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Co-digestion of Canna Indica Rhizome and Cow Manure: Kinetic Model Comparison

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Abstract—Empirical kinetic models have been successfully applied to describe the anaerobic co-digestion kinetics of canna rhizome and cow manure for biogas production. A diverse range of models were fitted to experimental data collected from batch assays at various ratios. To select the most appropriate model for each ratio, the statistical metrics R^2 and RMSE were employed. Among all the models evaluated, the Weibull model demonstrated superior performance in predicting kinetic parameters across all ratios, exhibiting the highest R^2 value (0.9988) and the lowest RMSE (0.9746) at the optimal ratio of 50 :50:200. The results obtained demonstrate that the co-digestion of these substrates is a promising pathway for bioenergy production, while valorizing agricultural residues. This study opens up interesting perspectives for the optimization of co-digestion processes and the energy transition.

Keywords—Biogas; Co-digestion; Canna indica rhizome; Cow manure; Kinetic models.

I. INTRODUCTION

The growing global energy crisis has sparked an incessant search for sustainable and renewable energy solutions. In this context, biogas, a clean and renewable fuel produced through anaerobic digestion of organic matter, represents a promising solution to reduce our dependence on fossil fuels [1]. However, the efficiency of biogas production is strongly influenced by the specific characteristics of the organic substrates used [9].

Our study focuses on the co-digestion of Canna indica rhizomes and cow manure, two readily available agricultural residues. Canna indica, a versatile tropical plant, has garnered attention for its potential as a feedstock for biogas production [10]. Cow manure, a ubiquitous by-product of livestock farming, is also recognized for its biogas production capabilities [14]. By combining these substrates, the co-digestion process is expected to enhance biogas yield, improve substrate digestibility, and optimize nutrient utilization [8].

In a previous study, we investigated the co-digestion potential of Canna indica rhizomes and cow manure, employing an existing mathematical model tailored to our system [17]. Building upon these initial findings, we delved deeper into our analysis by applying nine different empirical models, including Gompertz, Modified Gompertz, Logistic, Modified Logistic, Richards, First Order, Transference, Cone, and Weibull, to our experimental data. This multi-model approach enables us to obtain a more precise and detailed description of biogas production kinetics and to identify the most suitable model for our system ([4], [6], [12], [13], [18], [19], [21], [22], [23]).

Each of these models presents specific advantages and limitations. For instance, the Gompertz model, a classic approach that describes the cumulative biogas production over time, has been successfully applied in numerous studies but may not always capture the complexity of real-world data, particularly when dealing with substrates exhibiting non-standard growth patterns. The Logistic and Modified Logistic models are also commonly used to describe the sigmoidal shape of biogas production curves, but they may underestimate biogas yield when substrate digestibility is highly variable. The Richards model offers increased flexibility, allowing for asymmetric growth patterns, while the First Order model, although simple, often fails to capture the initial lag phase and subsequent exponential growth phase observed in many biogas production processes.

This comprehensive modeling approach will allow us to accurately predict biogas yields and extract critical kinetic parameters. The results of this study not only illuminate the feasibility and efficiency of co-digesting Canna indica rhizomes and cow manure but also contribute to a deeper understanding of the factors influencing biogas production kinetics ([2], [3], [7]). By identifying the optimal substrate ratio and the most appropriate kinetic model, this research provides valuable insights for the design, operation, and optimization of biogas facilities using agricultural residues ([13], [15]).

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In conclusion, our study aims to optimize biogas production from common agricultural residues, improve the understanding of factors influencing biogas production kinetics, and provide crucial data for the design and optimization of biogas facilities. Ultimately, our results support the transition towards a more sustainable and secure energy future ([5], [16], [20]) contributing to global efforts to develop renewable energy solutions and reduce our dependence on fossil fuels.

II. MATERIALS AND METHODS

A. Feedstocks

- Canna indica Rhizome :
  - The Canna indica rhizomes were sourced from Ambohitra village, located in the Andramasina district of Madagascar.
  - The rhizomes underwent washing and grinding.
- Cow Manure :
  - The cow manure was obtained from a local farm.
  - Pretreatment involved sieving and homogenizing the manure.

B. Co-digestion Methodology

- Substrate Mixtures: Canna indica rhizome and cow manure were combined in various ratios (Canna Rhizome RC: Cow Manure CM: Eau W) based on dry mass. The following ratios were used: (100:0:100), (100:0:200), (25:75:200) and (50:50:200)
- Anaerobic digestion occurred under mesophilic conditions (25-32°C) with a retention time ranging from 22 to 29 days.

C. Measurement

- Biogas production was quantified using the displacement method.
- Biogas production, composition, temperature, and pH of the reaction medium were monitored continuously throughout the study.

D. Kinetic Model : Models Description

To model biogas production, we selected nine commonly used kinetic models: Gompertz, Gompertz modified, Logistic, Modified Logistic, Richards, First-Order, Transference, Cone and Weibull. These mathematical models allow us to simulate and predict the time-dependent evolution of biogas production based on simplified assumptions of the underlying biological mechanisms of anaerobic codigestion.

