Batch Single-Stage Co-Digestion of Olive Mill Wastewater with Cattle Manure: Modeling, Simulation, and Validation

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ABSTRACT

The co-digestion of agri-food by-products, such as Olive Mill Waste (OMW) and Cattle Manure (CM), is an efficient method for waste management and biogas production. OMW, characterized by a high soluble organic content, low methane yield, and limited biodegradability, contrasts with the easily degradable properties of CM. The synergistic use of these wastes enhances the hydrolytic-acidogenic phase, increasing the availability of Volatile Fatty Acids (VFAs) and thereby boosting biogas production through bacterial fermentation of VFAs. This study introduces a novel mathematical model for mesophilic anaerobic co-digestion of OMW and CM in batch reactors. The uniqueness of the model lies in its ability to balance comprehensiveness with simplicity, implemented in MATLAB, for both precision and user-friendliness. Its focus on crucial factors, such as total VFA and methane generation, sets it apart in the field of anaerobic digestion modeling. The exceptional performance of the model is evidenced by its high accuracy in predicting experimental results, achieving impressive R^2 values of 0.96469 and 0.99133 for 50:50 and 75:25 OMW to CM ratios, respectively. These results demonstrated the robustness of the model in simulating key co-digestion parameters across varying substrate compositions. By enhancing the feasibility of numerical computation while maintaining high predictive accuracy, this approach represents a significant advance in biogas production optimization. The practical applicability and accuracy of the model make it a valuable tool for optimizing real-world waste management and renewable energy production processes, potentially leading to improved methane yields and overall biogas production.

Keywords-ADM1; simulation; amaerobic co-digestion; OMW

I. INTRODUCTION

Tunisia, which lacks significant reserves of oil, gas, and coal, is distinguished by its extensive olive production. Efforts have focused on improving the quality of olive oil and expanding olive cultivation [1]. However, the olive industry faces significant challenges owing to the large quantities of by-products, primarily Olive Mill Wastewater (OMW) and pomace, which are highly polluting because of their rich phenolic compounds. These by-products raise environmental concerns for their impact on aquatic ecosystems [2, 3]. Researchers are actively investigating methods for treating and processing OMW to mitigate this problem [4]. Anaerobic Digestion (AD) is highly valued for its ability to reduce pollutants and produce biogas that is used to generate renewable energy [5]. Biogas produced by AD has the potential to meet a significant portion of the world's natural gas demand [6]. The single-substrate AD processes encounter issues such as digester instability and low biogas yield. However, Anaerobic Co-Digestion (ACOD) of multiple substrates is a viable solution [7]. To understand and enhance AD processes, modern static and dynamic models such as AM2 [8] and ADM1 [9] play crucial roles. These models facilitate the simulation of AD behavior under varying conditions and ensure efficient control strategies for industrial facilities [9]. Despite its widespread use, the ADM1 model is nonlinear and complex, posing challenges for optimization. Therefore, a more concise alternative is needed. Efforts are ongoing to simplify the ADM1 model, while preserving its predictive capability and dynamic characteristics.

This study aims to develop a comprehensive yet simplified mathematical model to predict the dynamic behavior and optimize the performance of a batch reactor used for the mesophilic co-digestion of OMW and CM. The model balances accuracy and simplicity, facilitates numerical calculations, and provides reliable forecasts for reactor optimization.

II. METHODS

A. Raw Materials

OMW and CM were used as raw materials in this study. The OMW was sourced from a three-phase olive oil extraction unit in Hamma, Gabès, Tunisia, while the CM was collected from farms in the oases of Gabès, Tunisia.

B. Analytical Methods

The parameters pH, Total Chemical Oxygen Demand (TCOD), Total Solids (TS), Volatile Solids (VS), Total Alkalinity (TA), Total Kjeldahl Nitrogen, and Total Volatile Fatty Acid (TVFA) of OMW and CM were estimated utilizing standard methods [10]. Analyses were performed in triplicate and reported in mg of acetic acid equivalent per L (HAceq/L) and mg$CaCO_3$/L [11]. Table I lists the characteristics of the OMW and CM employed in this study.

C. OMW/CM Experimental Setup of Batch Anaerobic Digestion

The batch experiments were performed using 1 L digesters with a working volume of 800 mL. A schematic representation of the anaerobic digestion system is shown in Figure 1. Two co-substrates and two substrate mixtures were tested: RCM, ROMW, R50:50, and R75:25, each loaded according to Table II. These ratios were selected based on the optimal C/N ratio for the development of anaerobic processes [12]. In this study, mesophilic digestion was employed, maintaining a water bath at 38 ± 1 °C for optimal biodigestion. An electric heater regulated the temperature, while the pH of the mixture was adjusted to approximately 8.0 using nutrients and carbonates.

