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Kinetic Analysis of Biogas Production from Cow Manure Waste

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ABSTRACT

Biogas is the result of decomposing organic waste that can be used as alternative energy. One of the organic waste that has the potential to produce biogas is livestock waste. The purpose of this scientific article is to see the results of kinetic models on secondary data processing of biogas volume acquisition/day. This scientific article was conducted by processing secondary data on biogas production at several pH variations (N1 = 7.17, N2 = 7.22, N3 = 7.24) using several kinetic models, namely the Gompertz model, logistic model, and first-order model. The best results are obtained in the logistic model, where the objective function value is the smallest. For each variation of N1, N2, and N3, the SSE values obtained are 458.37, 423, and 309. For the Gompertz and logistic models have the same graphical shape which is sigmoid-shaped or "s" shaped, which indicates that there are three phases in the formation of biogas, namely the pause phase, the rapid growth phase, and the stable growth phase. For the first-order model, it has a linear graph shape which states that in this model, there is a simplification of stages, namely only the hydrolysis stage which follows a first-order pattern.

Keywords: *Alternative Energy, Biogas, First-Order Model, Gompertz Model, Logistic Model*

1. INTRODUCTION

Energy is an essential need for human life and its use continues to increase along with the increasing population. Energy also plays an important role in supporting human comfort and daily activities. In many countries, especially developing countries, there is an energy crisis due to high dependence on fossil fuels whose availability is limited (Fitri and Hamdi, 2024). Currently, fossil fuels are still the main source of energy, but their non-renewable nature causes their reserves to dwindle. Therefore, various efforts are made to develop renewable energy sources, one of which is through the utilization of waste from the livestock, agriculture, plantation and forestry sectors to be used as alternative energy such as biogas (Khaidir, 2016).

Biogas is a gas produced through the decomposition process of organic matter anaerobically by microorganisms. The composition of biogas consists of about 60% methane (CH_4), ±2% nitrogen (N) and oxygen (O_2), ±38% carbon dioxide (CO_2), and contains hydrogen sulfide (H_2S). Biogas is flammable like LPG. The manufacturing process is quite simple, namely by putting organic material such as animal or human feces into a tightly closed digester. After going through the fermentation process for a certain period of time, gas will be formed and can be utilized as an energy source. A digester or biodigester is where anaerobic fermentation by bacteria takes place, converting organic material into methane and carbon dioxide gas. The design of the biodigester must support the anaerobic process optimally (Kurniawati et al., 2021).

In the context of global energy transition, biogas has a strategic role because it supports the transition from fossil-based electricity systems to more environmentally friendly and renewable energy sources (Fitri and Hamdi, 2024). Biogas can be produced from various types of organic waste such as household garbage, agricultural waste, animal manure, and unused plantation waste. One of the most potential raw materials for biogas production is cow manure, because in addition to being environmentally friendly, it is also easily obtained and has a high methane content (Hassan et al., 2022). Therefore, the utilization of cow manure as a biogas feedstock is the most commonly used method and is considered efficient and economical (Rahmadi and Sudirman, 2014).

Kinetics analysis is necessary to understand the mechanism and rate of biochemical reactions in biogas production, such as hydrolysis, acidogenesis, and methanogenesis. By modelling parameters such as microbial growth rate (U), adaptation time (λ), or reaction constants (k), it is possible to predict system performance under various conditions. Kinetic models also help optimize digester design, reduce experimental costs, and validate laboratory and industrial-scale feasibility, evaluate the influence of external factors such as pH and temperature, and provide quantitative data for technical and economic decision-making. Kinetic modelling is the link between theory and application in improving biogas production efficiency (Velázquez-Martí et al., 2019).

Simple models are widely used in predicting biogas production in anaerobic digestion because they are easy to use, require less data, and are more practical to calculate. These models are based on experimental data and are able to estimate the amount and rate of biogas production without entering into complex biological processes. In this study, three models were used, namely the modified Gompertz model, Logistics, and First Order Reaction Kinetics.