Table I. Empirical-Kinetic models for Anaerobic Digestion tested in this work

Model Name	Model Equation	
Gompertz	$B(t) = B_0 exp\left[-exp\left(-K_G(t - T_i)\right)\right]$	$B(t)$ is the biogas production at time t; B_0 is the asymptotic level of biogas production, representing the maximum production capacity; K_G is the growth rate parameter, Ti is the inflection time parameter
Modified Gompertz	$B(t) = B_0 exp\left[-exp\left(\frac{R_{max} e}{B_0}(\lambda - t) + 1\right)\right]$	$B(t)$is cumulative biogas production (L); B_0 is the biogas production potential (L); R_{max} is the maximum biogas production rate (L/day) and λ is the duration of lag phase (day)
Logistic	$B(t) = \frac{B_0}{1 + exp\left[\frac{4R_{max}(\lambda - t)}{B_0} + 2\right]}$	The parameters have the same meaning as defined previously in Modified Gompertz model.
Modified Logistic	$B(t) = \frac{B_0}{1 + Ce^{-kt}}$	B(t) represents the cumulative biogas production at time t, $\boldsymbol{B_0}$ is the maximum achievable biogas production, C is a constant related to initial conditions, k is the specific growth rate.
Richards	$B(t) = \frac{B_0}{(1 + Ce^{-kt})^{\frac{1}{\theta}}}$	$B(t)$ represents the cumulative biogas production at time t, B_0 is the maximum achievable biogas production, C is a constant related to initial conditions, k is the specific growth rate, and θ is a shape parameter(θ = 1 simplifies to the logistic model; θ < 1 for slower initial growth, faster later; θ > 1 for faster initial, slower later growth).
First Order	$B(t) = B_0(1 - e^{-kt})$	B is the cumulative biogas yield at time t (L); B_0 is the methane potential of the substrate (L); k is the first-order biogas production rate constant (day^{-1}); t is digestion time (days).
Transference	$B(t) = B_0\left\{1 - exp\left[\frac{-R_{max}(t - \lambda)}{B_0}\right]\right\}$	The parameters have the same meaning as defined previously in Modified Gompertz model.
Cone	$B(t) = \frac{B_0}{1 + (kt)^{-n}}$	$B(t)$is cumulative biogas production (L); B_0 is the biogas production potential (L); k--A rate constant that determines how quickly biogas production reaches its maximum (day^{-1}); n- the shape of the biogas production curve..
Weibull	$B(t) = b_1 + b_2\left\{1 - exp\left[-\left(\frac{t}{b_3}\right)^{b_4}\right]\right\}$	$B(t)$ is the cumulative biogas production at time t, b1 is initial biogas production rate. b2 is the maximum biogas production capacity, b3 is the rate of biogas production increase and b4 is shape parameter for the production curve.

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https://ijpsat.org/
Vol. 47 No. 1 October 2024, pp. 195-208

E. Fitting and validation of kinetic models

To identify the optimal parameters of the kinetic models, a non-linear least squares optimization procedure [11] was implemented in MATLAB. This procedure aimed to minimize the difference between the predicted cumulative biogas production values from the models and the experimentally observed values. Once the parameters were optimized, the models' ability to accurately describe the biodegradation process was evaluated using a set of statistical criteria, including the coefficient of determination (R^2) and root mean square error (RMSE).

III. RESULTATS AND DISCUSSION

A. Biogaz Production Curves

Figures 1-9 illustrate the evolution of cumulative biogas production over time for different substrate ratios (100:0:100, 100:0:200, 25:75:200, 50:50:200) at various hydraulic retention times. This analysis helps to identify both the optimal ratio for maximizing biogas production and the best-fitting model that accurately describes the experimental data.

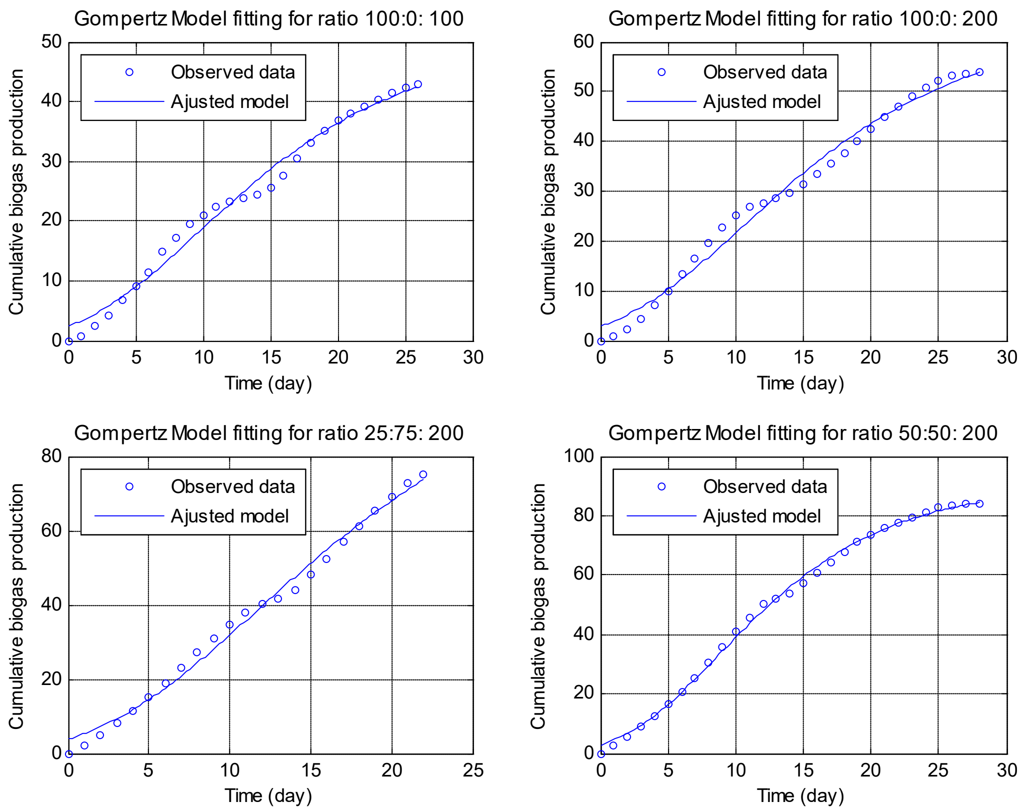

Fig.1. Gompertz model fitting for biogas production with varying substrate ratios

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Vol. 47 No. 1 October 2024, pp. 195-208

