4.6
Total influent	62.4	30%	86%	270	341	0.5	66	20	0.177	4.6

[1] $g_{TS}.g_{raw\ substrate}^{-1}$

[2] Volatile solid content expressed in $g_{volatile\ solids}.g_{TS}^{-1}$

[3] Biochemical Methane Potential.

Since, in the present biological model, the DHA step directly leads to acetate formation, VFA in Table 3 are supposed to be acetate equivalent (S_A). The COD biodegradability of the soluble

organic matter is assumed to be equal to 80%, within the range of values found in literature [32,33]. This means that in the soluble fraction, 53 $g_{COD}.kg^{-1}$ are biodegradable, among which are the 20 $g_{COD}.kg^{-1}$ of VFA. The soluble COD that is not VFA is considered to be easily hydrolysable compounds (X_r) like soluble polymers. The slowly degradable particulate matter (X_s) is assumed as the total biodegradable particulate matter. Knowing the TS and the volatile solid content (VS) of the raw substrate (particulate and soluble), the BMP of the raw substrate is 69.66 $NL.kg_{raw\ substrate}^{-1}$. According to the COD concentration of the raw substrate, this BMP is also equal to 0.204 $NL.g_{COD}^{-1}$. Theoretically, the methane production from total degradation of one gram of COD is equal to 0.350 $NL.g_{COD}^{-1}$ [34]. Assuming that about 7% of the biodegradable COD is converted into biomass during AD processes, the biodegradability of the organic matter in the raw substrate can be calculated as follows:

$$\%_{\text{Biodegradability-ra}} = \frac{0.204}{0.350*(1-0.07)} * 100 = 62.7\% \quad (34)$$

The biodegradable organic matter concentration in the raw substrate is thus equal to 214 $g_{COD}.kg^{-1}$. Since the biodegradable soluble organic matter concentration is equal to 53 $g_{COD}.kg^{-1}$, the total biodegradable particulate matter is equal to 161 $g_{COD}.kg^{-1}$. The global anions and cations concentration (S_{ions}) is calculated before running simulations in order to fit initial pH of the media through the electroneutrality equation (Eq. (32)). Model input values are gathered in Table 4. Concentrations of hydrolytic and methanogenic biomasses as well as the concentration of dissolved IC in the influent are supposed to be negligible compared to the concentrations in the digester.

Table 4: Model input variables characteristic of the influent described in Table 3.

Variable	Value	Units
X_I	114	$g_{COD}.kg^{-1}$
X_s	161	$g_{COD}.kg^{-1}$
X_r	33	$g_{COD}.kg^{-1}$
X_{bha}	0	$g_{COD}.kg^{-1}$
X_{bm}	0	$g_{COD}.kg^{-1}$
S_I	13	$g_{COD}.kg^{-1}$
S_A	20	$g_{COD}.kg^{-1}$
S_{CH4}	0	$g_{COD}.kg^{-1}$
S_{IC}	0	$mol.kg^{-1}$
S_N	0.177	$mol.kg^{-1}$
S_{ions}	-0.0488	$mol.kg^{-1}$
W_{in}	62 408	$kg.d^{-1}$
pH	4.6	-
TS	30	%

3.2. Results

The model previously introduced is a dynamic model that enables to follow the evolution of the different variables over time. This work is based on the results obtained in steady state conditions (after 400 days). The reactor is working at 55°C and has a working volume (V_d) of 1200 m^3, corresponding to a digestate mass (M_d) of 1 200 tons, and has a gas volume (V_{Gas}) of 300 m^3. In order to simulate the anaerobic digestion of the agricultural substrate presented in Table 3 and Table 4, the 12 kinetic and mass transfer parameters are those presented in Table 5. These typical values are chosen within the limits found in the literature and are used to achieve the simulation that gives the model outputs presented in Table 6.

Table 5: Setting of the model parameters values for the simulation of AD of agricultural substrate.

Kinetic parameters	**Values**	**Bibliographical study**	**Sources**
k_1 (d^{-1})	0.43	0.16-0.7	[35–38]
k_2 (d^{-1})	0.07	0.015-0.12	[20,30,37,39–42]
μ_{max} (d^{-1})	0.6	0.4-0.8	[8,43]
Ks ($g_{COD}.L^{-1}$)	0.3	0.2-0.4	[8,43]
k_4 (d^{-1})	0.02	0.01-0.03	[1]
k_5 (d^{-1})	0.02	0.01-0.03	[1]
k_La (d^{-1})	1.75	0.02-5	[4,44]
$pH_{LL.Xbha}$	5	4.5-5.8	[1]
$pH_{UL.Xbha}$	7.5	7-8.5	[1]
pH_{LL_Xbm}	6	5.5-6.7	[1]
$pH_{UL.Xbm}$	8.5	8-8.5	[1]
K_i ($mol.L^{-1}$)	0.098	0.0028-0.18	[45]

The initial conditions in the digester are the ones of the influent except biomass concentrations (X_{bha} and X_{bm}). In order to model a seeded digester and to prevent pH inhibition and biomass decay due to the low initial pH (Table 3), the initial concentrations X_{bha} and X_{bm} are set to relatively high values, respectively 30 $g_{COD}.kg^{-1}$ and 100 $g_{COD}.kg^{-1}$.

