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Towards Anaerobic Digestion (ADM No.1) Model's Extensions and Reductions with In-situ Gas Injection for Biomethane Production *

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Abstract: The necessity to focus and work with renewable energy for value-added product generation has gained interest in recent years, which has led to the development of mathematical models that allow a better understanding and optimization of these processes. In this work an extension of the anaerobic digestion model (ADM No. 1) with H₂ and CO external gas injection was proposed. Therefore, the modification of the volumetric mass transfer coefficient in terms of gas injection and the use of CO as a substrate of the process were proposed. Then, a model reduction was performed applying the principal process analysis (PPA) methodology with two threshold values $\delta=0.05$ and $\delta=0.1$. The R^2 , AIC_c criterium, and Global Relative Error (%Error) were used to compare the model and reductions performance. The threshold value $\delta=0.05$ presented the best results with an $R^2 > 0.99$ and AIC_c criterium of -114 compared to the experimental process. For the %Error, values of 2.32%, 1.38%, and 2.18% were achieved for H₂, CH₄, and CO outlet gas flowrates when the reduction $\delta=0.05$ is compared with the complete model. This reduction also allowed to decrease the simulation time from 1.94s to 0.82s. Thus, concluding that a first reduced model approximation is possible for the biomethanation process.

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Keywords: Biomethanation process, ADM No.1 extension, Gas injection, Model reduction, Biomethane production.

1. INTRODUCTION

The over-exploitation of non-renewable fossil-derived fuels associated with this increased energy demand has led to their progressive exhaustion worldwide. In addition, their use has generated multiple adverse effects on the environment, e.g., greenhouse gases emitted into the atmosphere that contributes to global warming effects, which has forced us to look for possible alternatives for renewable resources (Dar et al., 2021; Grimalt-Alemany et al., 2020; Hupfauf et al., 2020).

One of the alternatives studied to mitigate these impacts is the biomethanation process. It consists of a sequential degradation of organic compounds by a large variety of complex microorganisms that work synergistically and produce a mixture of CH₄ and CO₂, all in an oxygen-free environment (Dar et al., 2021).

This process entails four phases that transform biomasses into methane and CO₂: (i) hydrolysis, (ii) acidogenesis, (iii) acetogenesis, and (iv) methanogenesis. In the first phase, the fermentative bacteria excrete enzymes that dissolve complex material. In the second phase, these compounds are transformed into volatile fatty acids (VFA). In

the third phase, those VFA are converted into acetate, H₂, CO₂, and cell material. Finally, in the fourth phase, different substrates such as acetate, H₂, and CO₂ are converted by methanogenic archaea into CH₄ and new cell material.

In literature, several works employed models in the biomethanation process to use control strategies (Ashraf et al., 2020; Dev et al., 2019), analyze the degradation of raw materials or agro-industrial waste (Batstone et al., 2002; Rosen et al., 2006; Sun et al., 2021), or microbial consortium control (Grimalt-Alemany et al., 2020).

Another research area that gained interest in the last year is biogas injection to improve the biomethanation process efficiency (Jensen et al., 2018). Generally, the syngas (gas composed of H₂, CO₂, and CO) conversion efficiency into CH₄ increased from less than 68% up to 95% (Sun et al., 2021). Here, there are several challenges, like differentiating between the efficiency generated by gas injection or the conventional process (Rafrafi et al., 2020). However, through the model and simulation of the biomethanation process, it is possible to make differentiations easily.

In this study, an extension of the ADM No.1 model (ADM1_ME) is proposed. It includes the injection in-situ of gases, such as H₂ and CO, and the use of homoacetogenic bacteria and CO as a substrate of the process.

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This model considers a volumetric mass transfer coefficient in terms of the gas injected for all components in the gas phase. Finally, the model is reduced using the Principal Process Analysis (PPA) methodology proposed by Casagrande et al. (2015), which allows obtaining a simple model that preserves its phenomenology with the possibility to use it in optimization and control process, e.g., the development of optimal control strategies.