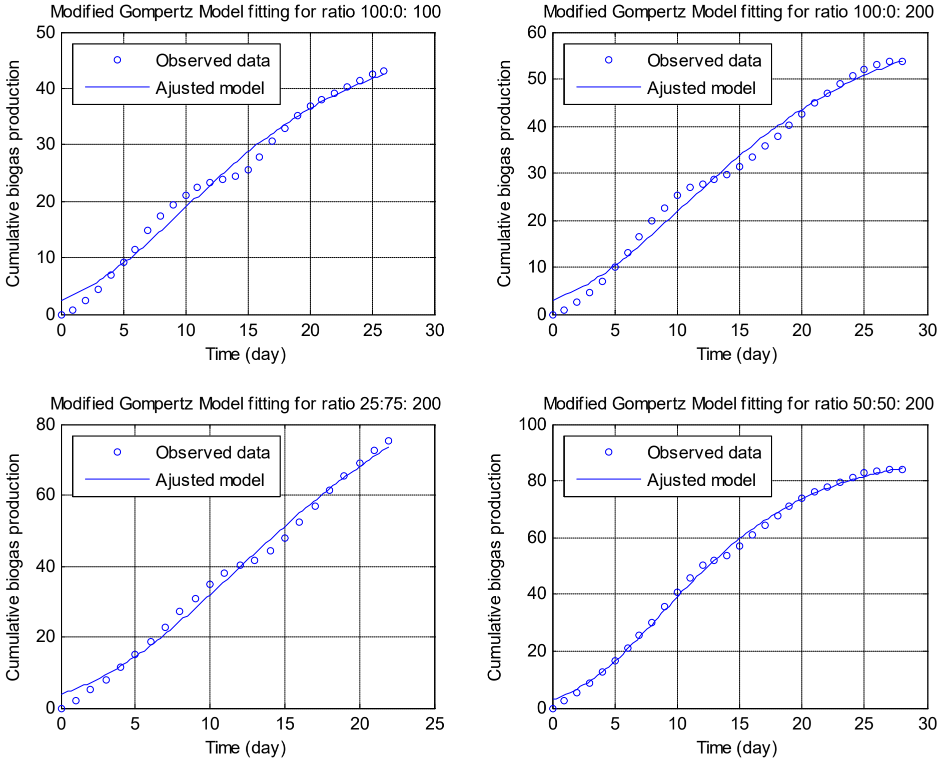

Fig.2. Modified Gompertz Model Fit for Biogas Production: Substrate Ratio Impact

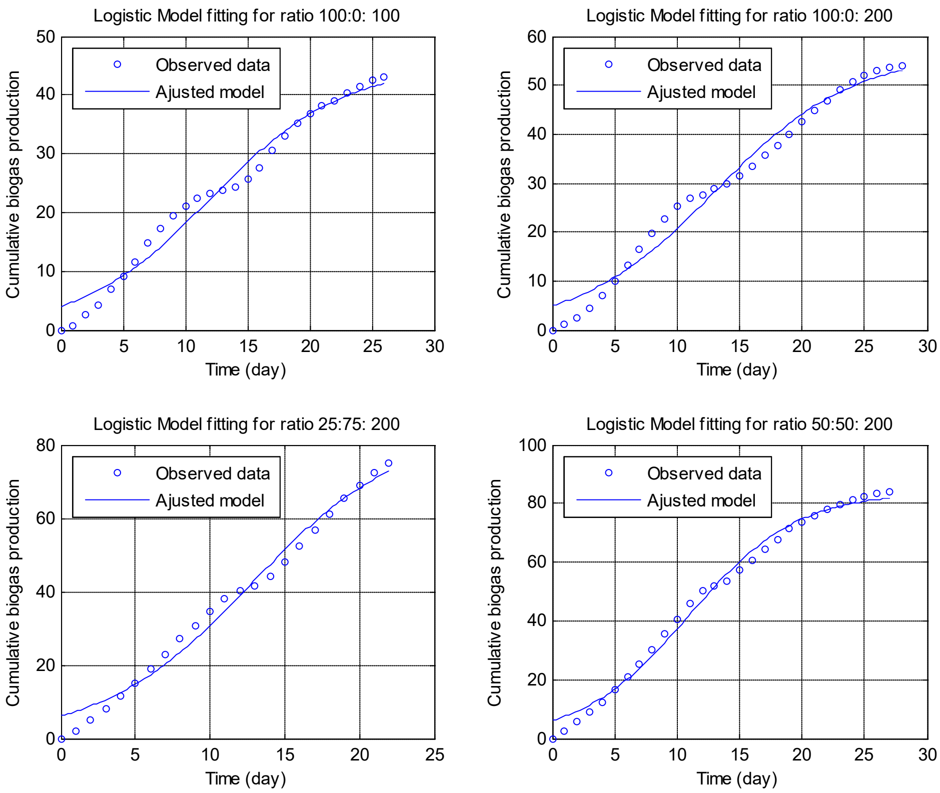

Fig.3. Fitting the Logistic Model to Biogas Production Data with Varying Substrate Compositions