For the chosen substrate (Table 4), the raw methane yield from the digestion of the agricultural substrate is about 0.17 $Nm^3_{CH4}.kg_{VS}^{-1}$ which corresponds to a degradation of the feedstock VS of 63%. This degradation percentage is of the same order of magnitude as the percentage encountered in the literature where values between 60% and 80% correspond to degradation percentage observed on full-scale plants treating agricultural wastes without a second digester [46]. Finally, the methane percentage in the biogas observed during the AD simulation is 53.14%. This result is consistent with values found in the literature, which are between 50% and 70% for full-scale AD of agricultural wastes [3,47]. Thus, the proposed simplified model enables to obtain typical results observed in AD processes similar than that considered in the present case study.

Table 6: Model output variables resulting from the simulation of the case study.

Particulate matter	
X_I ($g_{COD}.kg^{-1}$)	128.66
X_r ($g_{COD}.kg^{-1}$)	4.20
X_s ($g_{COD}.kg^{-1}$)	80.23
X_{bha} ($g_{COD}.kg^{-1}$)	9.54
X_{bm} ($g_{COD}.kg^{-1}$)	3.63
Soluble matter	
S_A ($g_{COD}.kg^{-1}$)	0.03
S_N ($mol.kg^{-1}$)	0.32
S_{H+} ($mol.kg^{-1}$)	7.70E-08
S_{IC} ($mol.kg^{-1}$)	0.31
S_{ions} ($mol.kg^{-1}$)	-0.05
S_{CH4} ($g_{COD}.kg^{-1}$)	3.64
S_I ($g_{COD}.kg^{-1}$)	15.51
Gas phase	
q_G ($Nm^{3}.d^{-1}$)	5007
G_{CH4} ($mol.L^{-1}$)	0.02
G_{CO2} ($mol.L^{-1}$)	0.02
G_{NH3} ($mol.L^{-1}$)	3.27E-05
$\%CH_4$	53.14%
$\%CO_2$	46.78%
$\%NH_3$	0.08%
Digester outputs	
pH	6.96
W_{biogas} ($kg.d^{-1}$)	6505
W_{out} ($kg.d^{-1}$)	55903

4. Method for global sensitivity analysis of the model by Definitive Screening Design

4.1. Kinetic and mass transfer parameter levels

The previous part shows the consistency of the model to represent the considered dry AD of a mixture of agricultural substrates. A global sensitivity analysis is implemented to determine the key model parameters that may strongly affect the simulation results and, therefore, to highlight the parameters that have to be carefully determined for the model to be reliable. In this work definitive screening design (DSD) method is used.

To perform the DSD method, three parameter levels are defined. These three levels (-1, 0, 1) correspond to parameter values (minimal, central, maximal) that allow to describe the range

of investigation. A bibliographical study (Table 5) has been carried out to choose reasonable ranges of the parameter values corresponding to the case studied in this work. The setting of the parameter levels is a delicate task since kinetic constants, especially hydrolysis constants (k_1 and k_2) and the maximum growth rate of methanogens (μ_{max}), depend on large extent of experimental conditions such as the inoculum [20], the moisture content [4,8,12], the temperature [43] or the mixing condition [22]. Among the large amount of published works on anaerobic digestion, the parameter ranges, presented in Table 7, have been determined using data identified on similar experimental conditions than that of the operating conditions of the process considered in this work i.e. thermophilic (55°C) condition, high solid content (>15%) and digestion of agricultural wastes. The central values correspond to those used in the case study presented in the previous part.

