An Integrated Modeling Approach for Biogas Production from Anaerobic Co-Digestion of Cattle Manure and Tomato Waste

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Abstract: This study develops and validates a multi-scale modeling framework to estimate biogas production from the anaerobic co-digestion (AcoD) of cattle manure and tomato crop waste (*Solanum lycopersicum L.*), an abundant and underutilized agricultural residue in Mexico. The modeling approach integrates three complementary mathematical models (Volume Averaging, Laplace Domain, and Modified Gompertz equation) which were fitted to experimental data previously reported in the literature. These data were obtained from batch bioreactors experiments conducted under different operational conditions (20% and 50% substrate on a dry basis, and pH 6.8 and 7.5). The models exhibited a strong fit (R^2: 0.84 – 0.97; RMSE = 0.10 – 1.10), supporting their suitability for describing both kinetic and transport phenomena. The Volume Averaging method enabled the estimation of transport parameters, including diffusion coefficients on the order of 1.6×10−6 m²/d, along with key reaction parameters. The Laplace Domain approach facilitated the dynamic characterization of the system through transfer functions, while the Modified Gompertz equation accurately captured biogas production kinetics. The results indicate that operating at 50% substrate concentration with pH control reduced the characteristic production time to approximately 30 days, which is less than half the time required for the 20% substrate condition (60-66 days) and achieved methane contents of up to 41%, approaching the established threshold for biogas as biofuel (45%), with V50a showing the highest methane fraction. The estimated kinetic and transport coefficients suggest a clear metabolic adaptation of the microbial consortia under optimal conditions. Overall, this integrated framework demonstrated its potential for the design and scale-up of AcoD systems, providing a link between physicochemical fundamentals and practical application in agricultural regions with high organic waste generation.

Keywords: biogas modeling, agricultural waste valorization, anaerobic co-digestion, tomato waste, sustainable energy

Nomenclature

Symbol	Description	Units
Latin Symbols		
A_ζ	Stimulus amplitude	d
c_A	Concentration of species A in the bioreactor volume	mol/m³
$\langle c_A \rangle$	Average concentration of species A	mol/m³
$\mathcal{D}_A$	Effective diffusion coefficient of gaseous species A	m²/d
d_R	Reactor diameter	m
k_p	Concentration divided by the characteristic time	mol/(m³·d)
L_R	Reactor length	m
R^2	Coefficient of determination	–
$RMSE$	Root Mean Square Error	L
s	Frequency domain variable (Laplace)	d⁻¹
t	Time	d
V_R	Reactor volume	m³
Greek Symbols		
α_A	Reactor properties divided by the volume fraction $(\alpha_A = L_R \mathcal{D}_A (\varepsilon V_R)^{-1})$	d⁻¹
ε	Volume fraction occupied in the bioreactor	–
κ_{eff}	Effective Michaelis-Menten saturation constant	mol/m³
λ_ψ	Lag phase in the Gompertz equation	d
μ_{eff}	Maximum effective reaction rate	mol/(m³·d)
μ_{A}	Reaction rate divided by the volume fraction $(\mu_{\text{A}} = \mu_{\text{eff}} \varepsilon^{-1})$	mol/(m³·d)
$\mu_{\text{max},\psi}$	Maximum specific production rate of biogas or methane	L/(gVS·d)
ψ_0	Specific maximum production potential	L/(gVS·d)
τ_p	Characteristic time of the process	d

Symbol	Description
Subscripts	
A	Species (Biogas or Methane)
eff	Effective
max	Maximum
R	Reactor
$V20, V50$	20% or 50% dry basis
a, b	pH conditions (a: 6.8, b: 7.5)
Acronym	**Description**
Abbreviations	
AD	Anaerobic Digestion
AcoD	Anaerobic Co-Digestion
BMP	Biochemical Methane Potential
COD	Chemical Oxygen Demand
TS	Total Solids
VS	Volatile Solids
VFA	Volatile Fatty Acids

Introduction

The global search for sustainable energy sources has positioned biogas as a key renewable fuel, particularly in agricultural regions where organic waste is abundant (Alghoul *et al*., 2019; Kumar and Samadder, 2020). In Mexico, approximately 13% of the workforce is dedicated to agriculture, generating significant amounts of organic residues that are generally disposed of without treatment (Mendivil-Garcia *et al*., 2020). This situation represents both an environmental challenge and an energy opportunity, especially considering that about one-third of the world's food production is wasted annually (Kumar and Samadder, 2020).

Anaerobic Digestion (AD) has become a promising technology for converting organic waste into biogas while contributing to the reduction of greenhouse gas emissions (Alburquerque *et al*., 2012; Kumar and Samadder, 2020; Elagroudy *et al*., 2020). The economic and energy interest in biogas lies in its methane fraction (CH_4), which constitutes between 50% and 70% of its composition and defines its calorific value. Therefore, the carbon-to-methane conversion efficiency is a critical parameter for the sustainability and profitability of the process (Börjesson and Mattiasson, 2008; Chaemchuen *et al*., 2016). In this context, the anaerobic co-digestion (AcoD) of animal manure with agricultural residues has been shown to improve both methane production and system stability, thanks to synergistic interactions between substrates (Esposito *et al*., 2012; Castro-Rivera *et al*., 2020). Among potential substrates, tomato crop waste (*Solanum lycopersicum L.*) is particularly attractive due to its high organic content and seasonal availability in farming areas (Castro-Rivera *et al*., 2020). In Mexico, where tomato production generates approximately 1.8 million tons of waste annually (SIAP, 2023), the energy valorization of these by-products represents a strategic opportunity to contribute to national energy transition goals (SENER, 2020). However, full-scale implementation requires modeling tools that capture both kinetic and transport phenomena.