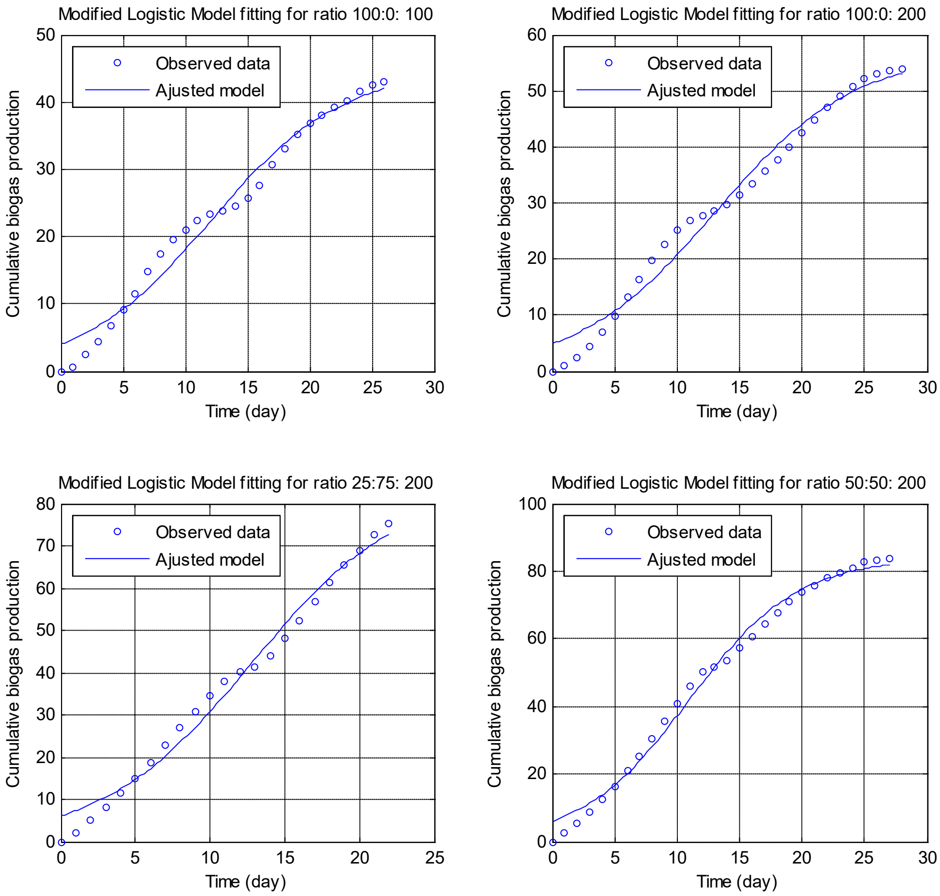

Fig.4. Modified Logistic Model: A Fitting Approach for Biogas Production with Diverse Substrate Ratios

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https://ijpsat.org/
Vol. 47 No. 1 October 2024, pp. 195-208

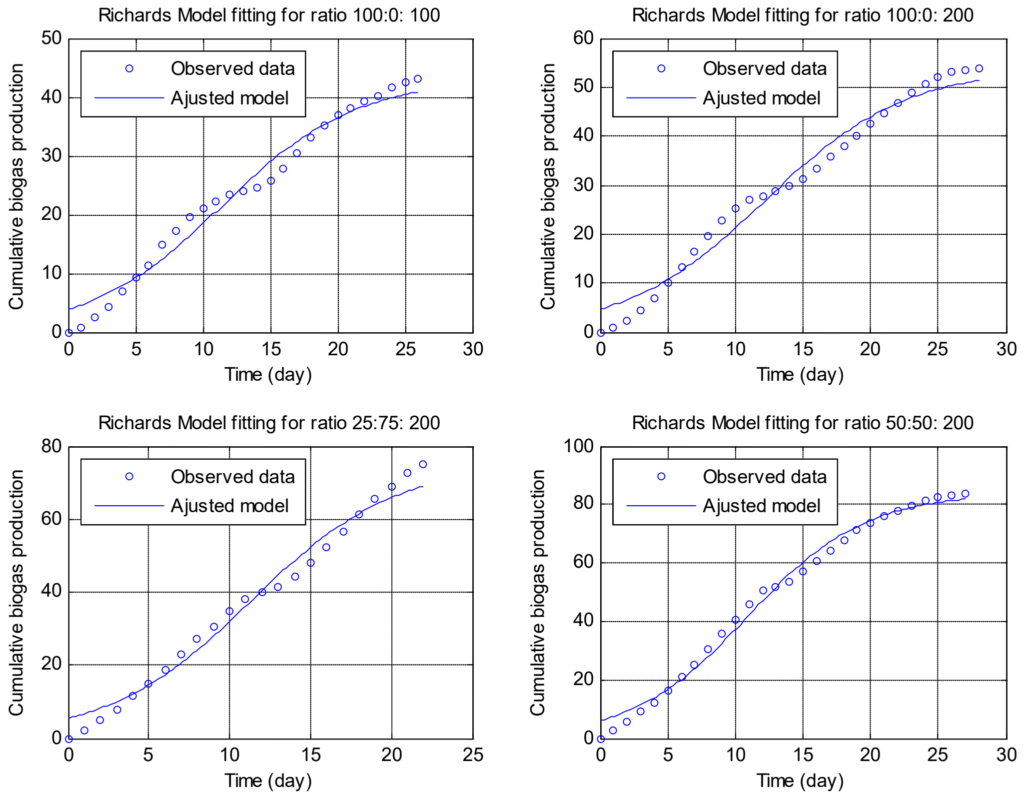

Fig.5. Fitting Biogas Production Data to the Richards Model with Varied Substrate Ratios

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https://ijpsat.org/
Vol. 47 No. 1 October 2024, pp. 195-208