2. EXPERIMENTAL DATA FROM LITERATURE REVIEW

Experimental data were taken from the literature (Sun et al., 2021). The entire experiment (first 32 days and stages I-V) was carried out in a working volume of $3.75 \times 10^{-2} m^3$. The bioreactor was operated at a hydraulic retention time (HRT) of 20 days at $37^\circ C$ for 207 days. The organic loading rate (OLR) was $10.66 kg_{COD}/m^3$ of glucose with an inlet liquid flowrate ($q_{liq,in}$) of $1.9 \times 10^{-3} m^3/d$. The gas injection was carried out in five stages, in which the injected gas flowrate ($q_{gas,in}$) and the gas loading rate (GLR), i.e., the COD kilograms (kg_{COD}) of H_2 and CO injected into the gas phase were varied in time. To model the process, the initial concentrations of H_2 and CO in gas phase ($S_{i,in}^g$) were calculated by using (1). All values are reported in Table 1.

$$S_{i,in}^g = \frac{GLR \cdot \phi_i \cdot \gamma_{COD,i}}{q_{gas,in} \cdot V_m} \quad (1)$$

where ϕ_i is the gas molar fraction of the component i , $\gamma_{COD,i}$ ($kg/kmol$) is the chemical oxygen demand (amount of oxygen needed to degrade the compound i into CO_2 and H_2O), V_m is the molar volume, for an ideal gas, $22.4 m^3/kmol$.

Table 1. Experimental conditions in each stage.
Taken from (Sun et al., 2021).

Stage	Time (Days)	Injected gas flowrate (m^3/d)	Gas loading rate (m^3/d) $\times 10^{-2}$	Initial concentration gas phase (kg_{COD}/m^3) $\times 10^{-3}$	
				H_2	CO
-	1-32	-	-	-	-
A	33-64	0.09	0.75	20.83	38.69
B	65-101	1.44	0.75	1.30	2.42
C	102-135	2.88	1.50	1.30	2.41
D	136-171	2.88	3.75	3.26	6.04
E	172-207	5.76	3.75	1.63	3.02

3. DEVELOPMENT MODEL

3.1 States, Inputs and Outputs in ADM1_ME

To model and simulate the biomethanation process, a bubble column reactor with a working volume of $3.75 \times 10^{-2} m^3$ is proposed. Operating at a HRT of 20 days at $37^\circ C$ for 207 days. The ADM1_ME presents sixteen state variables, reported in Table 2.

As input variables the ADM1_ME presents an OLR of $10.66 kg_{COD}/m^3$ of glucose, with an inlet liquid flowrate of $1.9 \times 10^{-3} m^3/d$. The injected gas flowrate was varied over time; values are reported in Table 1. As output variables, the model have the outlet gas flowrates of H_2 , CH_4 , and CO. The model assumptions are: the gas molar fraction volume is one-third of the working volume, the height of the bubble column reactor is $h_{reactor} = 1.2 m$, the reactor cross-sectional area $A = 3.13 \times 10^{-2} m^2$ is calculated for a bubble column reactor with the V_{liq} and $h_{reactor}$, and the

volumetric mass transfer coefficient for the first 32 days is $200 1/d$ (Rosen et al., 2006).

For each variable state mass balance is proposed:

Variable states in gas phase $S_{gas,i}$ were calculated by using (2)-(4),

$$\frac{dS_{gas,H_2}}{dt} = \frac{q_{gas,in}}{V_{gas}} S_{H_2,in}^g + \xi N_{H_2} - \frac{q_{gas}}{V_{gas}} S_{gas,H_2} \quad (2)$$

$$\frac{dS_{gas,CH_4}}{dt} = \frac{q_{gas,in}}{V_{gas}} S_{CH_4,in}^g + \xi N_{CH_4} - \frac{q_{gas}}{V_{gas}} S_{gas,CH_4} \quad (3)$$

$$\frac{dS_{gas,CO}}{dt} = \frac{q_{gas,in}}{V_{gas}} S_{CO,in}^g + \xi N_{CO} - \frac{q_{gas}}{V_{gas}} S_{gas,CO} \quad (4)$$

Variable states in liquid phase $S_{liq,i}$ were calculated by using (5)-(11),

$$\frac{dS_{liq,su}}{dt} = D(S_{su,in}^l - S_{liq,su}) - r_{su} \quad (5)$$

$$\frac{dS_{liq,bu}}{dt} = D(S_{bu,in}^l - S_{liq,bu}) + (1 - Y_{su})\beta_{bu,su}r_{su} - r_{bu} \quad (6)$$

$$\frac{dS_{liq,pro}}{dt} = D(S_{pro,in}^l - S_{liq,pro}) + (1 - Y_{su})\beta_{pro,su}r_{su} - r_{pro} \quad (7)$$

$$\begin{aligned} \frac{dS_{liq,ac}}{dt} = & D(S_{ac,in}^l - S_{liq,ac}) + (1 - Y_{su})\beta_{ac,su}r_{su} \\ & + (1 - Y_{bu})\beta_{ac,bu}r_{bu} + (1 - Y_{pro})\beta_{ac,pro}r_{pro} - r_{ac} \\ & + (1 - Y_{CO})\beta_{ac,CO}r_{CO} \end{aligned} \quad (8)$$