Mathematical modeling plays an essential role in understanding, optimizing, and scaling up AD processes (Hatata *et al*., 2021; Benítez-Olivares *et al*., 2016). Although various approaches exist, from complex kinetic models (Esposito *et al*., 2012; Hernández-Fydrych *et al*., 2021) to empirical formulations like the Gompertz equation (Zwietering *et al*., 1990), a gap persists in developing integrated frameworks that link fundamental transport phenomena with practical production kinetics. Most previous studies have focused on individual approximations; for example, Ravina *et al*. (2019) developed MATLAB software for biogas quantification; Nock *et al*. (2014) used mass transfer models to optimize biogas quality; and Hernández-Fydrych *et al*. (2019) applied kinetic models to slaughterhouse wastewater treatment.

The methodological novelty of this work lies in the synergistic integration of three complementary modeling perspectives: volume averaging to capture fundamental micro-scale transport phenomena, analysis in the Laplace domain to characterize the system's temporal dynamics, and the modified Gompertz equation to describe practical production kinetics. While previous studies have applied these methods in isolation (Ravina *et al*., 2019; Nock *et al*., 2014; Hernández-Fydrych *et al*., 2019), their combination into a unified framework overcomes the limitations of each individual approach, particularly for AcoD systems where synergistic substrate interactions introduce complex non-linearities (Esposito *et al*., 2012). This multi-scale approach provides not only kinetic parameters but also fundamental transport coefficients critical for bioreactor scale-up, an aspect often underestimated in the literature (Whitaker, 1999; Benítez-Olivares *et al*., 2016).

The main objectives of this work are:

1. To develop and validate an integrated multi-scale modeling framework that combines Volume Averaging, Laplace Domain, and Modified Gompertz approaches for biogas production from the AcoD of cattle manure and tomato crop waste.
2. To determine effective transport coefficients (diffusion coefficients $\mathcal{D}_A$, reaction rates μ_{eff}, and saturation constants κ_{eff}) under different operational conditions and establish their relationship with system performance.
3. To validate a multi-scale model for estimating biogas from AcoD of agricultural residues in developing regions.

Materials and Methods

Experimental System Description

This study is based on experimental data previously published by Castro-Rivera *et al*. (2020), obtained from a laboratory-scale system for biogas production through AcoD of cattle manure and tomato agricultural waste (*Solanum lycopersicum L.*). These data were used exclusively for analysis and mathematical modeling purposes, without conducting new experimental tests. In the original study (Castro-Rivera *et al*., 2020), experiments were conducted in 3 L plastic digesters with a working volume of 2.4 L and a 10% total solids concentration on a dry basis. The characterization of substrates (cattle manure and tomato peel) and effluents included determinations of chemical composition, pH, chemical oxygen demand (COD), total solids (TS), volatile solids (VS), substrate-to-inoculum ratio, alkalinity, and digestion time. A complete description of the experimental conditions is detailed in the original source (Castro-Rivera *et al*., 2020).

Briefly, in the reference work, each biodigester had a gas outlet and a liquid outlet for sampling. Before hermetic sealing, a nitrogen purge was performed for five minutes to remove dissolved oxygen and ensure anaerobic conditions. The digesters were maintained for 75 days at 30°C. Weekly, the biogas volume was measured according to the procedure described in Castro-Rivera *et al*. (2020), and its composition (CH_4 and CO_2) was determined by gas chromatography. The experimental design was completely randomized, with a factorial arrangement (2×2) and three replicates per treatment. The evaluated factors were the mixture of manure with tomato peel in proportions of 20/80% and 50/50% respectively, and the initial pH (6.8 and 7.5). For the purposes of the present modeling work, the corresponding data were grouped into four case studies:

- **V20a**: 20% dry basis, pH = 6.8
- **V20b**: 20% dry basis, adjusted pH = 7.5
- **V50a**: 50% dry basis, pH = 6.8
- **V50b**: 50% dry basis, adjusted pH = 7.5

From these data, three complementary mathematical models were implemented and evaluated to represent and analyze the behavior of biogas production and its methane fraction. The models considered were the Volume Averaging model, the Laplace Domain model, and the Modified Gompertz equation. Figure 1 illustrates the multi-scale modeling strategy implemented, integrating different levels of process description.

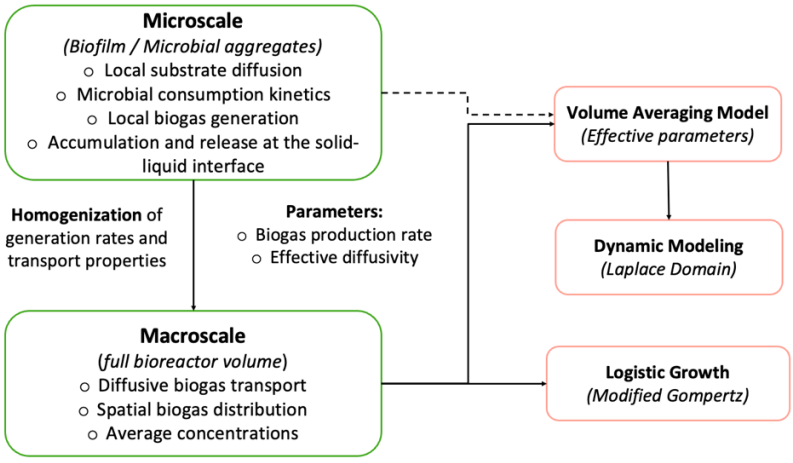

Figure 1. Schematic of the multi-scale modeling strategy implemented in this work

Mathematical Models

To adequately represent the formation and transport of biogas within the bioreactor, a multi-scale modeling strategy was developed that integrates local reaction and diffusion phenomena with the global system dynamics. The approach

is based on a conceptual separation between a micro-scale, where biochemical and transport processes occur within biofilms and microbial aggregates, and a macro-scale, which describes the behavior of biogas in the total reactor volume.