To assess how well a model represents the data, two main statistical indicators are used, namely the coefficient of determination (R^2) and the root mean square error (RMSPE). R^2 shows how much of the variation in the data is explained by the model while the closer to 1 the better the fit, with the benchmark usually being above 0.9 for a reliable model. Meanwhile, RMSPE gives an idea of the average error between model predictions and actual data, the smaller the value, the more accurate the model. These two parameters are used together to show that the model really describes the anaerobic digestion process precisely and accurately, and is able to predict biogas production results well. Through comparison of R^2 and RMSPE values, it can be determined which model best fits the experimental data (Mohammadianroshanfekr et al., 2024).

Research related to biogas production from cow manure waste has been studied by (Hassan et al., 2022). A number of other researchers have also developed various simulation models for biogas production, but these models generally require simultaneous solving of the mass balance equations for each substrate and microorganism population. This results in complex equations with many unknown variables. Therefore, a simpler model approach is needed to effectively represent the anaerobic digestion process. This scientific article has the novelty of simulating biogas production using a modified Gompertz model, a logistic model, and a first-order model. The three models showed good correlation values in calculating biogas production. The Gompertz, logistic, and first-order models were also able to estimate potential biogas production, maximum production, and production delay under various experimental conditions. The modified Gompertz model has been widely recognized as a commonly used modelling basis for simulating biogas production kinetics.

This article aims to examine the effect of pH on biogas production through kinetic analysis using three empirical models, namely modified Gompertz, logistic model and first order model. The three kinetic models are used to determine the value of kinetic constants that are useful to improve understanding of the effect of feed pH on biogas production from cow manure waste

2. METHODS

2.1 Secondary data collection

Secondary data were obtained from research conducted by (Hassan et al., 2022). This study was conducted by processing secondary data on biogas production at feed pH variations (N1= 7.17, N2= 7.22, N3= 7.24). Secondary data is presented in Table 1.

Table 1. Volume Biogas Per Hari (Hassan et al., 2022)

Retention Time (days)	Volume of Biogas Produced (ml)		
	N1 pH= 7.17 (mL)	N2 pH 7.22 (mL)	N3 pH= 7.24 (mL)
1	0	0	0
2	0	0	0
3	0	0	0
4	3	2	1
5	8	5	4
6	12	10	8
7	19	19	14
8	25	19	15
9	29	29	23
10	38	39	34
11	50	54	53
12	67	72	74
13	89	92	99
14	109	115	125
15	136	144	152
16	166	175	182
17	201	215	220
18	224	246	241
19	234	260	250
20	241	270	255
21	247	278	258

Note: the data displayed are cumulative biogas data generated from the processing of daily biogas data (Hassan et al., 2022)

2.2 Kinetic Analysis

This study uses three kinetic model approaches to see the dynamics of biogas formation in depth. The kinetic models used are the Gompertz model, logistic model, and first-order model. These three models are used to compare and assess the ability of each model to predict biogas accumulation based on available data. In kinetic analysis with a modelling approach, an objective function is used to assess the magnitude of the error between actual data and model predictions. In this study, the objective function used is Sum of Squared Error (SSE). Data processing in this study used Microsoft Excel to facilitate data analysis and visualization. The modified Gompertz model is an empirical model that describes cumulative biogas production over time (Li et al., 2015a). The resulting curve is sigmoidal or "S" shaped, which describes the lag phase, fast growth phase, and stable phase. The modified Gompertz model is listed in Equation 1 (Syaichurrozi et al., 2024).

$$y(t) = ym.exp\left\{-\exp\left[\frac{U.e}{ym}(\lambda - t) + 1\right]\right\} \quad (1)$$

The modified logistic model also shows a sigmoidal curve pattern like the Gompertz, but the emphasis is on how the production rate relates to the gas already produced and the total capacity that can be achieved. The model shows that the initial production rate increases, then slows down as the system approaches the production saturation point. The modified logistic model is shown in Equation 2 (Mohammadianroshanfekr et al., 2024).

$$y(t) = \frac{ym}{\left(1+exp\left[\frac{4U}{ym}(\lambda-t)+2\right]\right)} \quad (2)$$