TABLE I. CHARACTERISTICS OF THE OMW AND CM USED IN THIS STUDY

Parameter	OMW	CM
pH	5.2±0.2	8.2±0.3
TS (g/kg)	295.00±10.1	152.80±5.5
VS (g/kg)	262.6±13.1	121.55±7.0
TCOD (gO_2/kg)	160.25±3.1	96±5.1
TVFA (mgHAceq/L)	1426.20±3.5	890.12±1.5
TKN (gN/kg)	2.22±0.1	5.56±0.1
Soluble phenols (g/L)	5.8±0.1	1.12±0.02
Alkalinity ($gCaCO_3$/L)	3.12±0.2	9.50±0.15

The reactor had two outlets: one connected to a nitrogen gas bottle for 5 min to remove oxygen and establish anaerobic conditions, and the other (flask number three in Figure 1) collected the gases produced during fermentation. This outlet contained 0.1 N sulfuric acid to eliminate NH_3. The remaining gases (O_2, H_2, and CH_4) were collected in a sealed, inverted burette, while CO_2 and H_2S were bubbled through a NaOH (5M) and $Ca(OH)_2$ solution (number 4 in Figure 1) for capture. Gas collection commenced when solution 4 reached the top of the graded burette and gas was extracted using a vacuum pump. The sludge was then incubated for 35 d with OMW, and the experiment ended when the gas output dropped below 3 mL/24h. The daily gas volume in the burette during fermentation was recorded to calculate the biogas moles, and samples of the fermentation medium were collected from the reactors twice per week. Experiments were performed in triplicate.

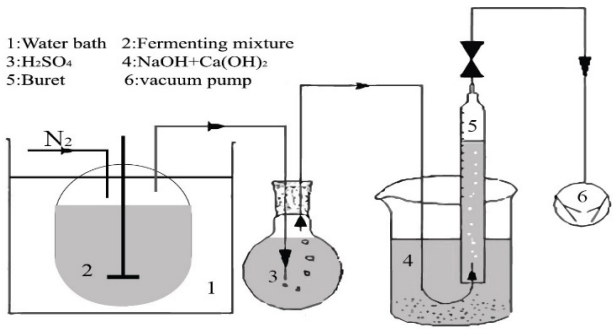

Fig. 1. Schematic of the anaerobic digestion system.

TABLE II. COMPOSITIONS OF CO -SUBSTRATES AND TWO SUBSTRATE MIXTURES (R50:50 AND R75:25)

Reactor	OMW (%)	CM (%)	Total phenols (g/L)
RCM	0	100	1.12±0.02
ROMW	100	0	5.8±0.1
R50 :50	50	50	2.17±0.1
R 75 :25	75	50	3.85±0.1

III. MODEL DISCRIPTION

A. Model Assumptions and Considerations

The model was developed based on the following assumptions and considerations [13], incorporating unsteady-state mass balance equations for components in both the liquid and gas phases as well as physicochemical equilibrium expressions. The following simplifying assumptions were made:

- The digester was closed.
- Agitation within the digester was constant.
- Biochemical processes occurred within the digester.
- The reactor was assumed to be uniform.
- The suspended biomass contributed to substrate degradation.
- Growth kinetics adhered to the Haldane model.
- Bacterial growth was limited by the availability of organic substrates.

This section outlines the mathematical model used to describe and simulate CH_4 production from ACOD of OMW and CM in the batch system. The model is inspired by ADM1 and the one-phase AD principles. It identifies five processes: hydrolysis of insoluble substrates, bacterial consumption of soluble substrates, breakdown of VFA, acetate formation and methane generation. Bacterial biomass is represented by $C_5H_9O_3N$, and VFAs include acetic, propionic, and butyric acids. Figure 2 illustrates the schematic of the model.

