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Kinetic Analysis of the Effect of pH on Biogas Production from Cow Manure Waste through Anaerobic Processes

Aufa Irsyad Priyatna*, Alzena Nasywa Firdaus, Siti Halimatu Sa'diyah, Iqbal Syaichurrozi

Chemical Engineering Department, Faculty of Engineering, Universitas Sultan Ageng Tirtayasa, Jl. Jend Sudirman km.03 Cilegon Banten 42435, Indonesia

Email: aufa.irsyad04@gmail.com (A.I.P.), alzena.cilegon@gmail.com (A.N.F.)
sitihalimatul579@gmail.com (S.H.S.), iqbal_syaichurrozi@untirta.ac.id (I.S.)

*Corresponding Author Email: aufa.irsyad04@gmail.com

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ABSTRACT

Biogas is the decomposition of organic waste by bacteria through an anaerobic fermentation process that can be managed to produce biogas in the form of methane gas (CH_4). This study aims to analyze the effect of pH variation on biogas production through anaerobic digestion using a kinetic modeling approach. Using secondary data from previous studies, three kinetic models Gompertz, First Order, and Logistic were applied to predict biogas volume at acidic pH 4.52, neutral (6.80), and alkaline (8.52). Alkaline pH (8.52) resulted in the highest biogas production at 2850 mL. At pH 8.52, Gompertz parameters such as production potential (4,231.24 mL), maximum rate (163.19 mL/day), and shortest lag phase (3.92 days) indicated the highest efficiency.

Keywords: *Anaerobic Digestion, Biogas, Kinetic Models, Organic Waste, pH*

1. INTRODUCTION

Increased energy demand has led to increased threats to the natural environment. Observed climate change, manifested as an increase in atmospheric temperature over time, is one of the major global threats. This phenomenon is called anthropogenic global warming. Proponents of this hypothesis argue that the time to avoid climate catastrophe is running out *(Kolenda et al., 2024).* Global warming has many negative impacts, such as decreased productivity, rising sea levels, and damage to agriculture, which ultimately have a negative impact on the economy. As a result of global warming, glaciers are melting and sea levels are rising. As a result, many coastal areas will be submerged, and the loss of settlements and infrastructure can be considered an economic loss (Li *et al.,* 2023).

Biogas has significant potential as a renewable energy source for industrial and domestic applications and as an efficient solution to the global energy crisis. Biogas is produced through the anaerobic fermentation of organic waste by bacteria, a process that can be managed to generate biogas in the form of methane gas (CH_4). Biogas, a byproduct of microbial metabolism, can be used in its raw form for heat and electricity generation or upgraded into biomethane and used for the production of value-added chemicals for energy and industrial process applications (Kumar Khanal *et al.,* 2021).

Kinetic analysis can be performed in terms of dynamic models that consider time as a variable. Numerical modeling investigates dynamic modeling and static modeling of systems without conducting practical experiments. There are several kinetic expressions used to describe anaerobic digestion that focus on different variables (Roberts *et al.,* 2023).

A study compared the modified Gompertz kinetic model and the first-order model in predicting biogas production from vinasse at various initial pH levels. The results showed that pH affected the input parameters of both models, with the Gompertz model showing the smallest variation in predictions compared to actual data. Another study also compared the two models in the treatment of recycled paper mill sludge through anaerobic digestion to produce methane and reduce environmental impact (Bakraoui *et al.,* 2020).

The purpose of this study is to analyze the effect of pH variation on biogas production through anaerobic digestion using a kinetic modeling approach. By utilizing secondary data from previous experiments, this study aims to evaluate how well the four kinetic models which are First Order, Logistic, and Gompertz predict biogas production volume under different pH conditions, as well as determine the most accurate model and optimal pH for maximizing biogas production.

2. METHODS

2.1 Secondary Data

This study uses a quantitative approach based on secondary data to evaluate the effect of pH on biogas production in the anaerobic digestion process. The secondary data analyzed were obtained from a scientific journal published by (Bahira *et al.,* 2018) which presented experimental results on pH variations and their relationship with the volume of biogas produced. The data included parameters such as time, pH values, and biogas production volume, which served as the basis for kinetic modeling. Table 1 provides detailed observations of biogas volume (mL) under different pH conditions categorized as acidic, neutral, and alkaline.