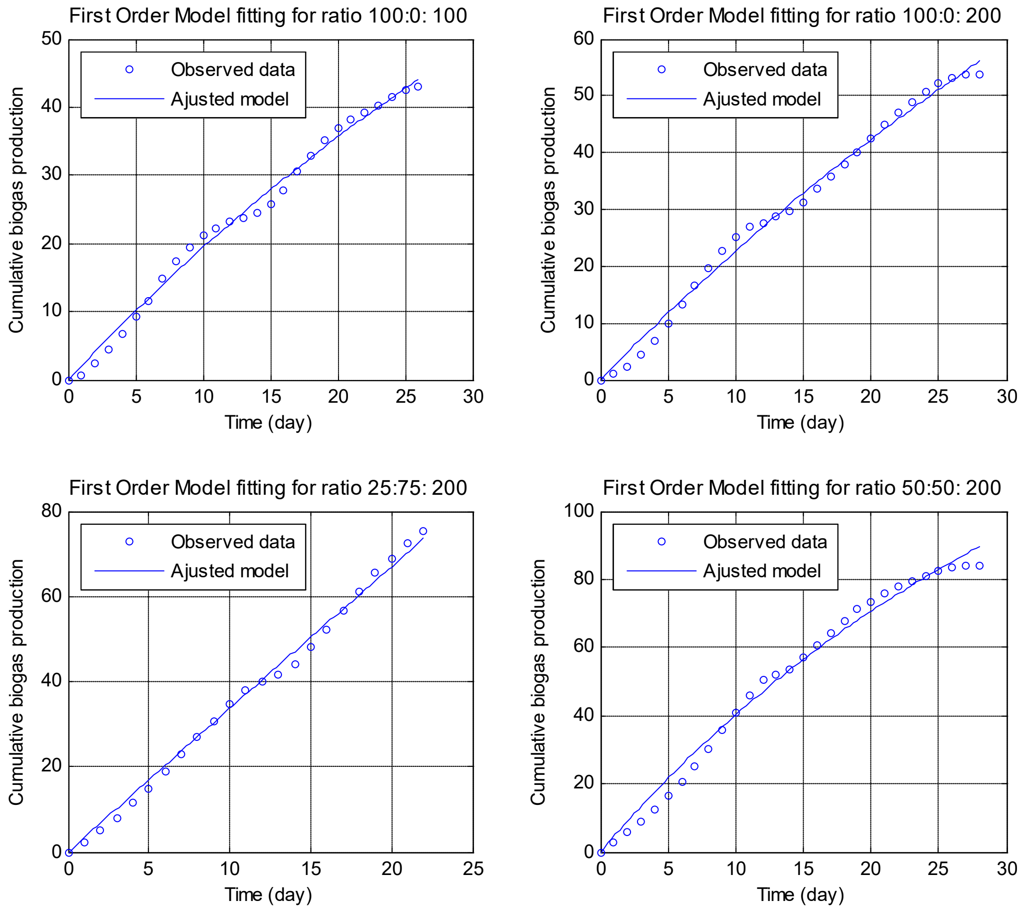

Fig.6. Impact of Substrate Ratios on Biogas Production: A First Order Model Fitting

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Vol. 47 No. 1 October 2024, pp. 195-208

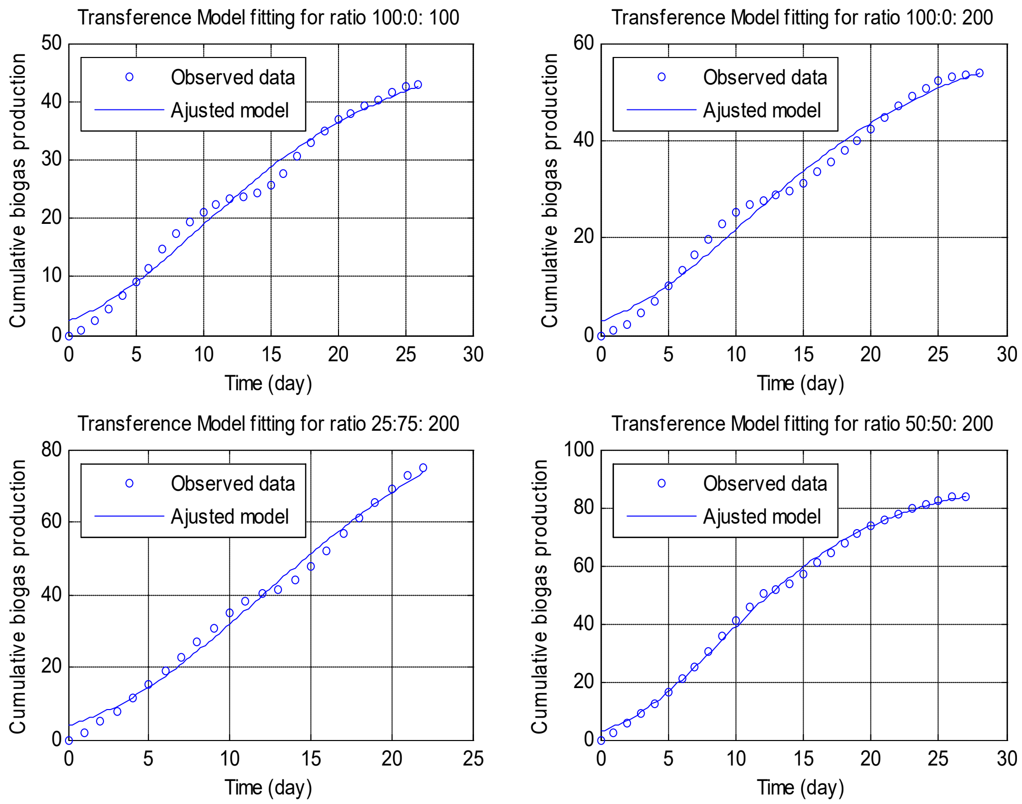

Fig.7. Impact of Substrate Ratios on Biogas Production: A transference Model fitting

International Journal of Progressive Sciences and Technologies (IJPSAT)
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https://ijpsat.org/
Vol. 47 No. 1 October 2024, pp. 195-208