At the micro-scale, the species of interest is the local concentration of biogas generated from microbial reactions. This stage explicitly considers the phenomena of substrate diffusion towards microbial structures, biochemical consumption via microbial kinetics, and localized biogas production. Additionally, the accumulation and release of gas at the solid-liquid interface is incorporated, allowing the capture of the intrinsic spatial heterogeneity of reactive microenvironments (Picioreanu *et al*., 1998).

The local biogas production rates and transport parameters obtained undergo a homogenization process, through which they are transformed into effective properties representative of the active reactor volume. These variables include the effective volumetric biogas generation rate, effective diffusivity, and other coefficients associated with gas transport and release.

At the macro-scale, these homogenized properties are incorporated into a model that describes the reactor dynamics and biogas transport at a global level. This model considers the effects of mixing, fluid circulation, bubble formation, as well as the diffusive transport of gas throughout the bioreactor volume. In this way, it is possible to predict the spatial distribution of biogas, its concentration gradients, and its accumulation or release during operation (Bird, Stewart, & Lightfoot, 2002; Velázquez-Martí *et al*., 2018).

Finally, a sequential coupling is established between both scales, where parameters estimated from the micro-scale (Volume Averaging model) serve as inputs for the macro-scale Laplace domain model. This ensures consistency between the fundamental transport phenomena and the global system dynamics.

Volume Averaging Model

The first model is based on the Volume Averaging method (Whitaker, 1999), which allows deriving transport equations at the bioreactor scale from the equations governing transport at the micro-scale. This approach considers three scale levels (Figure 2): the micro-scale ($r_{\beta\sigma}$), where microbial interactions occur; the intermediate region ($r_{\kappa\gamma}$); and the bioreactor scale.

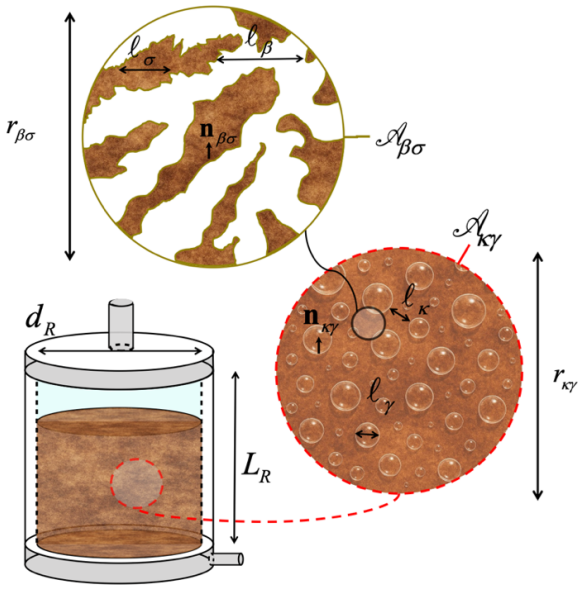

Figure 2. Diagram of the biodigester and the scaling used for the digestion of cattle manure and tomato crop waste. Where $r_{\beta\sigma}$ schematizes microbial interactions; $r_{\kappa\gamma}$ schematizes mass transport; d_R and L_R are the diameter and length of the reactor, respectively. Adapted from Castro-Rivera *et al*., 2020

Following the methodology established by Ochoa *et al*. (1986) and Benítez-Olivares *et al*. (2016), the volume averaging operator was applied to obtain a macroscopic mass transfer equation describing the accumulation of biogas in the bioreactor:

$$\varepsilon \frac{\partial \langle c_A \rangle}{\partial t} = \mathcal{D}_A \frac{\partial^2 \langle c_A \rangle}{\partial z^2} + \frac{\mu_{\text{eff}} \langle c_A \rangle}{\kappa_{\text{eff}} + \langle c_A \rangle} \quad \textbf{(1)}$$

where $\langle c_A \rangle$ is the average concentration of species *A* (biogas or methane) in [mol/m³], ε is the volume fraction occupied in the reactor, $\mathcal{D}_A$ is the effective diffusion coefficient in [m²/d], μ_{eff} is the maximum effective reaction rate in [mol/(m³·d)], and κ_{eff} is the Michaelis-Menten saturation constant in [mol/m³]. To consider the process throughout the reactor volume, the averaging operator is applied:

$$c_A = \frac{1}{V_R} \int_{V(t)} \langle c_A \rangle dV \quad \textbf{(2)}$$

obtaining the ordinary differential equation:

$$\varepsilon \frac{\partial c_A}{\partial t} = \frac{L_R}{V_R} \mathcal{D}_A c_A + \frac{\mu_{\text{eff}} c_A}{\kappa_{\text{eff}} + c_A} \quad \textbf{(3)}$$

The numerical solution of Equation 3 was implemented in MATLAB using both the Runge-Kutta method and the finite difference method, allowing the determination of the transport coefficients $\mathcal{D}_A$, μ_{eff}, and κ_{eff}.