The first-order kinetics model works by assuming that the rate of biogas production is directly proportional to the amount of organic substrate that can still be decomposed. This model simplifies the AD process to only one main stage, hydrolysis, which follows a first-order reaction pattern. The first order model is shown in Equation 3 (Velázquez-Martí et al., 2019).

$$y(t) = ym\,(1 - \exp(-k.t)) \quad (3)$$

The variables used in the model include y is the cumulative biogas yield at time (ml), time is t (days), maximum biogas yield is ym (ml), reaction rate constant is k (1/day), maximum production rate is U (ml/day), adaptation time is λ (days), and e denotes a mathematical constant (Neper/Euler Number). All these variables are used to understand and estimate the system behaviour quantitatively (Mohammadianroshanfekr et al., 2024).

To compare the models studied, the Sum of Squared Error (SSE) can be used to compare which model is better than the experimental biogas volume with the modelled biogas volume. The SSE formula is listed in Equation 4, where Pvi is the predicted value of methane volume and Mvi is the measured value of methane volume (Abdurrakhman and Wahyumulyaning Tiyas, 2017).

$$SSE = \sum(Mv_i - Pv_i)^2 \quad (4)$$

To compare the models studied, Root Mean Square Prediction Error (RMSPE) was calculated. The RMSPE value represents the deviation between the predicted value and the measured value. RMSPE can be calculated using Equation 5, where Pvi is the predicted value of methane volume, Mvi is the measured value of methane volume, and n is the number of measurements. RMSPE is calculated using the equation (El-Mashad, 2013).

$$RMSPE = \sqrt{\sum_{n-1}^{n}\frac{(Pv_i - Mv_i)^2}{n}} \quad (5)$$

The ability of the model to apply the variation of the dependent variable is used the coefficient of determination (R^2) method approach. In other words, the coefficient of determination measures how well a statistical model predicts an outcome. The R^2 measure is represented as a value between 0.0 and 1.0, where a value of 1.0 indicates perfect correlation. The closer the value of $R^2$is to 1.0, the more reliable the model is, while a value of 0.0 indicates that there is no relationship or dependency function between the two variables. Yi = 1st observation value, *Yi* = 1st guess value, γi = Average observation value n = number of observations. The R^2 can be calculated using Equation 6 (Putra and Setiawati, 2024).

$$R^2 = 1 - \frac{\sum_{i=1}^{n}(\mathrm{Yi}-Yi)^2}{\sum_{i=1}^{n}(Yi-\gamma i)^2} \text{ or } R^2 = RSQ(\sum Mv_i; Pv_i) \quad (6)$$

3. RESULTS AND DISCUSSION

The results obtained from several modelling experiments that have been carried out are presented in Table 1.

Table 2. Kinetic constants for modelling use modified Gompertz, modified logistics, and first-order kinetic models.

Parameter	Unit	N1 (pH 7.17)	N2 (pH 7.22)	N3 (pH 7.24)
Modified Gompertz Model				
ym	mL	360.29	418.08	321.48
U	mL/day	23.42	26.71	27.85
λ	Days	8.94	9.33	9.27
SSE	-	1300	1192	965
RMSPE	-	7.87	7.53	6.78
R^2	-	0.993	0.995	0.996
Modified Logistic Model				
ym	mL	277.81	315.62	277.89
U	mL/day	26.91	30.53	31.13
λ	Days	9.72	10.07	9.99
SSE	-	458.7	423	309
RMSPE	-	4.67	4.49	3.84
R^2	-	0.997	0.998	0.998
First-Order Kinetic Model				
ym	mL	27,892.26	42,412.44	34,097.36
k	1/day	0.000343	0.000245	0.000299
SSE	-	36,769	42,9246	46,106
RMSPE	-	41.84	48.83	46.86
R^2	-	0.900	0.895	0.900

Note: N is the pH of the feed

3.1 Kinetic Analysis

The best model is the logistic model. Where the SSE value is the smallest. The SSE values obtained are 458.37, 423, and 309. The graph of the results of the logistics modelling is shown in Figures 1 and 2.