In details, the hydrolysis constants (k_1 and k_2) must be consistent with the two fractions of particulate matter considered in this work, namely readily and slowly degradable (X_r and X_s). X_s can be considered as lignocellulosic wastes for their low bioaccessibility [48]. Therefore, the value of k_2 is associated to manure hydrolysis rates because of high concentration of undigested lignocellulosic material in this kind of substrate. As X_r is assimilated to simple polymers, k_1 is associated to cellulose hydrolysis constants or more generally to hydrolysis constants of substrates with higher concentrations of more accessible carbohydrates such as corn silage or grass silage [13,21]. Acetoclastic methanogenesis kinetics (μ_{max} and K_s) are set as recommended by the ADM1 for liquid anaerobic digestion. Nevertheless, several papers reveal that mass transfer limitation caused by a decrease in moisture content results in a diminution in the apparent methanogenesis rate [4,8,12,49]. An increase in TS from 20% to 35% may result in a decrease in methanogenic activity of 66% [49]. The value of μ_{max} proposed by the ADM1, 0.8 d^{-1}, is thus chosen as the upper level for the maximum specific growth rate for methanogens. Reductions of respectively 25 % and 50% are assumed to set the central value and the minimal value in the case of very high solid content causing mass transfer limitations [49]. The upper and lower levels of the first order decay constants (k_4 and k_5) and the pH inhibition limits correspond to the limits given by the ADM1. The values of the free ammonia inhibition constant (K_i) exhibit a large disparity in the concentration threshold of free ammonia (FAN) that degrades methanogens activity. A review has highlighted the existence of six different clusters corresponding to six K_i values [45]. The values of K_i

corresponding to livestock waste vary from 0.015 mol.L^{-1} to 0.18 mol.L^{-1}. Finally, mass transfer coefficient (k_La) has been less studied or even considered as non-limiting, which gives rise to a large range of values [4]. Moreover, the k_La value is directly linked to the moisture content, to the digester technology, to the medium physical properties and to the mixing condition of the system. Liquid-gas mass transfer coefficient of CO_2 of about 3 d^{-1} has been measured in a CSTR during liquid AD of activated sludge [50]. Similar k_La value has been found during the dry AD of municipal solid wastes (80% of moisture content) mixed by biogas injections [44]. Since a decrease of moisture content has a strongly negative impact on mass transfer phenomena [51], the value of 3 d^{-1} is here set as the upper level of k_La. The minimal value of 0.5 d^{-1} corresponds to k_La value calculated in the case of dry AD of municipal solid wastes without mixing system [44].

Table 7: Kinetic and mass transfer parameters and the associated levels for the DSD.

Kinetic parameters	**Min (-1)**	**Central (0)**	**Max (1)**
k_1 (d^{-1})	0.16	0.43	0.7
k_2 (d^{-1})	0.02	0.07	0.12
μ_{max} (d^{-1})	0.4	0.6	0.8
Ks (g_{COD}.L^{-1})	0.2	0.3	0.4
k_4 (d^{-1})	0.01	0.02	0.03
k_5 (d^{-1})	0.01	0.02	0.03
k_La (d^{-1})	0.5	1.75	3
$pH_{LL.Xbha}$	4.5	5	5.5
$pH_{UL.Xbha}$	7	7.5	8
pH_{LL_Xbm}	5.5	6	6.5
$pH_{UL.Xbm}$	8	8.5	9
K_i (mol.L^{-1})	0.015	0.098	0.18

4.2. Screening design of running simulations

The DSD has been constructed from the systematic approach developed by Phoa and Lin [25]. This construction method is based on the D-efficiency optimisation and provides design for any number of parameters. As the number of parameters is 12, the screening design matrix, noted X, presented in Table 8, implies 25 runs. Among the model outputs, the responses considered in the DSD are biogas production (q_G), pH and percentage of CH_4 in the biogas (%CH_4) because these variables are usually monitored on industrial digesters as indicators of

productivity and stability of the system. The further work is to assess the main effects of variations in the parameter levels on these model outputs.

4.3. Model outputs interpretation

For each model output of interest, multiple regression analysis is used to assess the main effect of each parameter present in the DSD. From the multiple regression, each model output value obtained from the running simulations, can be expressed as a function of the parameter values. The corresponding multiple linear regression model of each model output can be written as follows:

$$\hat{Y} = \beta_0 + \sum_{k=1}^{12} \beta_k x_k \quad (35)$$

where $\hat{Y}$ is the response given by multiple linear regression for a model output Y (q_G, pH or $\%CH_4$), β_0 is a constant, β_k is a constant giving the main effect of parameter k on Y and x_k is the level of parameter k. The coefficient β_k can be interpreted as the average growth rate of the model output Y depending on the level parameter x_k when all other regressors remain fixed. Coefficients β_k would be obtained with an infinite number of runs by continuously varying the parameters x_k in the considered intervals defined in Table 7. Since the present DSD matrix (Table 8) includes 25 runs, it is only possible to calculate estimates of the coefficients β_k namely $\widehat{\beta_k}$ which are obtained by multiple regression on each model output for the 25 runs. The response given by the multiple regression can be written as follows:

$$\hat{Y} = \widehat{\beta_0} + \sum_{k=1}^{12} \widehat{\beta_k} x_k \quad (36)$$

where $\widehat{\beta_0}$ is an estimate of β_0, $\widehat{\beta_k}$ is an estimate of the main effect of the parameter k on Y and x_k is the level of parameter k. For each run, each model output value Y_i can be expressed from the multiple regression and a residual term reflecting the difference between the value of the response given by the AD model and the value resulting from multiple linear regression:

$$Y_i = \hat{Y}_i + \hat{\varepsilon}_i \quad (37)$$

where Y_i is the observed AD model output value (q_G, pH or $\%CH_4$) for the ith run, $\hat{Y}_i$ is the response given by the multiple linear regression (q_G, pH or $\%CH_4$) for the ith run and $\widehat{\varepsilon_i}$ is the residual term for the ith run. The least square method is used to estimate the constants of each multiple linear regression carried out on each model output. Based on the assumption that

the residual term follows a normal distribution $N(0,\hat{\sigma}^2)$, it is established that the estimate $\widehat{\beta_k}$ follows a normal distribution $N(\beta_k,\sigma_{\beta,k}^2)$. The variance $\sigma_{\beta,k}^2$ is unknown but can be estimated from the experimental design matrix (X) and the calculation of the variance of the residual term ($\hat{\sigma}^2$) [52]:

$$\hat{\sigma}_{\beta,k}^2 = (X^T X)_{k,k}^{-1} \hat{\sigma}^2 \tag{38}$$

where $\hat{\sigma}_{\beta,k}^2$ is the estimate of the variance of $\widehat{\beta_k}$, $(X^T X)_{k,k}^{-1}$ is the diagonal term of the matrix $(X^T X)^{-1}$ corresponding to the parameter k and $\hat{\sigma}^2$ is the estimate of the residual term variance.

Once the multiple regression is done, estimates of the main effects ($\widehat{\beta_k}$) and the residual term are known. Because $\hat{\sigma}_{\beta,k}^2$ is an estimate of the real variance of $\widehat{\beta_k}$, the standardised probability density function of $\widehat{\beta_k}$ follows a Student t-distribution. The degrees of freedom of the Student t-distribution is 12 since the screening design includes 25 runs for 13 constants to set (from $\widehat{\beta_0}$ to $\widehat{\beta_{12}}$). The standardised probability density function can be written as follows:

$$L\left(\frac{\widehat{\beta_k}-\beta_k}{\hat{\sigma}_{\beta,k}^2}\right) = t_{12} \tag{39}$$

where t_{12} is the Student t-distribution with a degree of freedom equal to 12.

The significance of each coefficient $\widehat{\beta_k}$ on the corresponding model output Y is tested, based on the H_0 hypothesis which assumes that a given coefficient is not significant. Under the H_0 hypothesis, the main effect β_k of the parameter k on the model output Y is assumed to be null (in Eq. (39)). The corresponding t-value is calculated from Eq. (39) and its p-value is estimated. The p-value is the probability that the H_0 hypothesis is true: an effect is considered to be significant when $p < 0.05$ [52]. However, if a parameter effect had a p-value higher than but close to 0.05, the parameter would not be disregarded and its effect would be discussed.

All multiple linear regressions were performed using the MATLAB R2019a software with the "stepwiselm" function allowing to directly estimate the parameters with significant effect (p-value < 0.05) and to set the corresponding regression equation for each model output. For each regression, the Durbin-Watson test and the Shapiro test (p-value > 0.05) are performed on residuals terms to respectively detect the presence of autocorrelation and to confirm that the residuals are normally distributed.

5. Results and discussion

The DSD method is applied to the parameters defined in Table 7 resulting in 25 simulation runs. The parameter settings and the associated model outputs are listed in Table 8.

Table 8: Screening design matrix obtained for 12 variable parameters from the application of the construction method of Phoa and Lin [25] and the associated model outputs values for the biogas flowrate, the percentage of methane in the biogas and the pH.