Table 1. Biogas Volume

Day	Biogas Volume (mL)		
	Acidic (4.52)	Neutral (6.80)	Alkaline (8.52)
1	0	0	0
2	0	0	115
3	0	100	220
4	0	200	330
5	0	305	445
6	0	410	580
7	0	525	715
8	0	660	850
9	105	795	1,000
10	195	945	1,155
11	270	1,080	1,315
12	345	1,205	1,470
13	460	1,325	1,615
14	550	1,440	1,755
15	640	1,550	1,900
16	715	1,655	2,030
17	820	1,795	2,190
18	935	1,965	2,340
19	1,060	2,110	2,515
20	1,200	2,260	2,690
21	1,300	2,410	2,850

Source : (Bahira et al., 2018)

2.2 Kinetic Analysis

To gain a deeper understanding of the reaction rate and dynamics of biogas formation, this study applied three kinetic model approaches, namely First Order, Logistic, and Gompertz. These three models were used to compare and evaluate the extent to which each model could predict biogas accumulation based on the available data. In kinetic analysis using a modeling approach, the objective function serves to measure the degree of error between actual data and model predictions. In this study, the objective function applied was the Sum of Squared Errors (SSE). Data processing and model application were carried out using curve fitting methods with Microsoft Excel software. Table 2 presents the types of kinetic models applied in the analysis, which include Gompertz, First-Order, and Logistic models. These models are commonly used to describe growth and reaction patterns in biochemical processes. By applying these models to the experimental data, the study aimed to evaluate which model best represents the kinetic behavior of the system based on the fit quality, as indicated by the SSE value.

Table 2. Type of Kinetic Model

Models	Equation	Citation
Gompertz	$y(t) = ym.exp\left\{-exp\left[\frac{U.e}{ym}(\lambda - t) + 1\right]\right\}, t \geq 0$	(Syaichurrozi, 2018)
First Order	$Y = A\,(1 - exp\,(-k * t))$	(Roberts et al., 2023)
Logistic	$y = \frac{A}{\left[1 + exp\,exp\,\left[\frac{4\mu m}{A}(\lambda - t) + 2\right]\right]}$	(Roberts et al., 2023)
SSE	$SSE = \Sigma(Ydata - Ycount)^2$	(Dwi Werena et al., 2024)

Where:
y(t) = accumulation of biogas during fermentation time t days (mL)
ym = potential biogas production (mL)
U = maximum biogas production rate (mL/day)
A = maximum volume of biogas that can be produced during fermentation (mL)
μm = maximum biogas production rate (mL/day)
λ = lag phase period or minimum time required to produce biogas (days)
t = cumulative biogas production time (days)
e = mathematical constant (2.718282)
k = biogas rate constant (/day)
Ydata = Experimental Biogas Volume (mL)
Ycount = Model Biogas Volume (mL)

3. RESULTS AND DISCUSSION

This study aims to analyze the effect of pH variation on biogas production through anaerobic digestion using a kinetic modeling approach. The secondary data used were analyzed using three kinetic modeling approaches, namely the First Order, Logistic, and Gompertz models. Each modeling was conducted at pH variations of acidic (4.52), neutral (6.80), and alkaline (8.52). The modeling results were compared with experimental data obtained from a study (Bahira et al., 2018) to assess the accuracy of each model through the parameters of biogas production volume (Ym) and Sum of Squared Errors (SSE) as a measure of prediction error.