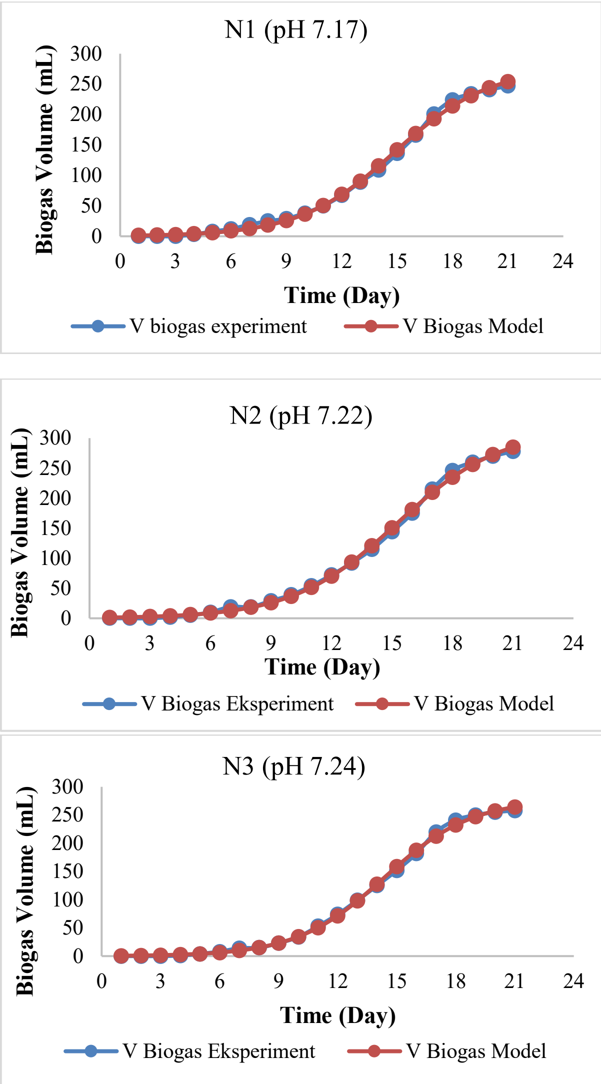

Fig 1. Logistic Modelling Results N1 (pH 7.17), N2 (pH 7.22), N3 (pH 7.24)

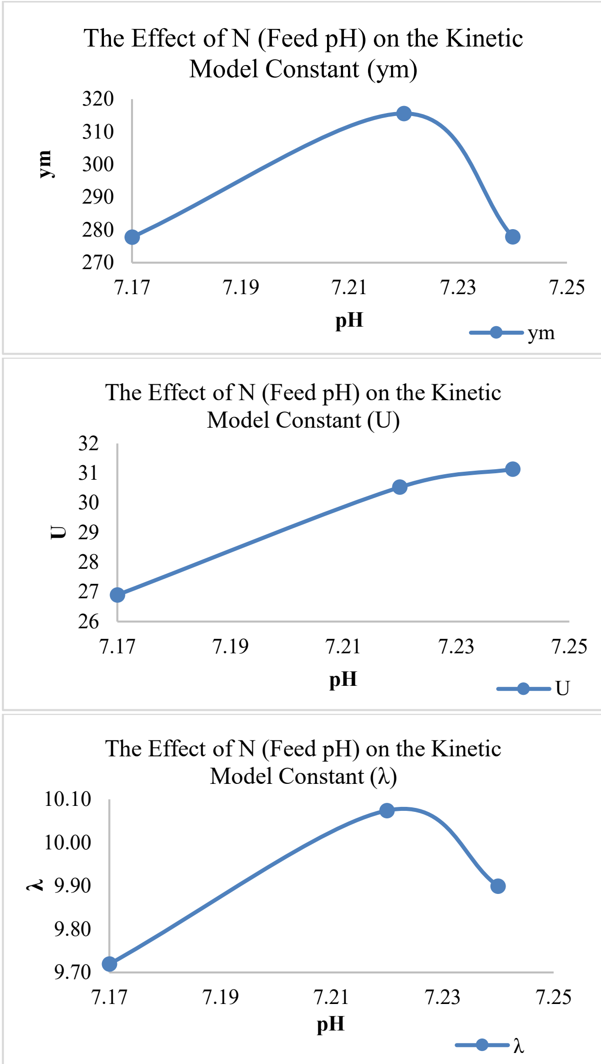

Fig. 2. Graph of the Effect of N (Feed pH) on ym, U, λ.