$$\frac{dS_{liq,CO}}{dt} = D(S_{CO,in}^l - S_{liq,CO}) - r_{CO} + N_{CO} \quad (9)$$

$$\begin{aligned} \frac{dS_{liq,CH_4}}{dt} = & D(S_{CH_4,in}^l - S_{liq,CH_4}) + (1 - Y_{ac})r_{ac} \\ & + (1 - Y_{H_2})r_{H_2} \end{aligned} \quad (10)$$

$$\begin{aligned} \frac{dS_{liq,H_2}}{dt} = & D(S_{H_2,in}^l - S_{liq,H_2}) + (1 - Y_{su})\beta_{H_2,su}r_{su} \\ & + (1 - Y_{bu})\beta_{H_2,bu}r_{bu} + (1 - Y_{pro})\beta_{H_2,pro}r_{pro} \\ & - r_{H_2} - N_{H_2} + (1 - Y_{CO})\beta_{H_2,CO}r_{CO} \end{aligned} \quad (11)$$

Variables states biomass growth X_k , were calculated by using (12)-(17),

$$\frac{dX_{su}}{dt} = \frac{q_{liq,in}}{V_{liq}} (X_{su,in} - X_{su}) + Y_{su}r_{su} + Y_{dec,su}r_{su} \quad (12)$$

$$\frac{dX_{bu}}{dt} = \frac{q_{liq,in}}{V_{liq}} (X_{bu,in} - X_{bu}) + Y_{bu}r_{bu} + Y_{dec,bu}r_{bu} \quad (13)$$

$$\frac{dX_{pro}}{dt} = \frac{q_{liq,in}}{V_{liq}} (X_{pro,in} - X_{pro}) + Y_{pro}r_{pro} + Y_{dec,pro}r_{pro} \quad (14)$$

$$\frac{dX_{ac}}{dt} = \frac{q_{liq,in}}{V_{liq}} (X_{ac,in} - X_{ac}) + Y_{ac}r_{ac} + Y_{dec,ac}r_{ac} \quad (15)$$

$$\frac{dX_{CO}}{dt} = \frac{q_{liq,in}}{V_{liq}} (X_{CO,in} - X_{CO}) + Y_{CO}r_{CO} + Y_{dec,CO}r_{CO} \quad (16)$$

$$\frac{dX_{H_2}}{dt} = \frac{q_{liq,in}}{V_{liq}} (X_{H_2,in} - X_{H_2}) + Y_{H_2}r_{H_2} + Y_{dec,H_2}r_{H_2} \quad (17)$$

where $\xi = V_{liq}/V_{gas}$, $D = q_{liq,in}/V_{liq}$, $q_{liq,in}$, and $q_{gas,in}$ are the inlet liquid and injected gas flowrates, V_{liq} (m^3) and V_{gas} (m^3) are the working and gas molar fraction volume, r_k ($kg_{COD}/m^3 d$) are the biochemical rates, $\beta_{j,k}$ are the stoichiometric coefficients, $S_{i,in}^g$ (kg_{COD}/m^3) and $S_{j,in}^g$ (kg_{COD}/m^3) are the inlet concentration of component i and j to the gas and liquid phase, $X_{k,in}$ (kg_{COD}/m^3) is the inlet concentration of biomass k , $r_{dec,k}$ (kg_{COD}/m^3) is the decay rate of biomass associated of component k , N_i (kg_{COD}/m^3) is the mass transfer rate of component i , Y_k ($kg_{COD,k}/kg_{COD,j}$) is the yield of biomass k , and q_{gas}

(m^3/d) is the total outlet gas flowrate calculated by using (18).

$$q_{gas} = K_P (P_{gas} - P_{atm} + q_{gas,in}) \quad (18)$$

where K_P ($m^3/bar d$) is a parameter related to the friction in the outlet gas flowrate (Rosen et al., 2006), P_{gas} (bar) and P_{atm} (bar) are the total gas and atmospheric pressure. Finally, using (19) is calculated the outlet gas flowrate of the component i .

$$q_{gas,i} = q_{gas} \left(\frac{p_{gas,i}}{P_{gas}} \right) \quad (19)$$

here $p_{gas,i}$ (bar) is the partial pressure of component i .

Table 2. Variable states in ADM1_ME.