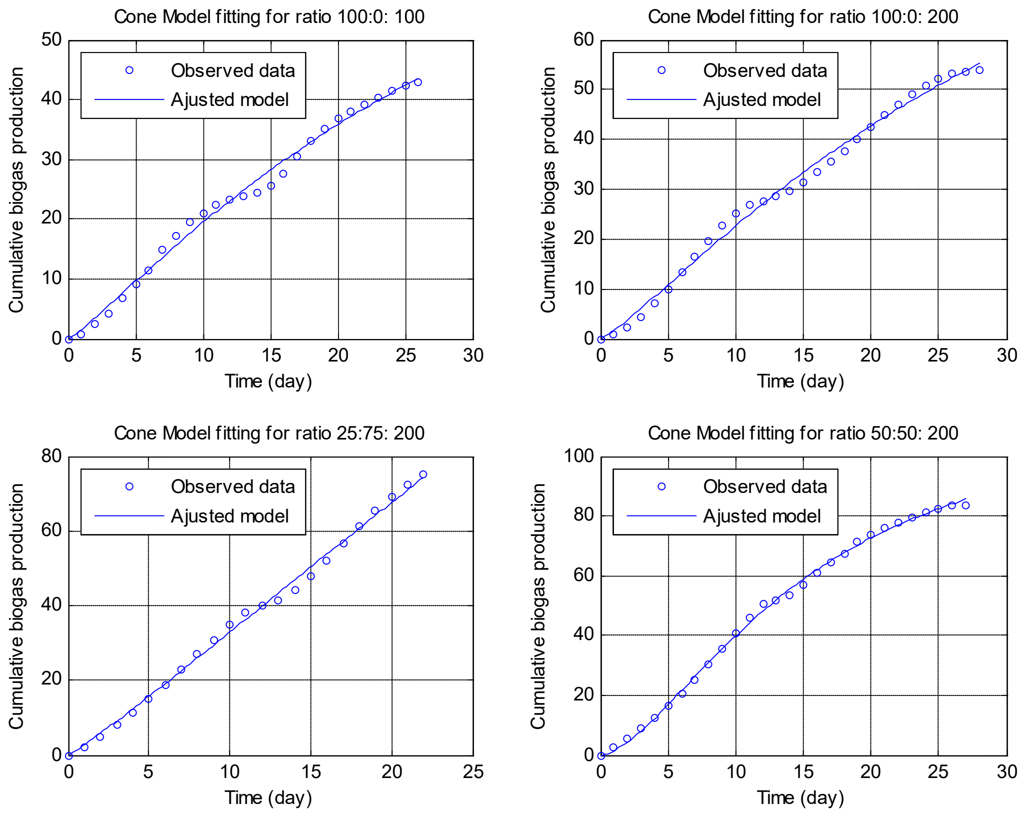

Fig. 8. Fitting the Cone Model to Biogas Production Data with Varying Substrate Compositions

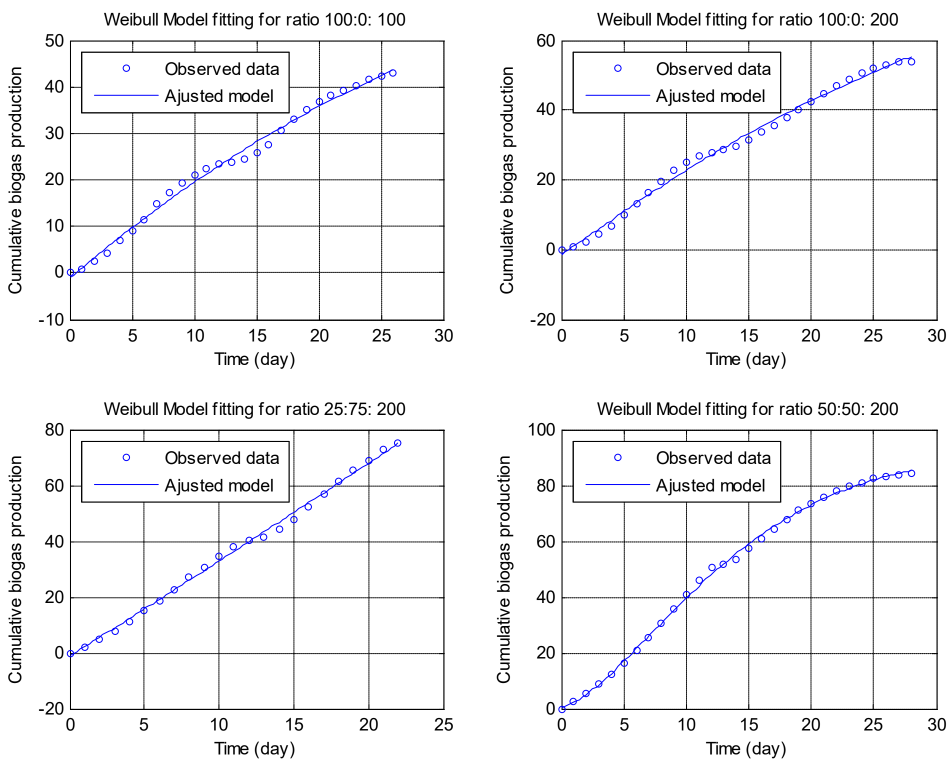

Fig. 9. Weibull Model: A Fitting Approach for Biogas Production with Diverse Substrate Ratios

In-depth analysis of the fitting curves reveals distinct behaviors depending on the models and substrate ratios.

- First Order model: Curves are nearly linear for all ratios, suggesting a relatively simple and stable biogas production kinetics.
- Cone and Weibull models :
    - Linearity for ratios 100:0:100, 100:0:200, and 25:75:200: these ratios induce nearly linear fitting curves, regardless of the model, indicating rapid degradation of dominant substrates without a significant lag phase.
    - Flattened S-shaped curve for ratio 50:50:200: This specific ratio induces a flattened S-shaped curve for Cone and Weibull models, suggesting a more complex kinetics, potentially due to substrate synergies, inhibitors, or shifts in microbial community.
- Other 6 models (Gompertz, Modified Gompertz, Logistic, Modified Logistic, Richards and Transference): For all ratios and remaining models, curves adopt a typical S-shape, characterized by an initial slow phase, followed by an exponential phase and a stationary phase. This classic S-shape is characteristic of microbial growth process.

A combination of factors influences biogas production kinetics. Substrate ratios modify organic matter composition and reaction conditions, while substrate heterogeneity adds complexity to the degradation process, affecting the shape of the fitted curves.

All models demonstrated strong alignment with the observed data across various substrate ratios, confirming their accuracy in predicting cumulative biogas production over time.