Model in the Laplace Domain

The second model is developed in the Laplace domain, providing an alternative approach to characterize system dynamics through transfer functions. Starting from Equation 3 and defining where $\alpha_A = L_R \mathcal{D}_A (\varepsilon V_R)^{-1}$ and $\mu_{\text{A}} = \mu_{\text{eff}} \varepsilon^{-1}$, we obtain:

$$\frac{dc_A}{dt} = \alpha_A c_A \frac{\mu_{\text{A}} c_A}{\kappa_{\text{eff}} + c_A} \quad \textbf{(4)}$$

The nonlinearity in the reaction term is linearized using a first-order Taylor expansion around an operating point $\bar{c}_A$:

$$f[c_A(t)] \approx f(\bar{c}_A) + \frac{df}{dc_A}[c_A(t) - \bar{c}_A] \quad \textbf{(5)}$$

Applying the Laplace transform (Widder, 2015),

$$k_p X(t) = \frac{\bar{c}_A}{\tau_p} \left[\frac{\mu_{\text{A}} \kappa_{\text{eff}}}{(\kappa_{\text{eff}} + \bar{c}_A)^2} - \frac{\mu_{\text{A}}}{\kappa_{\text{eff}} + \bar{c}_A} \right] \quad \textbf{(6)}$$

we obtain the standard form in the Laplace domain:

$$\tau_p \frac{dc_A}{dt} + c_A = k_p X(t) \quad \textbf{(7)}$$

whose Laplace transform results in:

$$\tilde{\zeta}_A = \frac{k_p}{\tau_p \left(s + \frac{1}{\tau_p} \right)} \tilde{\xi} \quad \textbf{(8)}$$

Where $\tilde{\zeta}_A = \mathcal{L}(\tilde{c}_A)$ and $\tilde{\xi} = \mathcal{L}(\tilde{X})$ are the variables in the Laplace domain, s [d^{-1}] is the frequency variable, τ_p [d] is the characteristic time of the process, and k_p [mol/(m^3·d)] condenses the concentration and reaction terms. Applying the inverse transform with $\tilde{\xi} = \frac{A_\zeta}{s}$, where A_ζ [d] is the stimulus amplitude, the temporal solution is obtained:

$$\tilde{\zeta}_A = A_\zeta k_p \left(1 - \exp^{-t/\tau_p}\right) \quad \textbf{(9)}$$

This equation provides an explicit relationship for cumulative biogas production as a function of time.

Modified Gompertz Equation

The third model employs the modified Gompertz equation (Zwietering *et al*., 1990), widely used to describe methane production kinetics in Biochemical Methane Potential (BMP) assays:

$$\psi(t) = \psi_0 \exp\left\{-\exp\left[\frac{\mu_{\max,\psi} \cdot e(1)}{\psi_0}(\lambda_\psi - t) + 1\right]\right\} \quad \textbf{(10)}$$

where $\psi(t)$ [L/gVS] is the accumulated biogas produced at time t, ψ_0 [L/gVS] is the maximum specific production potential, $\mu_{\max,\psi}$ [L/(gVS·d)] is the maximum specific production rate, and λ_ψ [d] is the lag phase.

While the lag phase was found to be negligible in most of our fitted cases, the Gompertz model was retained for three reasons: (1) it is the standard model in BMP assays, ensuring comparability with literature; (2) the three-parameter form provides slightly better fit during the transition from the initial to the exponential phase compared to two-parameter models like the logistic; and (3) the lag phase parameter, even when near zero, serves as a useful diagnostic indicator of rapid microbial adaptation. Nevertheless, we acknowledge that for systems consistently showing no lag, simpler first-order or logistic models could be equally valid and more parsimonious.

Numerical Implementation Strategy

Numerical implementation was carried out through algorithms developed in MATLAB that integrate the three modeling approaches:

- For the Volume Averaging model (Eq. 3), numerical methods for differential equations (Runge-Kutta and finite differences) were used.
- For the Laplace (Eq. 9) and Gompertz (Eq. 10) models, nonlinear regression was employed to estimate parameters by minimizing the mean square error.
- The coefficients obtained from the Volume Averaging model served as initial values for the Laplace model adjustment, establishing a connection between both approaches.
- The value of the volume fraction was kept constant at ε =0.8 for all cases, corresponding to the ratio between the reactor volume and the added organic matter.

Results and Discussion

This section presents the validation of the three proposed mathematical models against the experimental data of biogas production and its corresponding CH_4 fraction for the four case studies. The analysis focuses on the models' predictive capacity, the estimation of process parameters, and the effect of operational conditions on system performance.

Comparative Performance of the Modeling Approaches

The cumulative production values reported here (e.g., 2.4 L/gVS for V20a biogas) represent the total measured production over 75 days. The Gompertz parameter ψ_0 reported in Tables 1-4 represents the model-fitted asymptotic maximum, which may be slightly higher.

Figures 3 to 6 show the comparison between experimental data and predictions for biogas and methane production for the different case studies. In all scenarios, a qualitative and quantitative agreement between the modeled curves and experimental data is observed.

As observed in Figure 3, experiment V20a (20% substrate, pH 6.8) showed a prolonged period of very slow production, which could be visually interpreted as a latency phase. However, model fitting indicated a negligible statistical lag phase, suggesting this behavior is due to extremely slow kinetic rates rather than a true biological adaptation period. This low generation could be attributed to the microorganisms' adaptation period to the new substrate, which slowed the microbial growth rate, coupled with possible accumulation of volatile fatty acids (VFAs) that would have inhibited metabolic activity (Khadka *et al*., 2022). This behavior coincides with that reported by Esposito *et al*. (2012), who observed that suboptimal substrate concentrations, in combination with acidic pH, significantly reduce the metabolic activity of methanogenic consortia. Under these characteristics, the methane/biogas ratio was approximately 27%, a value below the 45% threshold proposed to consider biogas as a viable biofuel (Dueblein and Steinhauser, 2008), evidencing inefficient substrate conversion.