Variable States (kg_{COD}/m^3)		
1	H ₂ gas concentration	S_{gas,H_2}
2	CH ₄ gas concentration	S_{gas,CH_4}
3	CO gas concentration	$S_{gas,CO}$
4	Glucose liquid concentration	$S_{liq,glu}$
5	Butyrate liquid concentration	$S_{liq,bu}$
6	Propionate liquid concentration	$S_{liq,pro}$
7	H ₂ liquid concentration	S_{liq,H_2}
8	Acetate liquid concentration	$S_{liq,ac}$
9	CO liquid concentration	$S_{liq,CO}$
10	CH ₄ liquid concentration	S_{liq,CH_4}
11	Glucose biomass	X_{glu}
12	Butyrate biomass	X_{bu}
13	Propionate biomass	X_{pro}
14	Acetate biomass	X_{ac}
15	H ₂ biomass	X_{H_2}
16	CO biomass	X_{CO}

3.2 Biochemical Processes

In ADM1_ME, the gases injection becomes significant since it can affect the behavior of the biomethanation process. Therefore, the inclusion of CO was proposed as a substrate, which can be degraded by homoacetogenic bacteria to acetate or CH₄ obtention (Ashraf et al., 2020; Sun et al., 2021). Applying (20)-(25), the biochemical reaction rates are calculated as Monod kinetics type.

$$r_{su} = \frac{\mu_{m,su} S_{liq,su}}{K_{S_{su}} + S_{liq,su}} X_{su} \quad (20)$$

$$r_{bu} = \frac{\mu_{m,bu} S_{liq,bu}}{K_{S_{bu}} + S_{liq,bu}} X_{bu} I_{H_2, bu} I_{CO, H_2} \quad (21)$$

$$r_{pro} = \frac{\mu_{m,pro} S_{liq,pro}}{K_{S_{pro}} + S_{liq,pro}} X_{pro} I_{H_2, pro} I_{CO, H_2} \quad (22)$$

$$r_{ac} = \frac{\mu_{m,ac} S_{liq,ac}}{K_{S_{ac}} + S_{liq,ac}} X_{ac} I_{H_2, ac} I_{CO, ac} \quad (23)$$

$$r_{CO} = \frac{\mu_{m,CO} S_{liq,CO}}{K_{S_{CO}} + S_{liq,CO}} X_{CO} \quad (24)$$

$$r_{H_2} = \frac{\mu_{m,H_2} S_{liq,H_2}}{K_{S_{H_2}} + S_{liq,H_2}} X_{H_2} I_{CO, H_2} \quad (25)$$

where $\mu_{m,k}$ ($1/d$) is the maximum specific growth rate, K_{S_k} (kg_{COD}/m^3) is the saturation constant. The reaction rates of butyrate, propionate, and acetate express inhibition concerning H₂, through $I_{H_2, bu}$, $I_{H_2, pro}$, and $I_{H_2, ac}$, which can be calculated by using (26)-(28).

$$I_{H_2, bu} = \frac{1}{1 + S_{liq, H_2} / KI_{H_2, bu}} \quad (26)$$

$$I_{H_2, pro} = \frac{1}{1 + S_{liq, H_2} / KI_{H_2, pro}} \quad (27)$$

$$I_{H_2, ac} = \frac{1}{1 + S_{liq, H_2} / KI_{H_2, ac}} \quad (28)$$

The reaction rates of butyrate, propionate, and acetate express inhibition concerning CO, through $I_{CO, ac}$, and I_{CO, H_2} , which can be calculated by using (29)-(30).

$$I_{CO, ac} = \frac{1}{1 + S_{liq, CO} / KI_{CO, ac}} \quad (29)$$

$$I_{CO, H_2} = \frac{1}{1 + S_{liq, CO} / KI_{CO, H_2}} \quad (30)$$

where $KI_{H_2, bu}$, $KI_{H_2, pro}$, and $KI_{H_2, ac}$ are the inhibition constants by H₂ over butyrate, propionate, and acetate. $KI_{CO, ac}$, KI_{CO, H_2} are the inhibition constants by CO over acetate and H₂. And first order kinetics for decay biomass were proposed in (31) with $K_{k, dec}$ ($1/d$) as the decay biomass constant.