3.2. Discussion

3.2.1. Modelling Results of Biogas Production Using the Logistic Model

Research from this journal discusses a laboratory-scale digester designed using three plastic water bottles with a capacity of 750 mL with a concentration of 1500 g cow manure slurry per 3000 mL of distilled water for a retention time of three weeks. Biogas production started on the fourth day of fermentation and followed an increasing trend. It reached its peak on the seventeenth day before a gradual decline in production levels. The average weekly production of biogas was; days 1-7 (17.33 mL), days 8-14 (99.00 mL), days 15-21 (172.33 mL). The results obtained from this study also showed that Bacillus species were the most isolated bacteria (Hassan et al., 2022).

Modelling biogas production from the process of daily volume of biogas produced at a retention time of three weeks, namely N1 with a feed pH of 7.17, N2 with a feed pH of 7.22, and N3 with a feed pH of 7.24 using three types of kinetic models, namely modified Gompertz, modified logistic, and first-order kinetics models. The main objectives were to find out which model is most suitable for predicting biogas potential, evaluate the experimental results, and understand the factors affecting production yield. The findings are expected to contribute to optimizing anaerobic digestion (AD) systems.

The growth of microorganisms in the fermentation process proceeds through four stages, namely the lag, exponential, stationary, and death phases. In the lag phase, bacteria begin to adjust to their new environmental conditions. After that, in the exponential phase, bacterial activity increases rapidly until it reaches its peak. The stationary phase occurs when the number of bacteria that grow is proportional to those that die, so their activity tends to stabilize. Finally, in the death phase, microbial activity begins to decline as nutrient sources are depleted (Purnama and Sanatang., 2023.).

The Gompertz model, logistic model and first-order model were applied to the experimental results of biogas production to predict and estimate the kinetic coefficient for anaerobic digestion of cow manure as substrate. The experimental and predicted values of kinetic coefficients estimated using the three models are shown in Table 2. The results show that the biogas produced experimentally was well supported using the Logistic Model which was observed in both experimental and modeled values. The biogas prediction from the logistic model shows a higher correlation (Hadiyanto et al., 2023). From the three graphs, the logistic model visually closely follows the shape of the experimental data curve, both in the initial phase (slow), exponential phase (fast climbing), and stationary phase (flat). This shows that the model is able to describe microbial growth and biogas formation biologically. There is no significant difference between points in the lag and stationary phases, indicating that the prediction of daily cumulative volume is very accurate.

pH is one of the most crucial environmental factors in anaerobic fermentation, as it affects the activity of microorganisms (especially methanogens). The optimum pH range for methane production is generally 6.8-7.4. From the graphical data, it can be seen that at pH 7.22 and 7.24, biogas production is slightly higher and the model curve almost matches the experimental curve. This indicates that these conditions are closer to the optimum biological balance, so the gas accumulation increases steadily and the model is able to describe it better (Li et al., 2015).