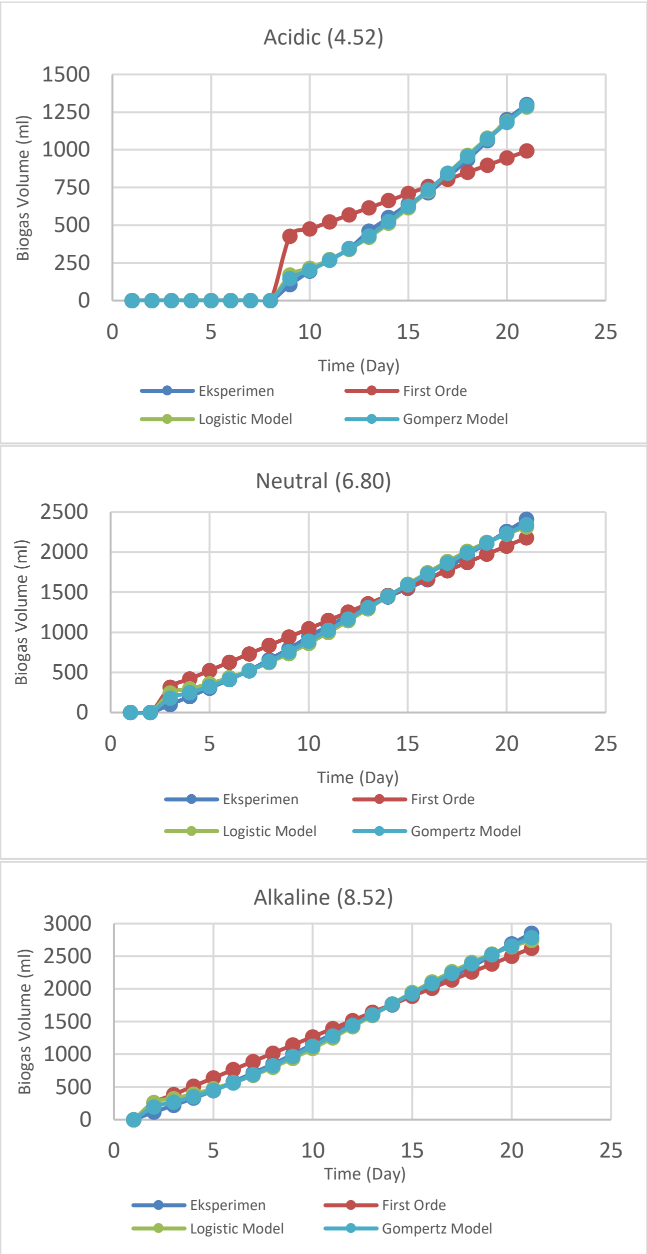

Fig 1. Effect of pH on Biogas Production Based on Experiments, First Order Modeling, Logistic Modeling, and Gompertz Modeling

Based on Figure 1, biogas production from cow manure is greatly influenced by the pH conditions of the digester environment, as pH plays an important role in the activity of methane-producing microorganisms. Based on experimental results, alkaline pH (8.52) was found to produce the highest biogas volume of 2,850 ml, compared to neutral pH (6.80) at 2,410 ml, and acidic pH (4.52) which only produced 1,300 ml. This indicates that mild alkaline conditions provide the most supportive environment for the growth and activity of methanogenic microorganisms responsible for methane production during anaerobic digestion. At acidic pH, microbial activity is inhibited because the low pH causes enzyme denaturation and disrupts cellular osmotic balance (Bahira *et al.,* 2018).

Further mathematical modeling using three approaches, namely First Order, Logistic, and Gompertz, further reinforced the experimental results. The parameter value Ym (biogas production potential) in the Gompertz model reached its highest value at pH 8.52, which was 4,231.24 ml, far above the neutral pH (3,552.66 ml) and acidic pH (2,648.67 ml). A similar trend was observed in the Logistic model, with the highest Ym value of 3,247. 93 ml at pH 8.52, compared to 2,758.12 ml at pH 6.80 and 1,746.87 ml at pH 4.52. This indicates that both experiments and mathematical simulations consistently conclude that alkaline pH yields the most optimal results. Another reason is that at pH 8.52, the system has the shortest lag time (λ), which is 3.92 days, so gas production begins earlier. Additionally, the maximum gas production rate (μ) is also highest under basic conditions (163.19 ml/day), indicating that fermentation reactions and microbial activity occur more quickly and efficiently (Budiyono *et al.,* 2014).