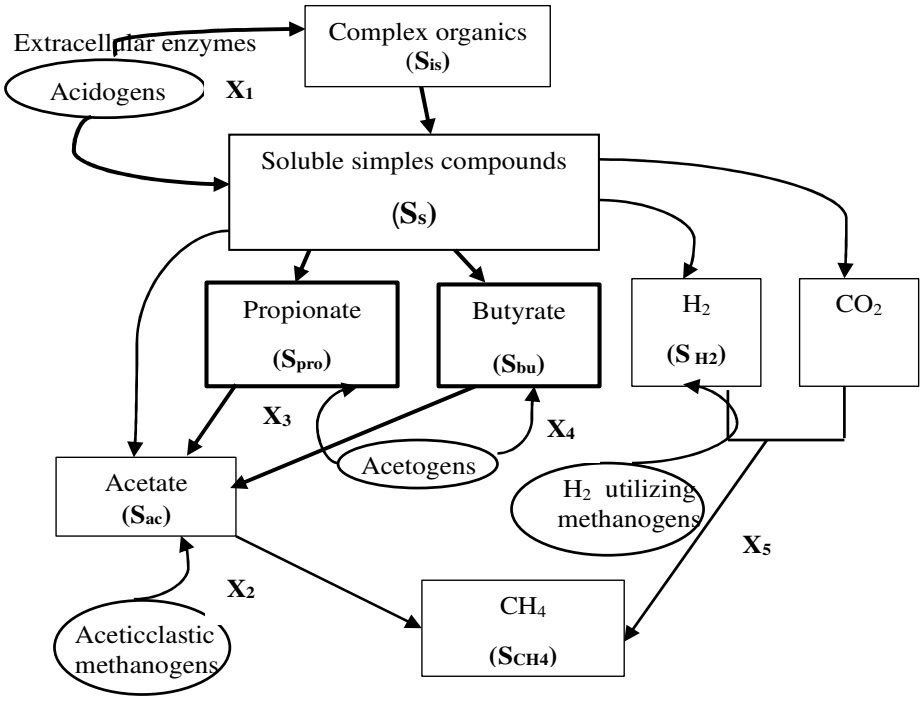

Fig. 2. The anaerobic model used for the anaerobic co-digestion of OMW with CM.

B. Substrate Degradation and Microorganism Growth

According to the model, hydrolysis of the given substrate can be described by the Contois function and then by a first-order equation, with Contois kinetics preferred for its consideration of biomass and substrate concentrations. The hydrolysis rate r_h is given by (1) in Table III. The subsequent utilization of soluble substrates and volatile acids, as well as anaerobic microorganism growth, followed Monod-type kinetics. The inhibition functions account for the accumulation of the product in relation to biomass, pH, and hydrogen inhibition, as detailed in (2)-(6) in Table III and Section C. The model also includes the mass balance of the digester headspace for H_2, CO_2, and CH_4, as described in (7)-(9), and biomass decay rates (10)-(14) [9]. The yield coefficients of the described steps associated with the consumption of each substrate reaction were calculated from the theoretical Adenosine Triphosphate (ATP) yields for each catabolic reaction, assuming that approximately 10 g of biomass are produced per mole of ATP generated [14].

C. Inhibitors

Specific inhibitors exclusively target methanogenic bacteria involved in later fermentation stages, leading to process termination, whereas nonspecific inhibitors affect all microorganisms [15]. As a result of the notable sensitivity of acetoclastic bacteria among anaerobic bacteria, research on pH inhibition in anaerobic treatment systems by hydrogen ions has predominantly focused on methanogenic bacteria. Their presence is crucial for the stability of the reactor. Mesophilic AD (35-37 °C) at nearly neutral pH (6.5-7.2) is typically used for models requiring operational stability and reduced

susceptibility to ammonia (NH_3), VFAs, and Long-Chain Fatty Acids (LCFA) inhibitions, controlling the growth of several bacterial populations in the following ways [13].