$$r_{k, dec} = K_{k, dec} X_k \quad (31)$$

3.3 Gas-liquid Mass Transfer Process

Volumetric Mass Transfer Coefficient. Following the modification of the gas injection, it is necessary to analyze its effect on the physicochemical part of the biomethanation process. Therefore, the volumetric mass transfer coefficients proposed by Batstone et al. (2002) and Sun et al. (2021) were modified. The principal reason is that it lacks a direct integration with the injection of gases into different process, which does not allow a physical behavior of the concept of mass transfer. Hence, volumetric mass transfer coefficient (k_{LAME}) was proposed to take into account the gas injection of the system in bubble column reactors (Klaas Van't, 1979) as,

$$k_{LAME} = \beta U_g^\alpha \quad (32)$$

here β and α are parameters that change with the conditions. U_g (m/d) is the superficial gas velocity, which can be calculated by using (33).

$$U_g = \frac{q_{gas, in}}{A} \quad (33)$$

where A (m^2) represents the reactor cross-sectional area. To differentiate the volumetric mass transfer coefficients for each component, applying (34) we computed the k_{LAME, CH_4} and $k_{LAME, CO}$ in terms of the k_{LAME, H_2} .

$$k_{LAME, i} = k_{LAME, H_2} \sqrt{\frac{D_i}{D_{H_2}}} \quad (34)$$

here D_i (m^2/s) indicates the diffusivity of component i .

Mass Transfer Rates. In this work, the mass transfer rates for H₂, CO and CH₄ can be calculated by using (35).

$$N_i = k_{LAME, i} (S_{liq, j} - \gamma_{COD, i} H_i P_{gas, i}) \quad (35)$$

where H_i is the Henry's law equilibrium constant. The signs of the mass transfer rates in the mass balance are maintained according to Batstone et al. (2002), and the direction of the mass transfer is controlled by the driving force, and depends on the existence or not of gas injection; the parameters used are reported in Table 3.

Table 3. Parameters in ADM1_ME.

Parameter	Value	Parameter	Value
$\beta_{bu,su}$	0.13	$\mu_{m,bu}(1/d)$	20
$\beta_{pro,su}$	0.27	$\mu_{m,pro}(1/d)$	13
$\beta_{ac,su}$	0.41	$\mu_{m,ac}(1/d)$	12.5
$\beta_{H_2,su}$	0.19	$\mu_{m,CO}(1/d)$	75
$\beta_{ac,bu}$	0.8	$\mu_{m,H_2}(1/d)$	90
$\beta_{H_2,bu}$	0.2	$K_{S_{su}}(kgCOD/m^3)$	0.02
$\beta_{ac,pro}$	0.57	$K_{S_{bu}}(kgCOD/m^3)$	0.3
$\beta_{H_2,pro}$	0.43	$K_{S_{pro}}(kgCOD/m^3)$	0.3
$\beta_{ac,CO}$	0.3	$K_{S_{ac}}(kgCOD/m^3)$	0.05
$\beta_{H_2,CO}$	0.7	$K_{S_{CO}}(kgCOD/m^3)$	8×10^{-6}
$Y_{su}(kgCOD,k/kgCOD,j)$	0.06	$K_{S_{H_2}}(kgCOD/m^3)$	1×10^{-6}
$Y_{bu}(kgCOD,k/kgCOD,j)$	0.06	$Kk_{dec}(1/d)$	0.02
$Y_{pro}(kgCOD,k/kgCOD,j)$	0.04	$KI_{H_2,bu}(kgCOD/m^3)$	1×10^{-5}
$Y_{ac}(kgCOD,k/kgCOD,j)$	0.05	$KI_{H_2,pro}(kgCOD/m^3)$	3.5×10^{-6}
$Y_{CO}(kgCOD,k/kgCOD,j)$	0.25	$KI_{H_2,ac}(kgCOD/m^3)$	1×10^{-6}
$Y_{H_2}(kgCOD,k/kgCOD,j)$	0.006	$KI_{CO,ac}(kgCOD/m^3)$	1×10^{-6}
$\mu_{m,su}(1/d)$	45	$KI_{CO,H_2}(kgCOD/m^3)$	1×10^{-6}

3.4 Parameter estimation

One of the main contributions in this research is the modification of the volumetric mass transfer coefficient. Therefore, the parameters K_P , β , and α in (18) and (32) were estimated for this case. With (36) is computed the sum of squared errors (*SSE*) using as adjusted variables the outlet gas flowrate of CH_4 , CO , and H_2 .

$$SSE_i = \frac{q_{gas,i}^e - q_{gas,i}}{\max(q_{gas,i}^e)} \quad (36)$$

where $q_{gas,i}^e$ is the experimental outlet gas flowrate, and $\max(q_{gas,i}^e)$ corresponds to the maximum experimental value. Once the SSE_i is determined for each outlet gas flowrate, the minimization of their sums, is performed by using (37) in order to reduce the error between the experimental and model data.