	Kinetic and mass transfer parameter levels ($x_{i,j}$)												**Model outputs (Y_i)**		
Runs	x_{k_1}	x_{k_2}	$x_{\mu_{max}}$	x_{K_s}	x_{k_7}	x_{k_8}	$x_{k_L a}$	$x_{pH_{LL,Xbha}}$	$x_{pH_{UL,Xbha}}$	$x_{pH_{LL,Xbm}}$	$x_{pH_{UL,Xbm}}$	x_{K_i}	q_G ($Nm^3.d^{-1}$)	$\%CH_4$	pH
1	0	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	2896	54.2	6.58
2	1	0	-1	-1	-1	-1	-1	1	1	1	1	1	4896	53.2	6.48
3	1	1	0	-1	-1	1	1	-1	-1	1	-1	1	4923	53.1	7.15
4	1	1	1	0	-1	-1	1	-1	1	-1	1	-1	5961	52.8	7.13
5	1	1	1	1	0	-1	-1	1	-1	1	-1	-1	5608	53.0	6.46
6	1	1	-1	1	1	0	-1	-1	1	-1	-1	1	5678	53.0	6.46
7	1	1	-1	-1	1	1	0	1	-1	-1	1	-1	5583	53.0	6.94
8	1	-1	1	1	-1	1	-1	0	-1	-1	1	1	3030	54.1	6.57
9	1	-1	1	-1	1	-1	1	1	0	-1	-1	1	3207	53.9	7.19
10	1	-1	-1	1	-1	1	1	1	1	0	-1	-1	3429	53.7	7.18
11	1	-1	1	-1	1	1	-1	-1	1	1	0	-1	3217	54.0	6.56
12	1	-1	-1	1	1	-1	1	-1	-1	1	1	0	2520	54.5	7.23
13	0	1	1	1	1	1	1	1	1	1	1	1	6066	52.8	7.13
14	-1	0	1	1	1	1	1	-1	-1	-1	-1	-1	3702	53.6	7.17
15	-1	-1	0	1	1	-1	-1	1	1	-1	1	-1	3015	54.1	6.57
16	-1	-1	-1	0	1	1	-1	1	-1	1	-1	1	2925	54.2	6.58
17	-1	-1	-1	-1	0	1	1	-1	1	-1	1	1	3130	53.9	7.20
18	-1	-1	1	-1	-1	0	1	1	-1	1	1	-1	2360	54.7	7.24
19	-1	-1	1	1	-1	-1	0	-1	1	1	-1	1	3140	54.0	7.03
20	-1	1	-1	-1	1	-1	1	0	1	1	-1	-1	5828	52.8	7.13
21	-1	1	-1	1	-1	1	-1	-1	0	1	1	-1	5389	53.1	6.46
22	-1	1	1	-1	1	-1	-1	-1	-1	0	1	1	5241	53.1	6.47
23	-1	1	-1	1	-1	-1	1	1	-1	-1	0	1	4923	53.1	7.15
24	-1	1	1	-1	-1	1	-1	1	1	-1	-1	0	5415	53.1	6.47
25	0	0	0	0	0	0	0	0	0	0	0	0	5007	53.1	6.96

To ensure that the results do not depend on the chosen set of runs presented in Table 8, several tests were carried out by varying the order of parameters in the DSD matrix. Despite slight differences in the coefficients values, conclusions of the sensitivity analysis were identical revealing the same significant parameters.

5.1. Biogas production

Over all the simulations, the value of biogas production varies between 2360 $Nm^3.d^{-1}$ and 6066 $Nm^3.d^{-1}$ for a mean value of 4284 $Nm^3.d^{-1}$. Lowest and highest specific methane yields correspond to the minimum and the maximum biogas productions and are respectively of 0.08 and 0.20 $Nm^3_{CH4}.kg_{VS}^{-1}$. The statistical analysis reveals that only variations in the kinetic parameters related to the hydrolysis step have significant effects on the overall biogas production values (Table 9). These parameters are the first order hydrolysis constants k_1, k_2 and the upper pH inhibition limit of the hydrolytic biomass $pH_{UL,Xbha}$. Effects of the other parameters of the model have a p-value greater than 0.05 and are therefore not considered to have a significant impact on the biogas production.

Table 9: Parameters with significant effect on the biogas production, each with its coefficient value (main effect) and the corresponding p-probability.

Model output	Parameter main effects			
	$\hat{\beta}_0$	$\hat{\beta}_{k_1}$	$\hat{\beta}_{k_2}$	$\hat{\beta}_{pH_{UL,Xbha}}$
q_G ($Nm^3.d^{-1}$)	4284 ($p < 0.0001$)	136 ($p = 0.0312$)	1261 ($p < 0.0001$)	276 ($p = 0.0001$)

The corresponding multiple linear equation of the biogas production as a function of x_{k_1}, x_{k_2} and $x_{pH_{UL,Xbha}}$ can be written as follows:

$$q_G = 4284 + 136\, x_{k_1} + 1261\, x_{k_2} + 276\, x_{pH_{UL,Xbha}} \quad (40)$$

The Durbin-Watson test and the Shapiro test performed on the residuals reveal that residuals are independent and follow a normal distribution.