TABLE III. RATE OF HYDROLYSIS AND CONSUMPTION OF SUBSTRATES

Definition of the model variables	Reaction rate
s_{is} (Insoluble substrate) mgCODS.l- X_1 Acidogens mg CODS. l^{-1}	$r_h = \frac{k_h s_{is}}{(k_{x_1} X_1 + s_{is})} X_1$ (1) Where k_h is hydrolysis rate constant and k_{x_1} is Contois constant
s_s (soluble substrate), X_1 Acidogens Y_{X_1,s_s}Acidogens yield on glucose	$r_s = \frac{1}{Y_{X_1,s_s}} \frac{\mu_s s_s}{K_{s,s} + s_s} X_1 \frac{1}{1+\frac{s_s}{k_{in}}} \cdot I_{pH_1} I_{pH_{1a}} \frac{1}{1+I_{H_2}}$ (2)
s_{ac} (CH_3COOH) X_2 Aceticlastic methanogens $Y_{X_2,s_{ac}}$Aceticlastic methanogens yield on acetic acid	$r_{ac} = \frac{1}{Y_{X_2,s_{ac}}} \frac{\mu_{ac} s_{ac}}{K_{s,ac}+s_{ac}} X_2$ $I_{pH_2} I_{pH_{2a}}$ (3)
s_{pro} (CH_3CH_2COOH), X_3 Propionate utilizing acetogens $Y_{X_3,s_{pro}}$propionic acid bacteria yield on propionic acid	$r_{pro} = \frac{1}{Y_{X_3,s_{pro}}} \frac{\mu_{pro} s_{pro}}{K_{s,pro} + s_{pro}} X_3$ $I_{pH_3} I_{pH_{3a}} \frac{1}{1+I_{H_2}}$ (4)
s_{bu} ($CH_3CH_2CH_2COOH$) X_4 Butyrate utilizing acetogens $Y_{X_4,s_{bu}}$ butyric acid bacteria yield on butyric acid	$r_{bu} = \frac{1}{Y_{X_4,s_{bu}}} \frac{\mu_{bu}}{K_{s,bu}+s_{bu}} X_4 I_{pH_4}$ $I_{pH_{4a}} \frac{1}{1+I_{H_2}}$ (5)
s_{H2} mol^{-1} X_5 Hydrogen utilizing methanogens $Y_{X_5,s_{H2}}$Methane yield on hydrogen	$r_6 = \frac{1}{Y_{X_5,s_{H2}}} \frac{\mu_{H2} s_{H2}}{K_{s,H2}+s_{H2}} X_5$ $I_{pH_5} I_{pH_{5a}}$ (6)
CO_2 Total (inorganic carbon in liquid phase) mol^{-1}, Y_{CO_2,s_s}, $Y_{CO_2,s_{ac}}$, $Y_{CO_2,s_{pro}}$, $Y_{CO_2,s_{bu}}$, $Y_{CO_2,s_{H2}}$: Hydrogen yield on glucose, acetic acid, propionic acid, butyric acid, hydrogen	rCO2 $= Y_{CO_2,s_s} r_s + Y_{CO_2,s_{ac}} r_{ac} + Y_{CO_2,s_{pro}} r_{pro} - Y_{CO_2,s_{bu}} r_{bu} - Y_{CO_2,s_{H2}} r_{H2}$ (7)
s_{CH4} (Methane)$Y_{CH_4,s_{ac}}$, $Y_{CH_4,s_{H2}}$: Methane yield on acetic acid, hydrogen	$r_{CH_4} = Y_{CH_4,s_{ac}} r_{ac} + Y_{CH_4,s_{H2}} r_6$ (8)
Y_{H_2,s_s} , $Y_{H_2,s_{pro}}$, $Y_{H_2,s_{bu}}$: Hydrogen yield on glucose, propionic acid, butyric acid	$r_{H_2} = Y_{H_2,s_s} r_s + Y_{H_2,s_{pro}} r_{pro} + Y_{H_2,s_{bu}} r_{bu} - r_{H2}$ (9)
Biomass decay rate	$r_{d_i} = k_{d_i} X_i \ \forall i=1,2,3,4,5$ (10)-(14)

1) pH Inhibition

This model assumes that microbial growth is inhibited by pH, and two types of pH inhibition functions have been used [16, 17].

For pH<7 (acidic range):

$$I_{pH_i} = \exp\left(-0.5\left(\frac{pH - pH_{m_i}}{pH_{sd_i}}\right)^2\right) \quad (15)$$

For pH>7 (alkaline range):

$$I_{pH_{ia}} = \exp\left(-0.5\left(\frac{pH_{m_{ia}} - pH}{pH_{sd_{ia}}}\right)^2\right) \quad (16)$$

where I_{pH} is pH inhibition function with i = 1, 2, 3, 4, 5 corresponding to X_1 to X_5, pH is the pH of the reactor, and pH_m and pH_{sd} are the mean and standard deviation of a pH inhibition function, respectively. The values of these constants are given in [13] and are utilized in the equations for calculating r_s, r_{ac}, r_{pro}, r_{bu}, and r_{H2} (Table III).

2) H_2 Inhibition

The authors in [18] found that hydrogen pressure impacts propionic and butyric acid degradation, potentially halting acetogenic activities. Additionally, in [19] it is suggested to incorporate hydrogen inhibition and regulation functions into bacterial models. Therefore:

$$I_{H_2} = (H_2)_{aq}\left[10^{\left[pH - \frac{1139}{T+273}\right]}\right] = 2000 P_{H_2} \quad (17)$$

where I_{H_2} is hydrogen inhibition and P_{H_2} is the partial pressure.