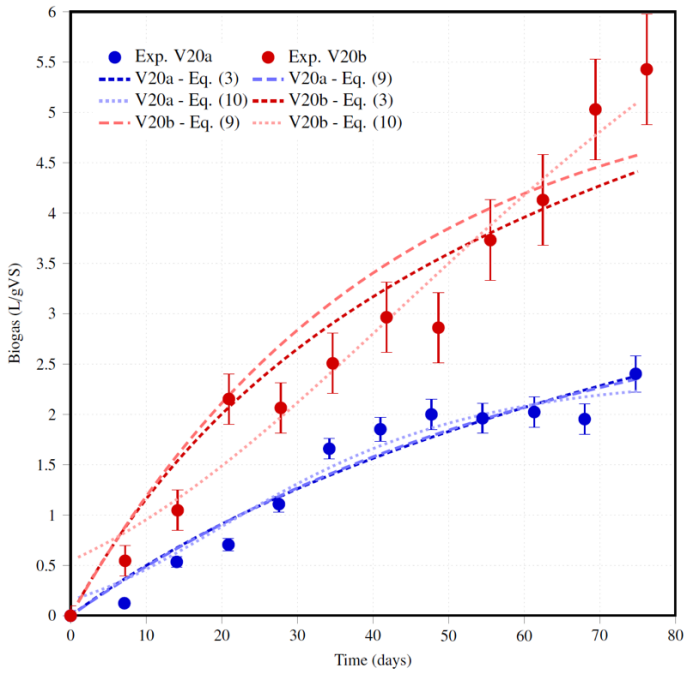

Figure 3. Cumulative biogas production for experiments V20a and V20b (20% manure on dry basis, pH = 6.8 and adjusted pH = 7.5, respectively). Points represent experimental values with error bars indicating observed variability. Lines show the fits of the three mathematical models: Volume Averaging (Eq. 3), Laplace Domain (Eq. 9), and Modified Gompertz (Eq. 10)

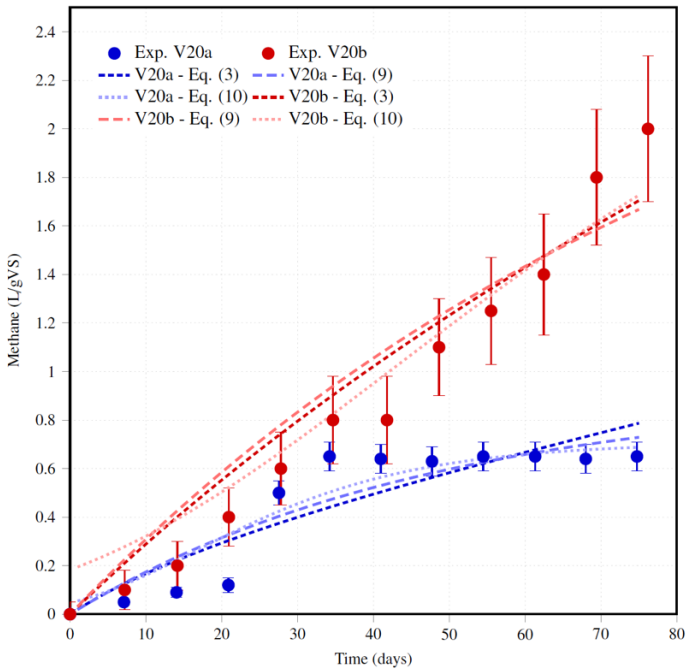

Figure 4. Cumulative methane production for experiments V20a and V20b (20% manure on dry basis, pH = 6.8 and adjusted pH = 7.5, respectively). Points represent experimental values with error bars indicating observed variability. Lines show the fits of the three mathematical models

pH control at 7.5 in experiment V20b (a) resulted in a 125% increase in biogas production compared to V20a. Under these conditions, a yield of 5.4 L/gVS of biogas was obtained, of which 2.0 L/gVS corresponded to CH_4. This increase could be attributed to greater microbial activity, as pH levels close to neutrality favor the balance of microbial consortia (Hernández-Fydrych *et al*. 2019). However, despite the increase in total biogas production, the methane/biogas ratio was only 37%. This value suggests that, although neutral pH increased metabolic activity, the 20% substrate concentration continued to be a limitation for conversion to CH_4, preventing achievement of the minimum percentage required to consider this biogas as a biofuel (González-Herrera *et al*. 2021).

In Figures 5 and 6 (V50a and V50b, respectively), the increase in substrate to 50% with improvements in system performance is observed. In V50a (pH 6.8), biogas production reached 8.1 L/gVS with a methane/biogas ratio of 41%, a value close to the 45% threshold. This behavior agrees with that reported by Castro-Rivera *et al*. (2020), who indicated that elevated substrate concentrations provide the necessary nutrient bioavailability to maintain robust microbial

activity even under suboptimal pH conditions. It is particularly relevant that V50a surpassed V20b in CH_4 conversion efficiency, evidencing that a higher substrate concentration can partially compensate for pH limitations (Li *et al*. 2022).

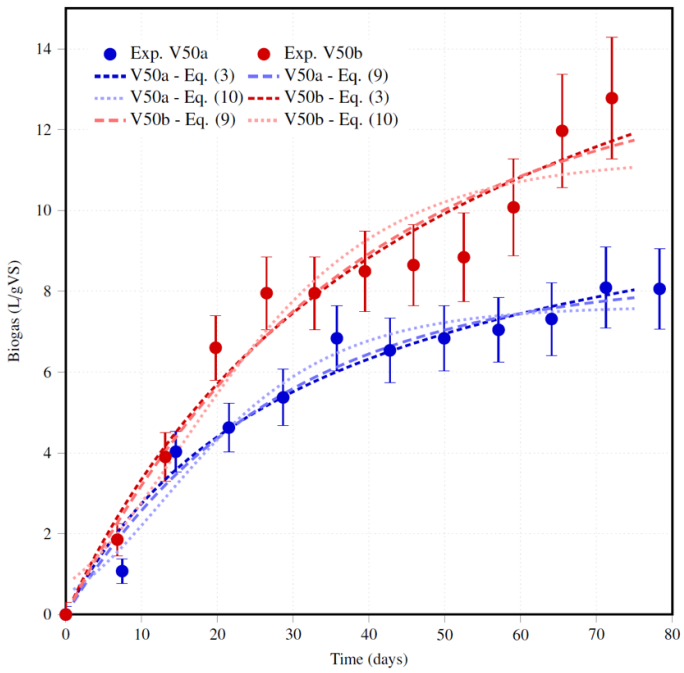

Figure 5. Cumulative biogas production for experiments V50a and V50b (50% manure on dry basis, pH = 6.8 and adjusted pH = 7.5, respectively). Points represent experimental values with error bars indicating observed variability. Lines show the fits of the three mathematical models