B. Analysis comparison

Table II. Kinetic parameter optimization and optimal ratio identification for anaerobic codigestion: a comparative model study

	Model	Ratio	B0	KG	Ti	Rmax	lambda	C	k	alpha	n	b1	b2	b3	b4	R^2	RMSE
1	Gompertz	100:0:100	49.8961	0.1128	9.7961	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	0.9850	1.6512
2	Gompertz	100:0:200	63.0390	0.1062	10.6156	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	0.9869	1.9649
3	Gompertz	25:75:200	104.3077	0.1020	11.6690	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	0.9913	2.1574
4	Gompertz	50:50:200	90.4116	0.1410	8.7909	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	0.9975	1.3860
5	M.Gompertz	100:0:100	49.8970	NaN	NaN	2.1115	9.7962	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	0.9850	1.6512
6	M.Gompertz	100:0:200	63.0392	NaN	NaN	2.5019	10.6156	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	0.9869	1.9649
7	M.Gompertz	25:75:200	104.3081	NaN	NaN	3.9534	11.6690	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	0.9913	2.1574
8	M.Gompertz	50:50:200	90.4116	NaN	NaN	4.7410	8.7909	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	0.9975	1.3860
9	Logistic	100:0:100	44.9211	NaN	NaN	2.1437	1.6332	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	0.9752	2.1280
10	Logistic	100:0:200	56.7358	NaN	NaN	2.5552	1.9686	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	0.9772	2.5959
11	Logistic	25:75:200	84.3904	NaN	NaN	4.2108	2.7596	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	0.9837	2.9448
12	Logistic	50:50:200	83.8602	NaN	NaN	4.8636	2.3520	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	0.9908	2.6460
13	M.Logistic	100:0:100	44.9196	NaN	NaN	NaN	NaN	10.0934	0.1909	NaN	NaN	NaN	NaN	NaN	NaN	0.9752	2.1280
14	M.Logistic	100:0:200	56.7346	NaN	NaN	NaN	NaN	10.5347	0.1802	NaN	NaN	NaN	NaN	NaN	NaN	0.9772	2.5959
15	M.Logistic	25:75:200	84.3898	NaN	NaN	NaN	NaN	12.8177	0.1996	NaN	NaN	NaN	NaN	NaN	NaN	0.9837	2.9448
16	M.Logistic	50:50:200	83.8590	NaN	NaN	NaN	NaN	12.7511	0.2320	NaN	NaN	NaN	NaN	NaN	NaN	0.9908	2.6460
17	Richards	100:0:100	42.9816	NaN	NaN	NaN	NaN	10.1025	0.4420	0.4571	NaN	NaN	NaN	NaN	NaN	0.9741	2.1713
18	Richards	100:0:200	53.8623	NaN	NaN	NaN	NaN	10.5355	0.4427	0.4345	NaN	NaN	NaN	NaN	NaN	0.9757	2.6792
19	Richards	25:75:200	75.2269	NaN	NaN	NaN	NaN	12.8262	0.4817	0.4676	NaN	NaN	NaN	NaN	NaN	0.9804	3.2331
20	Richards	50:50:200	83.8002	NaN	NaN	NaN	NaN	12.7497	0.3715	0.6250	NaN	NaN	NaN	NaN	NaN	0.9908	2.6461
21	First Order	100:0:100	120.4154	NaN	NaN	NaN	NaN	NaN	0.0175	NaN	NaN	NaN	NaN	NaN	NaN	0.9920	1.2074
22	First Order	100:0:200	166.6353	NaN	NaN	NaN	NaN	NaN	0.0146	NaN	NaN	NaN	NaN	NaN	NaN	0.9927	1.4645
23	First Order	25:75:200	1900.2000	NaN	NaN	NaN	NaN	NaN	0.0018	NaN	NaN	NaN	NaN	NaN	NaN	0.9948	1.6592
24	First Order	50:50:200	181.0300	NaN	NaN	NaN	NaN	NaN	0.0249	NaN	NaN	NaN	NaN	NaN	NaN	0.9905	2.6929
25	Transference	100:0:100	49.8969	NaN	NaN	2.0700	0.9286	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	0.9850	1.6512
26	Transference	100:0:200	63.0391	NaN	NaN	2.4628	1.1991	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	0.9869	1.9649
27	Transference	25:75:200	104.3079	NaN	NaN	3.9154	1.8697	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	0.9913	2.1574
28	Transference	50:50:200	90.4115	NaN	NaN	4.6891	1.6978	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	0.9975	1.3860
29	Cone	100:0:100	112.4791	NaN	NaN	NaN	NaN	NaN	0.0260	NaN	1.1618	NaN	NaN	NaN	NaN	0.9927	1.1513
30	Cone	100:0:200	131.2481	NaN	NaN	NaN	NaN	NaN	0.0274	NaN	1.2126	NaN	NaN	NaN	NaN	0.9940	1.3351
31	Cone	25:75:200	854.6486	NaN	NaN	NaN	NaN	NaN	0.0053	NaN	1.0980	NaN	NaN	NaN	NaN	0.9968	1.3072
32	Cone	50:50:200	120.0331	NaN	NaN	NaN	NaN	NaN	0.0651	NaN	1.6137	NaN	NaN	NaN	NaN	0.9986	1.0384
33	Weibull	100:0:100	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	-1.0645	89.0836	36.8753	1.0274	0.9930	1.1317
34	Weibull	100:0:200	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	-1.3387	103.4133	34.7252	1.0684	0.9942	1.3108
35	Weibull	25:75:200	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	-1.0692	1649.6000	37486.0000	1.0320	0.9971	1.2383
36	Weibull	50:50:200	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	0.0375	93.6189	15.1877	1.4645	0.9988	0.9746

M. Gompertz: Modified Gompertz; M. Logistic: Modified logistic

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Vol. 47 No. 1 October 2024, pp. 195-208

The research focuses on two key aspects: identifying the most suitable mathematical approach and determining the optimal substrate ratio. Four different proportions of rhizome, cow manure, and water were tested. By comparing various analytical models, the study seeks to identify the most effective predictive tool and its associated kinetic parameters, crucial for understanding and forecasting system performance.

1. General trends and results common to all models

The results obtained confirmed several trends common to all models:

- Dilution effect: The dilution rate had a significant impact on biogas production.
- Interest of the 100:0:200 ratio: The ratio composed solely of Canna indica rhizome and water (100:0:200) proved to be a valuable reference point for comparing other mixtures.
- Positive effect of cow manure and synergy: The addition of cow manure had a positive effect on biogas production, suggesting a synergy between the two substrates, for the 25:75:200 and 50:50:200 ratios.
- Optimal ratio: The 50:50:200 ratio (50% rhizome, 50% cow manure, and 200% water) was identified as the optimal ratio for the anaerobic co-digestion studied.
- Quality of fits: The models showed an excellent ability to predict biogas production, with R^2 greater than 0.98 in all cases. The RMSE were also low, ranging from 0.9746 to 2.9448.