It can be deduced from this equation that a variation in the level of k_2 (from 0 to -1 or from 0 to 1) is responsible for a variation in biogas production of 30% around the mean value while a variation in the levels of $pH_{UL,Xbha}$ and k_1 would be respectively responsible for variations of 6% and 3%. The positive sign in front of levels of the kinetic constants k_1 and k_2 in Eq. (40) indicates that an increase in hydrolysis rates, implying an increase in the acetate production, causes an increase in biogas production. An increase in the level of $pH_{UL,Xbha}$ has a positive impact on the biogas production. In fact, simulations demonstrate that, under the hypothesis of a perfectly

stirred reactor, the pH of the media at steady state resulting from the degradation of the influent used in this study is around 7 (Table 8). As the pH value is closed to $pH_{UL,Xbha}$ which gives the value of $I_{ph,Xbha}$ in Eq. (12), the higher the value of $pH_{UL,Xbha}$ is, the closer to 1 the value of $I_{ph,Xbha}$ is. Furthermore, variations in methanogenesis kinetic parameters do not appear to affect significantly biogas production. It shows that, within the limits of the sensitivity study (substrate characteristics and parameter variation ranges), almost all the acetate is converted by methanogens and that little or no inhibition occurs during the methanogenesis.

The results of the global sensitivity analysis performed on the biogas production have been compared to data from the literature. Schroyen et al. [17] carried out a global sensitivity analysis on the kinetic parameters of their simplified ADM1 model using Monte-Carlo sampling method. They reported that, the hydrolysis constant was the most influential parameter to simulate the methane production during the anaerobic digestion of lignocellulosic substrates. Weinrich et al. [53] have compared the complex structure of the ADM1 to different simplified model structures to simulate experimental data of AD of agricultural waste. They have proved that hydrolysis is the rate-limiting step during the uninhibited anaerobic digestion of complex particulate substrates since the reduction of the kinetics of the methanogenesis, acidogenesis and acetogenesis only have a little effect on the simulated biogas production. However, no similar results were found in the literature regarding the influence of $pH_{UL,Xbha}$ on the biogas production.

Thus, the first order kinetic constant k_2 has the larger impact on the biogas production. To rightly describe and predict biogas production from the anaerobic digestion of the previously presented substrate, this kinetic parameter as well as $pH_{UL,Xbha}$ should be precisely identified. The constant k_2 is substrate dependant but the large influence of its value on q_G suggests that it can be identified from experiments conducted in continuous flow for various substrates by following the biogas production.

5.2. Methane percentage in the biogas

Execution of the DSD matrix developed in Table 8 reveals the low variability of the methane percentage in the biogas (%CH_4) given by the biological modelling. Among the values obtained from the DSD application, the minimum, maximum and the mean value of %CH_4 are respectively 52.77%, 54.66% and 53.52%. In the biological model presented in this study, the

same number of moles of inorganic carbon and methane is produced during the hydrolysis and methanogenic steps. This leads to values of $\%CH_4$ close to 50%. The parameter variations of the first order hydrolysis constant k_2 and the upper pH inhibition limit of the hydrolytic biomass $pH_{UL,Xbha}$ are significantly responsible for the $\%CH_4$ variability (Table 10).

Table 10: Parameters with significant effect on the methane percentage in the biogas, each with its coefficient value (main effect) and the corresponding p-probability.

Model output	**Parameter main effects**		
	$\hat{\beta}_0$	$\hat{\beta}_{k_2}$	$\hat{\beta}_{pH_{UL,Xbha}}$
$\%CH_4$	53.52 ($p < 0.0001$)	- 0.57 ($p < 0.0001$)	- 0.14 ($p = 0.0019$)

Estimates of the main effects of these parameters on the $\%CH_4$ can be transcribed in the multiple linear equation of the methane percentage.

$$\%CH_4 = 53.52 - 0.57\, x_{k_2} - 0.14\, x_{pH_{UL,Xbha}} \quad (41)$$

The Durbin-Watson test and the Shapiro test carried out on the residuals terms of the regression reveal that residuals are independent and follow a normal distribution.