Three parameters were evaluated using the three models, The value of (ym) indicates the maximum capacity of biogas production. At pH 7.22, the ym value was highest (315.62 mL) because it was close to the optimum pH of methanogenic microbes. Cow manure substrate with neutral pH supports the degradation of compounds such as cellulose and protein by fermentative and methanogenic bacteria. This means that the closer the pH is to the optimum value, the greater the potential for conversion of the substrate to gas, so a logistic model with a sigmoid curve shape is very suitable to explain this. The maximum rate of biogas production (U) was also highest at pH 7.24 (31.13 mL/day). This shows that the curve in N3 climbs faster at the beginning of the growth phase than N1, because the microorganisms start to work faster in producing gas per time, although the maximum production capacity is slightly below N2. The value of λ that is close to 10 days indicates that the microorganisms need some adaptation time before they start actively producing gas. The logistic model accommodates this lag phase with a flat sigmoid curve at the beginning. The biogas produced with pH 7.22 at N2 shows a longer lag time which indicates that the microbes need a longer adaptation time. In this lag phase, bacteria are in the process of acclimatization to environmental conditions. Microbes need carbon and energy sources that can be obtained from substrates. This explains that increasing the portion of substrate and increasing pH will increase the potential constant for biogas formation (ym) and indicates that the lag period (λ) is actually slightly longer at pH 7.22 and 7.24, which indicates that although total biogas production is higher at this pH, microorganisms need a slightly longer initial adaptation time than at pH 7.17. This could be influenced by the dynamics of the microbial community or the initial conditions of the substrate that do not directly support the activity of methanogens, besides that the optimum pH does not always guarantee the fastest adaptation, this is due to other factors such as microbial competition, NH_4^+ content, or the initial acidity of the cow manure substrate that hinders initial adaptation (Hadiyanto et al., 2023).

The smallest SSE and RMSPE values occurred at pH 7.24, which means that the model is very suitable to describe the actual biogas pattern. In contrast, the first-order model has a large SSE and RMSPE because it cannot adjust the shape of the biological curve that actually occurs. R^2 values close to 1 (between 0.997-0.998) indicate that the logistic model is very good at explaining data variation. The Logistic model fits the experimental data with high precision and suitability due to its sigmoidal shape curve which can well describe the lag, exponential, and stationary phases during the digestion process (Li et al., 2015).

3.2.2. Comparison of Biogas Volume of Gompertz, Logistic and First-Order Modelling Results

Comparison graph of biogas volume modelling results for each pH variation (N1, N2 and N3) in each model is shown in Figures 3, 4, and 5.