2. Quantifying model differences through constant analysis

The figure presents a comprehensive analysis of biogas production for a ratio of 50:50:200, comparing nine different mathematical models against observed data. The graph illustrates the cumulative biogas production in liters over a period of 28 days. The observed data points are represented by white circles, while the various models are depicted by lines of different colours and styles.

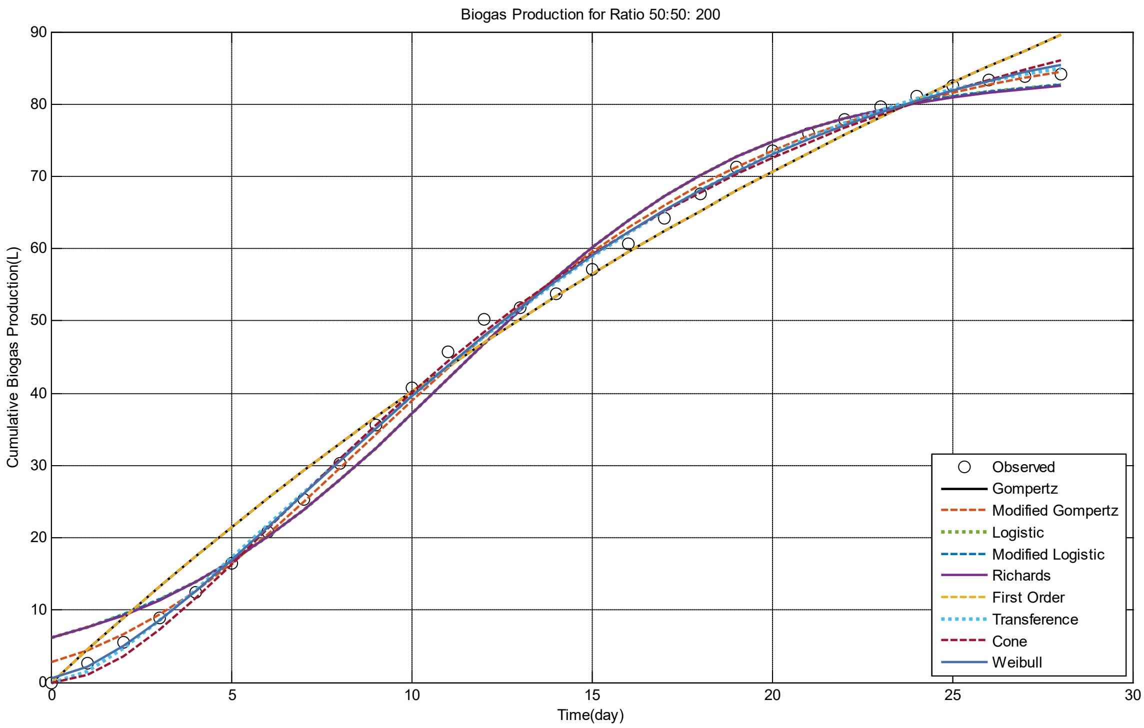

Fig. 10 Model fitting: comparison

Upon examination, we can discern three distinct phases in the biogas production process. The initial lag phase, lasting approximately 0-5 days, is characterized by slow biogas production as microorganisms adapt to the substrate. This is followed by an exponential phase from roughly day 5 to day 20, where biogas production increases rapidly. The inflection point, indicating the maximum rate of production, occurs around days 10-12. Finally, a stationary phase is observed after day 20, where production slows and approaches a plateau as easily biodegradable organic matter is depleted.

Most models indeed closely follow the trend of the observed data. The Gompertz, Modified Gompertz, Logistic, Modified Logistic, Cone and Weibull models show particularly good fits throughout the entire process.

The Richards model shows a good fit overall but slightly overestimates production in the very early stages (0-5 days) and underestimates it slightly in the later stages (after 20 days).

The First Order model noticeably overestimates production in the early and middle stages (0-15 days) and then underestimates it in the later stages.

The Transference model follows the observed data quite well, with only minor deviations.

Most models converge satisfactorily with the observed data towards the end of the process, around 25-28 days.

The graph indicates a final biogas production of approximately 85 liters after 28 days, with the most intense production occurring between days 5 and 20. Overall, the models demonstrate good alignment with the observed data, though slight variations are noticeable across different phases of the production process.

3. Identification of the best performing mathematical model

We evaluated each analytical approach using R^2 and RMSE, selecting the model where the former is close to 1 and the latter is minimal, ensuring the best fit between predictions and observed data.

Regardless of how R^2 and RMSE were weighted, our analysis consistently identified the Weibull model as the most suitable for describing our dataset.

IV. CONCLUSION

A comparative analysis of empirical models for biogas production from canna rhizome and cow manure reveals valuable insights into their predictive capabilities.

Among the models evaluated, the Weibull model demonstrated superior performance in predicting kinetic parameters. This finding confirms the optimal ratio of 50:50:200 previously identified in our earlier research [17]. This ratio offers a promising avenue for further optimization, it would be interesting to delve deeper into variations around this optimal ratio to identify new synergies between substrates and further optimize the co-digestion process.

While the Weibull model excelled under these conditions, it's essential to note that these results are specific to the experimental setup. Future research could delve into other kinetic models, such as mechanistic models, and examine additional factors influencing biogas production to gain a deeper understanding of the underlying co-digestion mechanisms. Moreover, larger-scale validation is necessary to assess the applicability of these findings in real-world conditions.

Combining canna rhizomes with various organic waste streams, such as brewery grains, coffee grounds, and sewage sludge, or different types of manure, in anaerobic co-digestion offers numerous benefits. This approach can enhance biogas production, improve digestate quality, stabilize the co-digestion process, and contribute to a more circular economy and a sustainable energy future.

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