Differences in concentration in the gas phase are mainly due to differences in Henry's law constants of CO_2 and CH_4 (at 55°C, H_{CH4}= 0.0009 $mol.atm^{-1}.L^{-1}$ [54] and H_{CO2}=0.0180 $mol.atm^{-1}.L^{-1}$ [55]) and to the proportion of inorganic carbon produced as bicarbonate. Increases in k_2 and $pH_{UL,Xbha}$ result in a combined increase in inorganic carbon production and a decrease in pH. However, as the pH decreases, the concentration of inorganic carbon in acid form, namely CO_2, increases and therefore the quantity of CO_2 that desorbs is greater, which means that the proportion of CO_2 in the gas increases to the detriment of $\%CH_4$. Nevertheless, as said before, methane percentage in biogas is not significantly influenced by the model parameter values in the investigated ranges: this output is therefore not relevant, in the range of this study, to identify the parameters of the model.

5.3. pH

The pH values observed during the simulations range from 6.46 to 7.24 around a mean value of 6.86. No pH value falls into an acidic range which explains the low impact of pH_{LL} values on the different model outputs. Variations in the level of parameters k_2 and k_La have significant effects on the pH value observed in steady state (Table 11).

Table 11: Parameters with significant effect on the pH in the reactor, each with its coefficient value (main effect) and the corresponding p-probability.

Model output	Parameter main effects		
	$\hat{\beta}_0$	$\hat{\beta}_{k_2}$	$\hat{\beta}_{k_L a}$
pH	6.86 ($p < 0.0001$)	- 0.04 ($p = 0.0003$)	0.33 ($p < 0.0001$)

The equation corresponding to the multiple linear regression made on the pH values is:

$$\mathrm{pH} = 6.86 - 0.04\, x_{k_2} + 0.33\, x_{k_L a} \quad (42)$$

The Durbin-Watson test performed on the residuals terms of the regression reveals that residuals are independent. However, the Shapiro test (not detailed) has shown that residuals do not follow a Gaussian distribution. By adding the square term of only one of the two selected parameters (x_{kLa}^2), the Shapiro test reveals that residuals follow a normal distribution. This confirms that the screening analysis of the pH can be carried out by these parameters alone

This shows that the main effect of k_2 is 8 times lower than the main effect of k_La. The main effect of k_2 is a combination of the influences of the inorganic nitrogen, acetate and inorganic carbon productions on the pH. Since no inhibition of the methanogenesis occurs, the acetate is mostly consumed by methanogens. Thus, the concentrations of inorganic carbon and nitrogen insure the medium alkalinity. An increase in k_2 leads to a slight increase in the proportion of inorganic carbon to inorganic nitrogen and thus a decrease in pH. In the observed pH range (between 6.49 and 7.25), the free ammonia (NH_3) fraction is extremely low. It means that the positive main effect of the k_La is linked to a higher CO_2 desorption when k_La increases.

The volumetric liquid/gas mass transfer coefficient value suggested in the ADM1 is 200 d^{-1} [4]. This reflects the low mass transfer limitation that may occur in wet anaerobic digestion. However, it has been demonstrated in several papers that a limitation to the transfer of gaseous species due to the high TS or to mixing problems may occur in the case of dry anaerobic digestion [4,49]. The sensitivity analysis highlights that for low ranges of k_La value the CO_2 oversaturation has the greater impact on the media alkalinity. This result is consistent with the work of Pauss et al. [50] which shows that low k_La values imply insoluble gas over-concentrations such as CH_4 and H_2 but also CO_2 responsible of medium acidification. In order to simulate the inhibitory effects of pH, caused by CO_2 accumulation, occurring during the dry anaerobic digestion of cardboards, Abbassi-Guendouz et al. [4] had to drastically reduced the k_La value of the ADM1. These literature data confirm that the k_La value can be significant to model the pH evolution of digestion media of high solid content substrates.

Since the mass transfer coefficient has the most significant impact on the pH media, it can be deduced that k_La could be identified by fitting the pH of experiments conducted in continuous flow.

6. Conclusion

The present work shows the reliability of a global sensitivity analysis methodology to assess model parameters that significantly influence anaerobic digestion model outputs. This method uses Definitive Screening Design technique, as its major advantage is the estimation of unbiased main effects of parameter variations on model outputs from a low number of runs. The global sensitivity analysis method is performed on the kinetic and mass transfer parameters of a simplified ADM1 model for dry AD of agricultural wastes. The statistical multiple regression analysis is used to estimate the significant main effects of the parameters on chosen significant model outputs (biogas flowrate, methane percentage in the biogas and pH).

The implementation of this global sensitivity analysis method reveals that hydrolysis constant k_2 as well as $pH_{UL,Xbha}$ should mainly be targeted for identification due to their significant influences on the biogas production given by the model. The mass transfer coefficient k_La is found to have a significant impact on the pH of the media whereas the methane percentage given by the model presents a low variability whatever the parameter values are.