This was added to the rate equations for butyric acid utilization (r_{bu}), propionic acid utilization (r_{pro}), and soluble substrate (r_s).

3) Product Inhibition

The model incorporates product inhibition to explain organic acid build-up at neutral pH, using "non-competitive inhibition" to describe high acetic acid concentration, as evidenced in (2) in Table III.

D. Acid-Base Equations

The pH plays a crucial role in anaerobic digestion [19]. To determine these levels, an alternative method can be deployed by solving the charge balance equation:

$$s_{cat^+} + s_{H^+} + s_{NH_4^+} - s_{HCO_3^-} - \frac{s_{ac^-}}{64} - \frac{s_{pro^-}}{112} - \frac{s_{bu^-}}{160} - s_{OH^-} - s_{an^-} = 0 \quad (18)$$

where $s_{OH^-} = \frac{k_w}{s_{H^+}}$, , $pH = -\log_{10} s_{H^+}$ and s_{ac^-}, s_{pro^-}, s_{bu^-}, $s_{NH_4^+}$, and $s_{HCO_3^-}$are the concentrations of the respective ions.

E. Biogas Production

The gas transfer rates for gaseous substances (H_2 and CO_2) transferred from the liquid phase to the gas phase were calculated as described in [13].

$$r_{T,H_2} = (K_l a)_{H_2}\left(\frac{P_{H_2}}{H_{H_2}} - S_{H_2,aq}\right) \quad (19)$$

$$r_{T,CO_2} = (K_l a)_{CO_2}\left(\frac{P_{CO_2}}{H_{CO_2}} - S_{CO_2,aq}\right) \quad (20)$$

where $r_{T,i}$is the transfer rate of dissolved gas i, $(K_l a)_i$ is the overall mass transfer coefficient of gas i (day^{-1}), $K_{H,i}$ is the Henry's law coefficient of gas i ($kmol/m^3bar$), $S_{i,aq}$ is the concentration of component i dissolved in liquid ($kmol/m^3$), and P_i is the partial pressure of component i (bar) calculated from the ideal gas law. Using dynamic gas-liquid transfer equations, the biogas production (CH_4, CO_2, and H_2) is directly computed based on the soluble concentrations and can be calculated as observed in the following equation:

$$q_G = \frac{V_L}{1-P_{H2O}} RT_{op}\left(r_{CH_4} - \frac{r_{T,H_2}}{16} - r_{T,CO_2}\right) \quad (21)$$

All adjustment parameters related to the gas transfer can be found in [9].

F. Differential Equations in the Implementation of Batch Digester

According to simplifications and modifications of the ADM1 model, the model was reduced to a set of 8 differential equations for the soluble substrate (liquid form) and 5 for the particulate substrate (solid form):

$$\frac{dSis}{dt} = -r_1 \quad (22)$$

$$\frac{dSs}{dt} = (1-\alpha)r_1 - r_2 \quad (23)$$

$$\frac{dS_{ac}}{dt} = Y_{S_{ac},S_s} r_2 - r_3 + Y_{S_{ac},S_{pro}} r_4 + Y_{S_{ac},S_{bu}} r_5 \quad (24)$$