$$SSE_{total} = \sum_{i=1}^n SSE_i \quad (37)$$

4. ADM1_ME REDUCTION METHODOLOGY

Non-linear models could presents difficulties for use in the online optimization and control process because they have several parameters and equations that need high time calculations. In literature, some research proposes a model reduction to improve time calculation (Bernard and Bastin, 2005). In this study, the methodology proposed by Casagrande et al. (2015) was applied. Principal Process Analysis (PPA) is a methodology that allows analyzing the key processes. Consider the following ordinary differential equation (ODE) model of biological network,

$$\frac{dS}{dt} = F(S, p) \quad (38)$$

where $S = (S_1, S_2, \dots, S_n) \in R^n$ is the vector of variable states, $S^0 = (S_1^0, S_1^0, \dots, S_n^0) \in R^n$ is the vector of the initial conditions, p^b is the vector of parameters. Each equation is decomposed into a sum of biological processes as,

$$\frac{dS_n}{dt} = \sum_j f_{i,n}(S, p) \quad (39)$$

where $f_{i,n}$ represents the i process involved in the dynamical evolution of the n variable of the system over a period $[0, t]$. As example, the variable state acetate in the liquid phase is rewritten as,

$$\frac{dS_8}{dt} = f_{1,8} + f_{2,8} + f_{3,8} + f_{4,8} + f_{5,8} + f_{6,8} + f_{7,8} \quad (40)$$

with $f_{1,8} = DS_{in,ac}$, $f_{2,8} = -DS_{in,ac}$, \dots $f_{7,8} = (1 - Y_{CO})\beta_{ac,CO}r_{CO}$. Once the decomposition of the state variable into the different processes has been carried out, the analysis of the weight of each one is performed, i.e., a criterion must be proposed that allows weighing the influence of the different processes $f_{i,j}$ on the time evolution of each variable S_n .

$$W_{i,n}(t, p) = \frac{|f_{i,n}(S(t), p)|}{|\sum_i f_{i,n}(S(t), p)|} \quad (41)$$

where $0 \leq W_{i,n}(t, p) \leq 1$ and $\sum_i W_{i,n}(t, p) = 1$. Commonly to consider or discard processes in the reduction methodology, a threshold value (δ) is necessary. If $W_{i,n} < \delta$, the process $f_{i,n}$ might be discarded in the state n , else must be considered. Casagrande et al. (2015) proposed to use a threshold value of 10%. Two criteria were used to compare the model and its reductions. The Global Relative Error (% Error) calculated as,

$$\%Error = \frac{\sum |y_{n,model} - y_{n,model,re}|}{\sum |y_{n,model,re}|} \cdot 100\% \quad (42)$$

And the AIC_c criterium calculated as,

$$AIC_c = AIC + \frac{2K(K+1)}{n-K-1} \quad (43)$$

This criterium permit compare the models by taking into account the number of variables and parameters in each model, and sample size (Burnham and Anderson, 2004). AIC can be calculated by using (44).

$$AIC = 2K + n [\log(2\pi) + 1 - \log(n) + \log(WSSE)] \quad (44)$$

K is the number of parameters in each model, n is the number of data to compare the models (sample size), and $WSSE$ is the weighted sum of squared errors.

5. RESULTS AND DISCUSSION

5.1 Parameter Estimation

The models were run in a processor Intel(R) Core(TM) i7-8665U CPU @ 1.90GHz 2.11 GHz. For the parameters estimation the *fmincon* function from MATLAB was used, and the parameters β , α , and K_P , were estimated by minimize the function SSE_{total} . The initial value of β , and α , 0.467 and 0.82, were taken from (Klaas Van't, 1979), for superficial gas velocity less than 0.1 m/s, and the value of K_P , 5×10^4 ($m^3/bard$) was taken from (Rosen et al., 2006). Finally, a $SSE_{total}=5.46$ was achieved, and the estimated value of β , α , and K_P were 11, 0.95, and 6×10^4 ($m^3/bard$), respectively.

5.2 ADM1_ME Proposal and Reduction Development

In this work, two threshold values were evaluated, $\delta=0.05$, and $\delta=0.1$, meaning that $f_{i,n}$ must be discarded if the weight ($W_{i,n}$) is less than 5% or 10%, respectively. Table 4 presents the %Error for the outputs model, q_{gas,CH_4} , q_{gas,H_2} , and $q_{gas,CO}$. The maximal %Error was 2.32% for H_2 with $\delta=0.05$, respect to 27.52% with $\delta=0.1$. It is possible to conclude that the reduction with a threshold $\delta=0.05$ presents a better adjustment concerning $\delta=0.1$.