Furthermore, the low impact of the hydrolysis constant k_1 on model outputs suggests that the model could be further simplified. Results of the global sensitivity analysis also highlight that there is no significant inhibition of methanogenesis during the AD of the agricultural waste considered in the study. Complementary work should be addressed on the simplified model to measure the influence of input conditions, notably the organic nitrogen content, on the global sensitivity analysis results. It would allow to check if potential inhibition issues modify the global sensitivity analysis results. Finally, the low number of runs required for the present method makes its application easy to any type of model from simplified to more complex models. The low computational time and reliability of the method presented enables its application to any type of digestion model.

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Notations

d	Density of the digestion media
G_{CH4}	Gaseous CH_4 concentration ($mol.L^{-1}$)
G_{CO2}	Gaseous CO_2 concentration ($mol.L^{-1}$)
G_{NH3}	Gaseous NH_3 concentration ($mol.L^{-1}$)
H_i	Henry's law constant for component i ($mol.atm^{-1}.L^{-1}$)
$K_{a,i}$	Acid-base equilibrium constant for component i ($mol.L^{-1}$)
K_i	Half inhibition concentration of free ammonia for methanogens ($mol.L^{-1}$)
k_La	Liquid-gas mass transfer coefficient (d^{-1})

K_s Half saturation constant of methanogens for acetate ($mol.L^{-1}$)

k_1 First order hydrolysis rate constant for readily degradable particulate (d^{-1})

k_2 First order hydrolysis rate constant for slowly degradable particulate (d^{-1})

k_4 First order decay rate constant of hydrolytic biomass (d^{-1})

k_5 First order decay rate constant of methanogens (d^{-1})

MC Moisture Content (%)

M_d Mass of media in the reactor (kg)

P_{atm} Total pressure (atm)

P_{CH4} CH_4 partial pressure (atm)

P_{CO2} CO_2 partial pressure (atm)

P_{NH3} NH_3 partial pressure (atm)

$pH_{LL,i}$ Lower limit of pH for 50% inhibitory effect on biomass i

$pH_{UL,i}$ Upper limit of pH for 50% inhibitory effect on biomass i

q_G Biogas production flowrate ($m^3.d^{-1}$)

R Gas law constant (8.2058 x 10-2 $L.atm.K^{-1}.mol^{-1}$)

r_j Kinetic rate of process j ($g_{COD}.kg^{-1}.d^{-1}$ or $mol.kg^{-1}.d^{-1}$ for inorganic carbon or nitrogen)

S_A Acetate concentration ($g_{COD}.kg^{-1}$)

S_{CH4} Methane concentration ($g_{COD}.kg^{-1}$)

S_{CO2} Soluble carbon dioxide concentration ($mol.kg^{-1}$)

S_{H+} Hydronium concentration ($mol.L^{-1}$)

S_I Soluble inert concentration ($g_{COD}.kg^{-1}$)

S_{IC} Total inorganic carbon concentration ($mol.kg^{-1}$)

S_{ions} Inactive ionic species concentration ($mol.L^{-1}$)

S_N Total inorganic nitrogen concentration ($mol.kg^{-1}$)

S_{NH3} Soluble free ammonia concentration ($mol.kg^{-1}$)

T Temperature (K)

TS Total solid content (%)

V_d Volume of media in the reactor (m^3)

V_{Gas} Volume of the gas phase in the reactor (m^3)

W_{biogas} Biogas mass flowrate ($kg.d^{-1}$)

W_{in} Influent mass flowrate ($kg.d^{-1}$)

W_{out} Raw digestate mass flowrate ($kg.d^{-1}$)

X_{bha} Hydrolytic biomass concentration ($g_{COD}.kg^{-1}$)

X_{bm} Methanogenic biomass concentration ($g_{COD}.kg^{-1}$)

X_I Particulate inert concentration ($g_{COD}.kg^{-1}$)

X_r Readily degradable particulate concentration ($g_{COD}.kg^{-1}$)

X_s Slowly degradable particulate concentration ($g_{COD}.kg^{-1}$)

$\alpha_{1,i}$ Stoichiometric coefficient of component i from readily degradable particulate

$\alpha_{2,i}$ Stoichiometric coefficient of component i from slowly degradable particulate

$\alpha_{3,i}$ Stoichiometric coefficient of component i from degradable soluble

$\alpha_{4,i}$ Stoichiometric coefficient of component i from decay of hydrolytic biomass

$\alpha_{5,i}$ Stoichiometric coefficient of component i from decay of methanogenic biomass

μ_{max} Monod maximum specific growth rate for methanogens (d^{-1})

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