$$\frac{dS_{pro}}{dt} = Y_{S_{pro},S_s} r_2 - r_4 \quad (25)$$

$$\frac{dS_{bu}}{dt} = Y_{S_{bu}S_s} r_2 - r_5 \quad (26)$$

$$\frac{dS_{H2}}{dt} = r_{H_2} + r_{H_2,T} \quad (27)$$

$$\frac{dS_{CH4}}{dt} = r_{CH_4} \quad (28)$$

$$\frac{dR_{S_{is}}}{dt} = \alpha r_1 \quad (29)$$

$$\frac{dX1}{dt} = Y_{X_1 S_s}\, r_2 - r_{d_1} \quad (30$$

$$\frac{dX2}{dt} = Y_{X_2 S_{ac}}\, r_{ac} - r_{d_2} \quad (31)$$

$$\frac{dX3}{dt} = Y_{X_3 S_{pro}} r_{pro} - r_{d_3} \quad (32)$$

$$\frac{dX4}{dt} = Y_{X_4 S_{bu}}\, r_{bu} - r_{d_4} \quad (33)$$

$$\frac{dX5}{dt} = Y_{X_5 S_{H_2}}\, r_{H2} - r_{d_5} \quad (34)$$

where α is the refractory fraction of insoluble substrate, Y_{S_{ac},S_s} is the acetic acid yield on glucose, $Y_{S_{ac},S_{pro}}$ is the acetic yield on propionic acid, $Y_{S_{ac},S_{bu}}$ is the acetic acid yield on butyric acid, Y_{S_{pro},S_s} is the propionic acid yield on glucose, and Y_{S_{bu},S_s} is butyric acid yield on glucose. To simplify the model, it is possible to reduce the number of variables and associated equations by differentiating (18) and rearranging the terms to obtain (35). This equation allows for direct integration, with S_{H+} being the only state variable in the acid-base processes.

$$\frac{dH^+}{dt} = -2\frac{dCO_3^{2-}}{dt} + \frac{dHCO_3^-}{dt} + \frac{dOH^-}{dt} + \frac{dAC^-}{dt} + \frac{dPr^-}{dt} + \frac{dBu^-}{dt} - \frac{dNH_4^+}{dt} - 2\frac{dCa}{dt} \quad (35)$$

For liquid-gas mass balance in the headspace:

$$\frac{dy_{H_2}}{dt} = -\frac{q_G}{V_G} y_{H_2} - \frac{V_L}{V_G} RT_{op} r_{T,H_2} \quad (36)$$

$$\frac{dy_{CH4}}{dt} = -\frac{q_G}{V_G} y_{CH4} + \frac{V_L}{V_G} RT_{op} r_{CH_4} \quad (37)$$

$$\frac{dy_{CO2}}{dt} = -\frac{q_G}{V_G} y_{CO2} - \frac{V_L}{V_G} RT_{op}\, r_{T,CO_2} \quad (38)$$

$$\frac{dy_{N2}}{dt} = -\frac{q_G}{V_G} y_{N2} \quad (39)$$

Furthermore, since ammonia is necessary for the growth of microorganisms, the model also considers the ammonia emitted during the hydrolysis stage. During degradation, other cations, such as alkali metals, can be released, which in the model are grouped with calcium ions.

$$\frac{dCa}{dt} = Y_{Ca} r_{is} \quad (40)$$

$$\frac{dN_T}{dt} = Y_{N,T} r_{is} \quad (41)$$

$$\frac{dCO_2T}{dt} = r_{CO_2} + r_{CO_2,T} \quad (42)$$

The total number of differential equations to be solved is thus reduced to 21 from the 35 equations in the differential equation system of ADM1. All differential equations in this model were integrated using the ODE15s solver, which is an integrated function of MATLAB. The ODE15 solver deploys a backward differentiation formula to solve the "stiffness" problem.

IV. RESULTS AND DISCUSSION

A. Co-Digestion of Olive-Mill Wastewater and Cattle Manure

Table IV summarizes the culture medium characteristics and the results of physicochemical test fermentation. Table IV presents analytical data collected both before and after the anaerobic co-digestion of OMW with CM. This demonstrates changes in the culture medium due to variations in pH, a decrease in organic material, and a decline in polyphenols, as well as gas generation.

TABLE IV. CHARACTERISTICS OF THE CULTURE MEDIUM

Substrate		pH	TCOD	Phenols	TVFA (g HAc/L)
RCM	before	8.1	62.72	1.12	0.89
	after	7.8	43.2	0.95	0.25
ROMW	before	8,1	159.3	5.8	1.42
	after	7.8	128.6	4.3	1.01
R 50 :50	before	8.1	121.52	3.85	2.3
	after	7.95	97.22	2.65	1.15
R 75 :25	before	8.1	140.32	2.17	2.1
	after	7.9	89.4	1.72	0.99

B. Model Input and Initial Conditions

The initial conditions reflecting the state variables are essential to accurately solve the differential equations of the system. Calibration is required because of the complexity of these variables, which ensures alignment with the experimental data. The model follows the ADM1 framework, with default parameters mainly taken from [9] and [20]. The stoichiometric parameters were adjusted according to Table IV to reflect the composition of OMW and CM. The kinetic parameters for the hydrolysis phases were set to values reported in the literature [20]. The constants for the pH inhibition function were derived using the parameter estimation routine developed by [21]. In this model, other cations, such as alkali metals, were grouped as calcium ions. The VFA kinetic parameters (μ, K_s) were estimated by considering both batch experimental runs and modeling the experimental data to modify the kinetic parameter values. Figure 3 displays the evolution of specific growth rates as a function of the substrate concentration [22]. The biomass

specific growth rates were obtained by fitting experimental data to the Monod equation, which describes the relationship between substrate concentration (S) and growth rate (μ). This equation can be rearranged into a linear function suitable for the Lineweaver-Burk plot, as demonstrated in [23]. The data shown in Figure 3 were used for this purpose. The results of the model simulation using the Monod equation were summarized and presented in Table V.