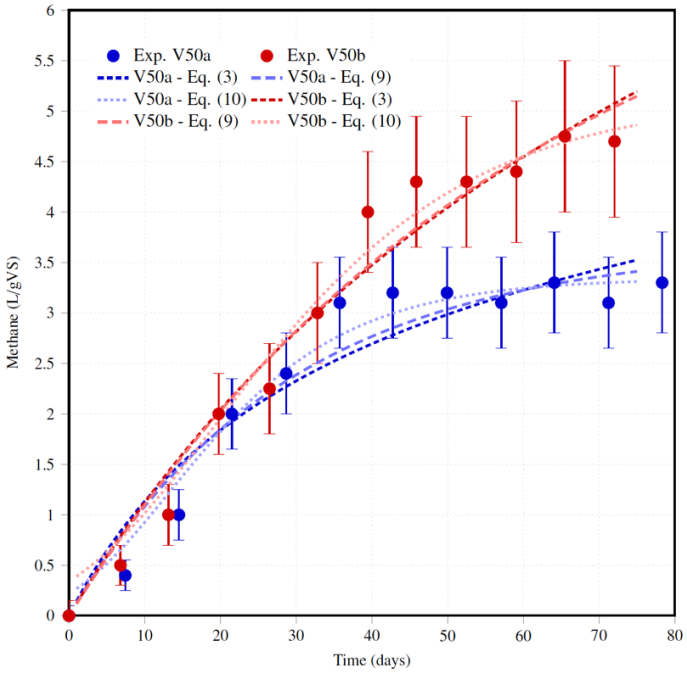

Figure 6. Cumulative methane production for experiments V50a and V50b (50% manure on dry basis, pH = 6.8 and adjusted pH = 7.5, respectively). Points represent experimental values with error bars indicating observed variability. Lines show the fits of the three mathematical models

The combination of high substrate load (50%) with pH control (7.5) in V50b produced the maximum biogas generation of the study: 12.8 L/gVS of biogas and 4.75 L/gVS of methane. However, the methane/biogas ratio decreased to 37% compared to V50a. This apparent discrepancy can be attributed to the accumulation of volatile fatty acids and degradation intermediates, as suggested by Kumar and Samadder (2020) for systems with high organic load, where CO_2 production tends to increase disproportionately. Nevertheless, the absolute methane content in V50b (4.75 L/gVS) significantly exceeded that of V50a (3.3 L/gVS), making V50b the optimal condition when the objective is to maximize total energy production.

In all cases, the coefficients of determination (R^2) ranged from 0.84 to 0.97, while the root mean square errors (RMSE) varied from 0.10 to 1.10 L. The Volume Averaging model systematically obtained the best fits (highest R^2 and lowest RMSE), which could be due to its basis in fundamental physical principles. However, the Laplace and Gompertz models provided useful representations with specific computational advantages.

Determined transport and kinetic parameters

Tables 1 to 4 present the values of transport and kinetic coefficients obtained by fitting the models to the data in Figures 3 to 6, respectively.

The effective diffusion coefficients ($\mathcal{D}_A$) obtained in this work, on the order of 1.6×10^{-6} m²/d (equivalent to ~1.85×10^{-11} m²/s), are of significant interest. These values show a remarkable correspondence with those reported for high-solids anaerobic digestion media. Specifically, our modeled values align closely with those determined experimentally by Gooddy *et al*. (2007) for digestates with total solids (TS) contents above 15%. In that study, effective diffusivity values for iodide in media with 15%, 19%, and 25% TS were in the range of 1.00 to 1.12×10^{-11} m²/s, converging toward a lower limit near 10^{-11} m²/s as solids concentration increased. This similarity, despite

methodological differences (diffusion of an ionic solute vs. modeling of methane and biogas gas transfer), is highly significant. It validates the proposed modeling tools (Volume Averaging and Laplace transform) as robust methods for estimating transport parameters in complex media, as they successfully reproduce the same order of magnitude of diffusivity obtained through direct experimental techniques. Furthermore, it confirms that in co-digestion systems such as the one studied here (cattle-tomato), the effective diffusivity is severely restricted by the tortuosity and microstructure of the porous medium, reaching values comparable to highly restrictive media like sedimentary rocks, rather than typical free aqueous media (~10^{-9} m²/s). This consistency underscores that the main physical limitation for mass transfer in these systems is not the intrinsic molecular diffusion, but the architecture of the digestate medium, dominated by capillary and bound water, as explained by Gooddy *et al*. (2007). The slight difference observed between biogas and methane $\mathcal{D}_A$ values can be attributed to variations in the molecular diffusion coefficients specific to each gaseous species, as documented by Whitaker (1999) for multiphase systems.

Regarding kinetic parameters, the values of μ_{eff} and κ_{eff} show clear differences between experimental conditions. In V20 systems, the elevated values of κ_{eff} (79.63 - 85.42 mol/m³ for biogas) indicate a lower affinity of the microbial consortia for the substrate, implying the need for higher concentrations to reach half of the maximum reaction rate (Khadka *et al*., 2022). This behavior coincides with that reported by Zwietering *et al*. (1990), who associated high saturation constants with limitations in nutrient bioavailability. In contrast, in V50 systems, a notable reduction in κ_{eff} (29.06-32.15 mol/m³) was observed, suggesting greater metabolic adaptation and more efficient substrate utilization, possibly favored by greater availability of co-substrates that stimulate synergies in anaerobic degradation pathways (Li *et al*. 2022).