Table 4. %Error for outlet gas flowrates in ADM1_ME reductions.

Model Outputs	% Error ($\delta = 0.05$)	%Error ($\delta = 0.1$)
$q_{gas,CH4}$	1.38	26.15
$q_{gas,H2}$	2.32	27.53
$q_{gas,CO}$	2.18	26.80

Table 5. R^2 , AIC_c , and simulation time for ADM1_ME and its reductions.

Criterion	ADM1_ME	ADM1_ME ($\delta = 0.05$)	ADM1_ME ($\delta = 0.1$)
R^2	0.9951	0.9945	0.9785
AIC	-197.1335	-134.0685	74.9102
AIC_c	-176.1335	-114.0518	94.9634
$t_{simu}(s)$	1.94	0.8247	1.0429

t_{simu} : Simulation time

From the statistical point of view (see Table 5), the ADM1_ME model presents a better adjustment, followed by the reduction with $\delta=0.05$ and finally $\delta=0.1$. If we focus on the R^2 , it is possible to conclude that the ADM1_ME model and the reduction with $\delta=0.05$ adjust the experimental data ($R^2 > 0.99$) and can be used to represent the process. However, it is necessary to consider other aspects. For this reason, the AIC and AIC_c have an important role.

AIC and AIC_c values for the reduction $\delta=0.1$ permit us to conclude that this model reduction presents a lack in the representation of the experimental process. For the ADM1_ME and the reduction $\delta=0.05$, AIC of -176.13 and -114.01 were achieved, meaning that both of them represent properly the experimental process. In addition, the use of $\delta=0.05$ achieved a decrease in the simulation time from 1.94 s to 0.82 s.

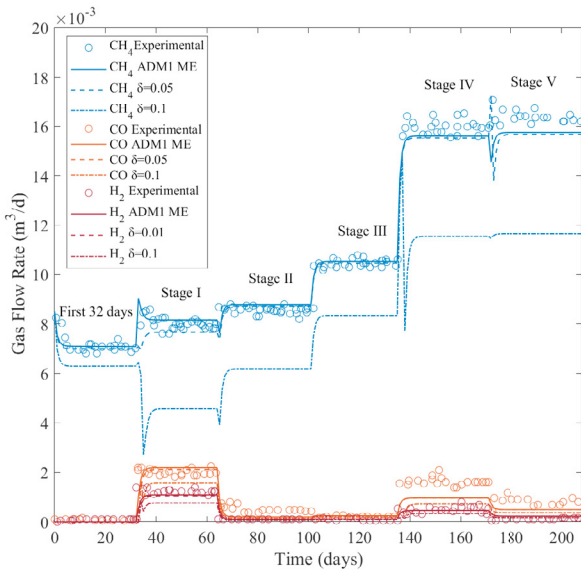


Fig. 1. Outlet gas flowrates $q_{gas,H2}$, $q_{gas,CH4}$, and $q_{gas,CO}$ in ADM1_ME (-), and reductions $\delta=0.05$ (- -), $\delta=0.1$ (- · -).

Figure 1 presents the dynamic behavior of the adjusted variables $q_{gas,H2}$, $q_{gas,CH4}$, and $q_{gas,CO}$. It is observed how the adjusted ADM1_ME model manages to reproduce

the experimental data for all stages and the first 32 days of the process. It is also evident how a reduction with $\delta=0.05$ replicates the experimental data, even better than the ADM1_ME at the beginning of stage I. The reduction $\delta=0.1$ fails to reproduce the experimental data, especially for $q_{gas,CH4}$ and $q_{gas,CO}$. These differences are associated with the removed processes in the reduction. A detailed explanation is presented in section 6.2.

6. DEEP INSIDE IN THE ADM1_ME AND ITS REDUCTIONS

6.1 Gas percent in ADM1_ME

A comparison between ADM1_ME and its reduction in terms of gas percent for H_2 , CH_4 , and CO is presented in Table 6. The %Error for all components with $\delta=0.05$ is less than 17%, concerning 19% with $\delta=0.1$. For $\delta=0.05$, the best accuracy was achieved for CH_4 gas percent, with %Error of 1.68% concerning 10.37% and 16.70% obtained for H_2 and CO gas percents, variables directly implicated in the gas injection.

Table 6. %Error for H_2 , CH_4 , and CO percent between ADM1_ME and its reduction.