TABLE V. KINETIC CONSTANTS OF ANAEROBIC DIGESTION OF BUTYRATE, ACETATE AND PROPIONATE ORGANIC ACID SALTS

Model/Equation		$\frac{\mu_{max,i}\,S}{K_{s,i}+S}.X_1.$	
	Butyrate	Acetate	Propionate
μ_{max} (d^{-1})	0.1	0.13	0.09
K_s (mgCOD/L)	892	642	1468

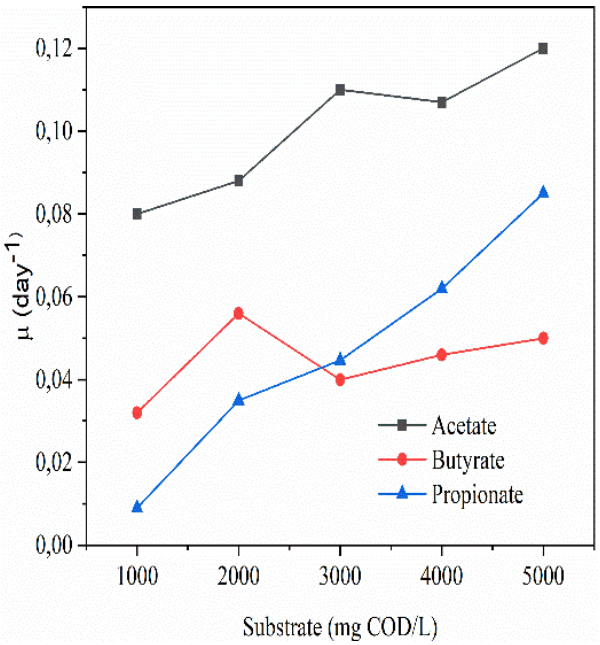

Fig. 3. The evolution of specific growth rates as a function of substrate concentration.

C. *Simulation of the Process and Comparison with the Experimental Data*

The graphs and data (Figure 4) provide valuable insights into the dynamics of TVFA production during the anaerobic co-digestion of OMW and CM. The model shows strong predictive capabilities across various substrate ratios, with R-squared values ranging from 0.80626 to 0.98523. The R75:25 (OMW) ratio fits best, reflecting higher TVFA concentrations than individual substrates. The model accurately captures TVFA dynamics, from initial increases during the acidogenic and acetate phases to decreases during methanogenic activity, which is crucial to optimizing the biogas production efficiency.

The graphical representation (Figure 5) and accompanying analysis provided valuable insights into the model's performance for predicting methane production in the co-digestion of OMW and CM. The model demonstrated strong predictive capability, particularly for the R75:25 (OMW) ratio, achieving an impressive R-square value of 0.99133. This ratio exhibits excellent agreement between the simulated and experimental data throughout the 35-day period.