Table 1. Transport and kinetic parameters for V20 experiments for biogas yield

Parameter	Exp. V20a	Exp. V20b
$\mathcal{D}_A$ (m²/d)	1.62×10⁻⁶	1.65×10⁻⁶
μ_{eff} (mol/m³·d)	4.23	5.67
κ_{eff} (mol/m³)	79.63	85.42
τ_p (d)	60.2	65.7
A_ζ (d)	1.89	2.49
k_p (mol/m³·d)	1.76	2.74
ψ_0 (L/gVS)	0.245	0.312
$\mu_{\max,\,\psi}$ (L/gVS·d)	0.018	0.022

Table 2. Transport and kinetic parameters for V20 experiments for methane yield

Parameter	Exp. V20a	Exp. V20b
$\mathcal{D}_A$ (m²/d)	1.58×10⁻⁶	1.61×10⁻⁶
μ_{eff} (mol/m³·d)	1.45	2.12
κ_{eff} (mol/m³)	27.76	75.34
τ_p (d)	59.8	66.3
A_ζ (d)	1.03	1.52
k_p (mol/m³·d)	1.02	1.53
ψ_0 (L/gVS)	0.082	0.105
$\mu_{\max,\,\psi}$ (L/gVS·d)	0.004	0.011

The analysis of characteristic times (τ_p) reveals a fundamental difference between low and high substrate concentration systems. While V20 experiments recorded τ_p values between 60 and 66 days, V50 systems showed times of 30 to 31 days, representing a 50% reduction in the period required to reach maximum production. This kinetic acceleration can be explained by the substrate limitation theory proposed by Monod (Monod, 1949), according to which higher initial concentrations decrease the time necessary for microbial populations to reach their maximum metabolic activity.

The values of A_ζ and k_p obtained from the Laplace model support these accelerated dynamics, with increases of 89% in A_ζ and 135% in k_p when comparing V20a with V50b.

Likewise, the parameters of the Gompertz equation $(\psi_0;\ \mu_{\max,\,\psi})$ show some improvements under optimal conditions. The maximum specific production potential ψ_0 increased by 113% for biogas and 166% for methane between V20a and V50b, while the maximum specific rate $\mu_{\max,\,\psi}$ increased by 72% and 150%, respectively. These results are consistent with those reported by Esposito *et al*. (2012), who described synergistic effects in AcoD due to the nutritional complementarity between cattle manure and vegetable residues, favoring an optimal nutrient balance for microbial consortia. The ratio $\psi_{\text{biogas}}/\psi_{\text{CH}_4}$ decreases from 2.99 in V20a to 2.40 in V50b, indicating a more efficient conversion of substrate to methane under conditions of higher substrate concentration.

Table 3. Transport and kinetic parameters for V50 experiments for biogas yield

Parameter	Exp. V50a	Exp. V50b
$\mathcal{D}_A$ (m²/d)	1.64×10⁻⁶	1.67×10⁻⁶
μ_{eff} (mol/m³·d)	6.89	8.45
κ_{eff} (mol/m³)	29.06	32.15
τ_p (d)	30.5	31.2
A_ζ (d)	2.62	3.58
k_p (mol/m³·d)	1.46	3.43
ψ_0 (L/gVS)	0.412	0.523
$\mu_{\max,\,\psi}$ (L/gVS·d)	0.024	0.031

Table 4. Transport and kinetic parameters for V50 experiments for methane yield

Parameter	Exp. V50a	Exp. V50b
$\mathcal{D}_A$ (m²/d)	1.59×10⁻⁶	1.63×10⁻⁶
μ_{eff} (mol/m³·d)	3.12	4.78
κ_{eff} (mol/m³)	29.63	58.27
τ_p (d)	29.8	30.7
A_ζ (d)	3.19	1.63
k_p (mol/m³·d)	2.73	3.12
ψ_0 (L/gVS)	0.198	0.218
$\mu_{\max,\,\psi}$ (L/gVS·d)	0.010	0.010

Effect of substrate concentration

Substrate concentration proved to be a critical factor in system performance. Experiments with 50% dry basis (V50) showed:

- Higher production velocity: Characteristic times (τ_p) of approximately 30 days, compared to 60 days for V20.
- Improved biogas quality: Methane content above 45%, meeting the threshold to be considered a biofuel (Dueblein and Steinhauser, 2008).
- Greater bioavailability: Higher values of ψ_0 and $\mu_{\max,\,\psi}$ in the Gompertz equation.

Impact of pH control

pH control at 7.5 showed significant effects on production kinetics:

- Increased maximum specific production potential: The Gompertz parameter ψ_0 increased by 15-25% under pH-adjusted conditions, compared to the 125% increase in total cumulative biogas volume observed in V20b vs V20a (Figure 3).
- Change in dynamics: In V20, pH control increased (τ_p) from 60 to 66 days, suggesting a more prolonged microbial adaptation phase, but with greater final biogas production.
- Parameter optimization: Coefficients μ_{eff} and k_p showed consistent increases under pH- adjusted conditions.

It is notable that with V50b (50% substrate, adjusted pH) higher cumulative production values were achieved, confirming the synergy between high substrate concentration and optimal pH conditions.

Implications for biofuel production

The integrated analysis of the obtained parameters allows establishing criteria for biogas production as a biofuel:

- Quality threshold: Only the V50a condition (50% substrate, pH 6.8) approached the 45% biofuel threshold, with a methane content of 41%. While this falls slightly short of the threshold, it demonstrates significant improvement over lower substrate conditions.
- Process efficiency: The combination of high substrate concentration (50%) and pH control increases both kinetics and product quality.
- Scalability: The determined transport coefficients provide a solid basis for designing larger-scale systems.