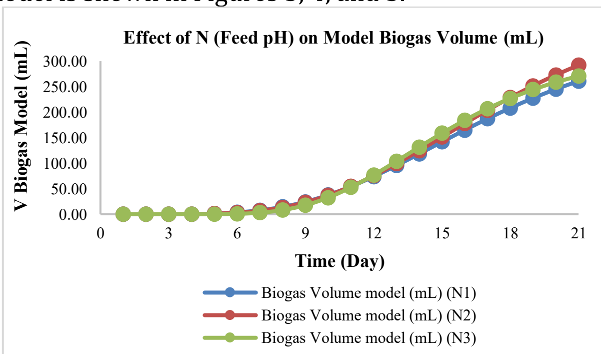

Fig 3. Gompertz Model Biogas Volume Graph

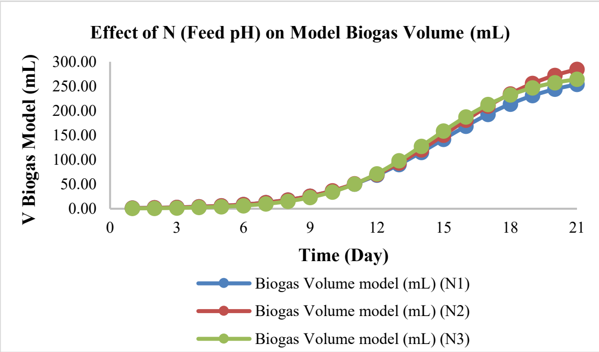

Fig 4. Logistic Model Biogas Volume Graph

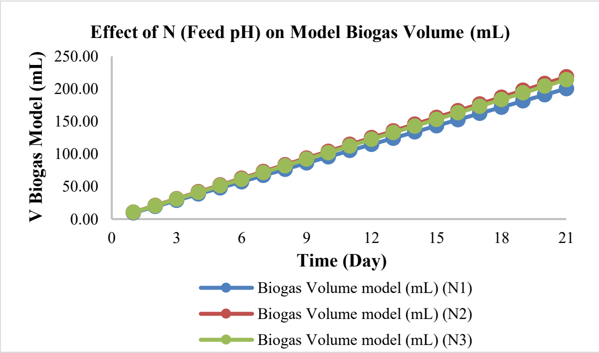

Fig 5. First-Order Model Biogas Volume Graph

It can be seen in the three graphs above, the graphs of the Gompertz and logistic models are the same shape, namely sigmoid. As for the first-order model graph, the graph tends to be close to linear. The resulting Gompertz model graph is sigmoidal or in the shape of the letter "S" describing the pause phase, the rapid growth phase, and the stable phase. This model is accurate enough to show how the gas is formed from the beginning until the process stabilizes. In the logistic model graph, the shape of the graph is also the same as the Gompertz model, which is "S" shaped, but the emphasis is on how the production rate relates to the gas already produced and the total capacity that can be achieved. This model shows that the initial production rate increases, then slows down as the system approaches the production saturation point (Mohammadianroshanfekr et al., 2024). In the first-order model graph, the shape of the graph tends to be linear. The first-order kinetics model works by assuming that the rate of biogas production is directly proportional to the amount of organic substrate that can still be decomposed. This model simplifies the AD process to only one main stage, hydrolysis, which follows a first-order reaction pattern (Velázquez-Martí et al., 2019).

At pH 7.22 (N2) and 7.24 (N3), biogas production was higher than at pH 7.17 (N1), which the model showed through a faster increasing curve and a larger final biogas volume. This makes sense because microbes work more efficiently in neutral to slightly alkaline conditions, in accordance with research (Li et al., 2015) cow manure contains organic matter and in situ microbes that can work optimally if pH conditions are favorable.

The Modified Gompertz Model shows a sigmoid (S) curve shape that reflects the biological phases: lag phase, exponential phase, and stationary phase. This model is suitable to describe the dynamics of microbial growth in anaerobic fermentation. At pH N2 and N3, it was seen that gas growth was faster and steeper in the lag phase indicating a good biological response to increasing pH (Nielfa et al., 2015.)

The Modified Logistic Model also shows a sigmoid curve similar to Gompertz, but slightly more symmetrical. From the graph, the logistic model gives results that are very close to the experimental data. The model captured the saturation point well, showing stable gas production after day 15. This is consistent with the fermentation condition of cow manure substrate, which generally reaches peak production after 10-17 days (Hassan et al., 2022).

The First-Order Kinetic Model shows exponential linear growth without any lag phase. This is not suitable for complex biological systems such as cow manure fermentation. The graphs show that at all pH variations, the model overpredicts both high and low initial and final times. This is because the model only assumes that the gas production rate is proportional to the amount of undegraded substrate, without considering microbial dynamics or environmental adaptation. The first-order model is relatively simple as it only assumes that the hydrolysis process is the decisive stage. The downside is that it does not take into account the lag phase, so under certain conditions, this model can be less accurate. This model shows that although it is not complex, it can still be used effectively for systems with rapid substrate degradation (Mohammadianroshanfekr et al., 2024).

In general, the three models performed quite well with high R^2 values and were similar although not close to one. However, modified logistics has the best performance in terms of R^2which requires adaptation of microorganisms. In addition, the logistic model also has the lowest SSE and RMSPE values which indicate the highest level of accuracy in predicting experimental data.

4. CONCLUSION

Of the three models, all models showed good results. The logistic model is the best and most superior model among the three models because it is able to represent the lag, exponential, and stationary phases biologically and predict biogas volume with high precision following the microbial growth pattern. Gompertz and logistic models have the same graphical form, which is sigmoid or "s" shaped. For the first-order model, the shape of the graph is linear, which states that in this model there is a simplification of stages, namely only the hydrolysis stage which follows a first-order pattern. Modelling of biogas production shows that the highest ym value is at pH 7.22, which indicates the maximum capacity of biogas production is greatest when pH conditions are close to neutral. The highest U value was at pH 7.24, indicating the fastest gas production rate, while the λ value was slightly larger at high pH (7.22 and 7.24), indicating that the microorganisms needed a slightly longer initial adaptation time. Statistically, the logistic model provided the lowest SSE and RMSPE values, as well as the highest

R^2 value (close to 1) indicating excellent model accuracy and fit compared to Gompertz and first-order.

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