Component Percent	% Error ($\delta=0.05$)	% Error ($\delta=0.1$)
H_2 gas percent	10.37	17.00
CH_4 gas percent	1.68	1.52
CO gas percent	16.70	19.11

Table 7 presents the %Error for $q_{gas,H2}$, $q_{gas,CH4}$, and $q_{gas,CO}$ for the model and its reductions concerning the experimental data from the literature. The ADM1_ME achieved %Error up to 17%, in relation to the reduction $\delta=0.05$ and $\delta=0.1$, where errors less than 18%, and 46% were achieved.

Table 7. %Error for ADM1_ME and its reduction respect to experimental data.

Component	% Error (Sun et al., 2021)	% Error (ADM1_ME)	% Error ($\delta=0.05$)	% Error ($\delta=0.1$)
$q_{gas,H2}$	24.84	17.02	17.77	43.62
$q_{gas,CH4}$	1.86	2.92	1.32	27.64
$q_{gas,CO}$	12.63	13.55	12.70	45.15

6.2 Principal Differences Between ADM1_ME Reductions

The differences in the reductions are given by the removed processes in the variable states $S_{liq,ac}$ and $S_{gas,H2}$. $S_{liq,ac}$ is composed of seven processes $f_{1,8}$, $f_{2,8}$, ..., and $f_{7,8}$, previously described. In $\delta=0.1$ is suggested to eliminate the terms $f_{4,8} = (1 - Y_{bu})\beta_{ac,bu}r_{bu}$ in all stages, $f_{5,8} = (1 - Y_{pro})\beta_{ac,pro}r_{pro}$ in the stages IV and V, and $f_{7,8} = (1 - Y_{CO})\beta_{ac,co}r_{CO}$ for stages I, II, and III. Which generate a significant loss in the acetate variable and influence the $q_{gas,CH4}$. For this reason, all the state variables associated with acetate show marked differences.

Similarly happens with the state $S_{liq,H2}$. It is composed of 8 processes $f_{1,11} = D(S_{H2,in}^l)$, $f_{2,11} = -D(S_{liq,H2})$, $f_{3,11} = (1 - Y_{su})\beta_{H2,su}r_{su}$, $f_{4,11} = (1 - Y_{bu})\beta_{H2,bu}r_{bu}$, $f_{5,11} = +(1 - Y_{pro})\beta_{H2,pro}r_{pro}$, $f_{6,11} = -r_{H2}$, $f_{7,11} = -N_{H2}$, and $f_{8,11} = +(1 - Y_{CO})\beta_{H2,co}r_{CO}$. Both threshold

values suggest eliminating $f_{4,11}$, but only $\delta=0.1$ suggest eliminating $f_{5,11}$, and this change generates notable differences, especially in stage I.

6.3 Comparison of ADM1_ME with other models

The ADM1_ME and the Sun et al. (2021) models have a good representation of the experimental process. %Error of 17.02% and 2.92% for q_{gas,H_2} , and q_{gas,CH_4} , were achieved with the ADM1_ME. In the Sun et al. (2021) model, %Error of 24.84% and 1.86% were respectively achieved. In the case of $q_{gas,CO}$, the Sun et al. (2021) model presents an error of 12.63% concerning 13.55% with the ADM1_ME (see Table 7). Finally, it is possible to conclude that the modified equation to represent the volumetric mass transfer coefficient with the injection of gases and the estimation of its parameters permits a better approximation of the experimental process.

7. CONCLUSIONS

The extended model (ADM1 ME) and its reduction allowed to generate advances in the understanding in the modeling of the biomethanation process with gases injection such as H_2 and CO , in addition, the modification of the volumetric mass transfer coefficient dependent on the injected gas flowrate was proposed.

The model was adjusted to the experimental data selected from the literature, where an SSE of 5.46 was obtained by adjustment of the parameters β , α , and K_P , which are directly associated with the proposed equation for the volumetric mass transfer coefficient.

The PPA methodology was applied, with two threshold values, $\delta=0.1$ and $\delta=0.05$. For the second one, $R^2 > 0.99$, ACI_c of -114, and simulation time of 0.82s were achieved, respect to $R^2 > 0.99$, ACI_c of -176.13, and simulation time of 1.94s obtained in the ADM1_ME. This makes the reduction $\delta=0.05$ suitable to represent the biomethanation process. However, it is necessary to take care with the selection of the threshold values. Changes from a threshold value of $\delta=0.05$ to $\delta=0.1$ can generate important variations. Therefore, the selection of the threshold must be analyzed in detail.

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