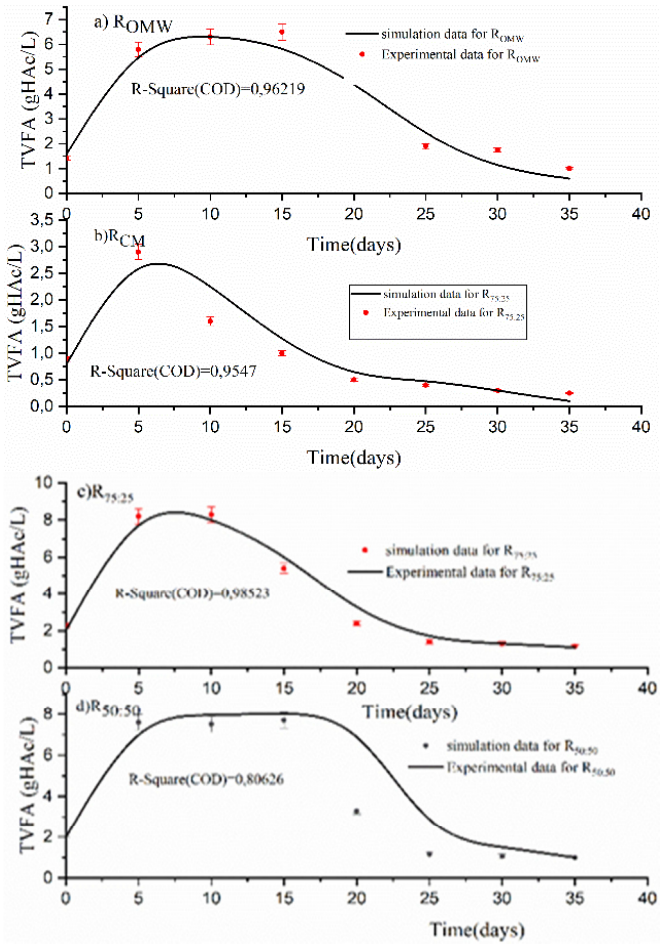

Fig. 4. Total VFA evolution and comparison of the experimental and simulated values for the co-substrate (a, b) and mixtures of co-digestion (c, d).

The R50:50 ratio also performs well, with an R-squared of 0.96469, although it manifests some deviations between days 15-25, where the model underestimates methane production. These discrepancies can be attributed to the sensitive parameters of the model. Despite these slight deviations, the general trend in methane production was accurately captured for both ratios. The superior performance of the R75:25 ratio in terms of model fit is consistent with previous observations. However, it is important to note that optimal model performance does not always translate directly to optimal real-world outcomes. These results underscore the potential of the model as a valuable tool for predicting biogas production in anaerobic co-digestion processes while also highlighting areas for potential refinement, particularly in parameter sensitivity analysis for varying substrate ratios.

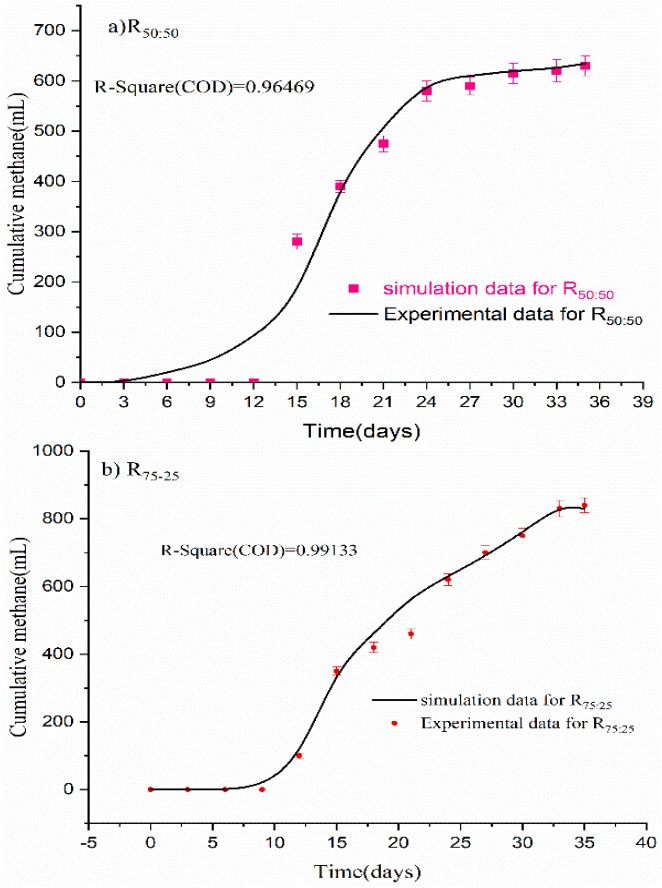

Fig. 5. Validation of simulation results with experimental data: (a) R50-50 and (b) R75-25.

V. CONCLUSIONS

This study demonstrated the feasibility of co-digesting Olive Mill Wastewater (OMW) and Cattle Manure (CM) at mesophilic temperatures. Methane production and yield were higher for mixed substrates than for the individual substrates. The substrate with a 75:25 ratio (OMW:CM) exhibited the best performance in terms of model fit and biogas production. A simplified mathematical model based on the ADM1 model was developed to simulate the behavior of a bioreactor for anaerobic co-digestion of OMW and CM. The simulation results were acceptable and successfully reproduced the experimental trends. The model was validated using data from two specific substrate mixtures. It demonstrated high accuracy in predicting biogas production rates and other crucial process parameters such as Volatile Fatty Acids (VFAs). This validation confirms the reliability and applicability of the model for practical use.

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