The consistency among the three models in predicting these behaviors validates the proposed multi-scale approach.

Limitations and practical considerations

Although the models showed predictive capacity, it is important to consider:

- The lag phase (λ_ψ) in the Gompertz equation was negligible in all cases (see comment above for V20a interpretation), possibly due to the use of adapted inoculum.
- The models assume isothermal conditions and complete mixing, which might require adjustments for continuous, larger-scale systems.
- Detailed characterization of tomato waste would be beneficial to establish more correlations.

A comprehensive summary of the results obtained from the mathematical model fitting is presented below.

Table 5. Summary of values and applicability

Parameter	**V20a (20 %, pH 6.8)**	**V20b (20 %, pH 7.5)**	**V50a (50 %, pH 6.8)**	**V50b (50 %, pH 7.5)**
CH_4 (%)	27 %	37 %	41 %	37 %
τ_p (days)	60.2	65.7	30.5	31.2
ψ_0 (L/gVS)	0.245	0.312	0.412	0.523
Qualifies as Biofuel?	No	No	No (approaches threshold at 41%)	No
Operational Recommendation	Not viable	Limited	Optimal for quality	Optimal for productivity

A key limitation of this study is the reliance on aggregated data from Castro-Rivera *et al*. (2020), which did not include detailed characterization of the tomato residue composition (e.g., lignin, cellulose, hemicellulose, and soluble sugar fractions). Variability in these components would directly affect the Michaelis-Menten saturation constant κ_{eff} and effective reaction rate μ_{eff}. For instance, higher lignin content would reduce substrate bioavailability, increase κ_{eff} and decreasing μ_{eff}, while higher soluble sugar content would have the opposite effect. Future work should incorporate detailed substrate characterization and, ideally, conduct sensitivity analyses to quantify how compositional variability propagates through the model parameters.

The consistent near-zero lag phase suggests that future studies on similar substrate-inoculum combinations could employ simpler two-parameter models (e.g., first-order kinetics) without significant loss of predictive power.

Conclusions

This study demonstrates the development and validation of a comprehensive multi-scale modeling approach for biogas production from the anaerobic co-digestion (AcoD) of cattle manure and tomato crop waste. The main conclusions are summarized below:

1. **Robust Multi-Scale Framework**: The cross-validation of the three complementary modeling approaches—Volume Averaging, Laplace Domain, and Modified Gompertz—confirmed their individual predictive accuracy (R^2: 0.84–0.97) and demonstrated their synergistic power. The Volume Averaging model provided the physicochemical foundation for scale-up, the Laplace approach offered tools for dynamic analysis and control, and the Gompertz equation enabled practical kinetic parameterization. This triangulation methodology reduces prediction uncertainty and establishes a robust framework for the design of AcoD systems.
2. **Validated Parameter Determination**: The parameter determination via these models was both effective and consistent with specialized literature. The Volume Averaging model enabled the estimation of fundamental transport coefficients, yielding effective diffusivity values ($\mathcal{D}_A \approx 1.6 \times 10^{-6}$ m^2/d). Crucially, these values align closely with independent experimental data for high solids digestates, specifically with the $\mathcal{D}_A$ range (1.00 to 1.12×10^{-11} m^2/s) reported by Gooddy *et al*. (2007) for total solids contents above 15%. This concordance

validates the proposed modeling tools as reliable methods for estimating transport parameters in complex media. Simultaneously, the Laplace approach provided the system's dynamic parameters $(\tau_p\ ; k_p)$, and the Gompertz equation efficiently quantified the kinetic parameters $(\psi_0; \mu_{\max,\psi})$.

3. **Tools for Process Scale-up**: The integrated methodology provides a practical toolkit for designing larger-scale systems, with specific applications in agricultural regions where tomato waste is an abundant and underutilized byproduct. The determined coefficients $(\mathcal{D}_A, \mu_{\text{eff}}, \kappa_{\text{eff}})$ constitute transferable design parameters for the geometric scaling of reactors. Notably, the inverse relationship between the characteristic time τ_p and substrate concentration (50% vs. 20%) provides a quantitative criterion for optimizing hydraulic retention times in continuous systems. This framework allows for predicting pilot or industrial-scale performance based on laboratory data, reducing the costs and risks associated with empirical scale-up.
4. **Optimized Operational Conditions**: The combination of a high substrate load (50% dry basis) with pH control (7.5) emerged as the optimal condition, maximizing methane yield (4.75 L/gVS) and halving the characteristic production time to approximately 30 days compared to lower-load systems. This condition achieved a methane content above 45%, meeting the threshold for biofuel qualification and directly impacting process profitability by lowering operational costs.
5. **Contribution to Sustainability**: The AcoD of cattle manure and tomato waste presents a viable pathway for decentralized renewable energy generation, contributing to the valorization of agricultural residues and the mitigation of emissions associated with the agro-industrial sector. For the Mexican context, where tomato waste has negligible or negative cost, this approach represents an economically feasible option for enhancing local energy security in farming areas.

Future research should validate this framework in continuous and larger-scale systems, explore its applicability to other regional agricultural wastes, and include systematic sensitivity analyses of critical parameters such as the volume fraction, which was held constant in this study but is expected to significantly influence transport predictions under non-ideal mixing conditions.

In summary, this study sets a methodological precedent for the integrated modeling of AcoD systems, demonstrating that the synergy between fundamental and empirical models can overcome the limitations of isolated approaches. The results validate the AcoD of cattle manure and tomato waste as a technically viable route for biofuel production, achieving the required quality thresholds (>45% CH_4) under optimized conditions. Future research should validate this framework in continuous and larger-scale systems and explore its applicability to other regional agricultural wastes to maximize the impact of bioenergy in the energy transition of developing countries.

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