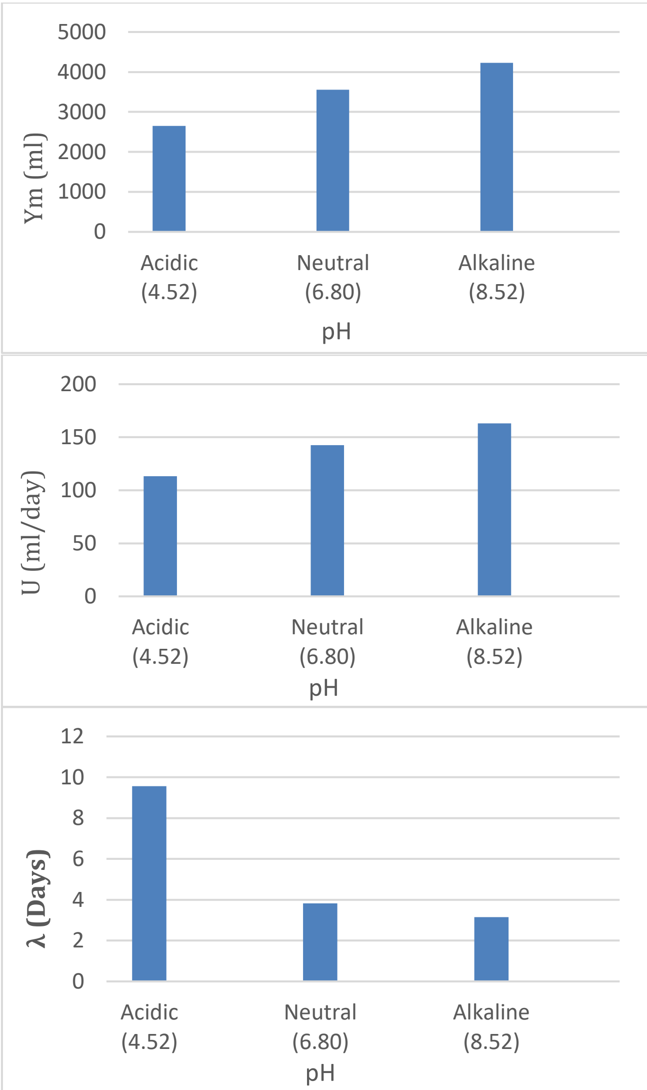

Fig 2. Effect of Variable Constants on Gompertz Kinetic Modeling

Based on Figure 2, it can be explained that in the Gompertz model, there are three main parameters that influence biogas production predictions, namely Ym (maximum gas production potential), μ (maximum production rate), and λ (lag phase or initial production delay). These three parameters provide a comprehensive overview of the biological process dynamics within the digester. First, the value of Ym as an indicator of maximum gas production potential shows that basic pH (8.52) has the highest potential at 4,231.24 ml, indicating that this condition supports maximum conversion of substrate into gas. This is not only because microorganism grow better, but also because the enzymes involved in the final stage of methanogenesis function optimally at slightly basic pH. Second, μ, as the maximum production rate, has the highest value at a basic pH of 163.19 ml/day, compared to neutral pH (142.57) and acidic pH (113.32). This means that the rate of gas volume growth at pH 8.52 is faster than the other two conditions. This rate is important as it indicates conversion efficiency during the exponential phase, where substrates such as acetic acid, CO_2, and H_2 are rapidly converted into methane by methanogens. Third, λ (lag phase) is an important factor as it indicates the time required before active gas production begins. At basic pH, the λ value was recorded at only 3.92 days, significantly faster than at neutral pH (4.53 days) and acidic pH (9.87 days). The shorter the lag phase, the faster the system operates, indicating that microorganisms do not require a long adaptation period under alkaline conditions. This is likely because pH 8.52 aligns with the optimal range for methanogenic microbial activity, typically ranging from 7.0 to 8.5 (Chandra *et al.,* 2012; Gerardi, 2003).

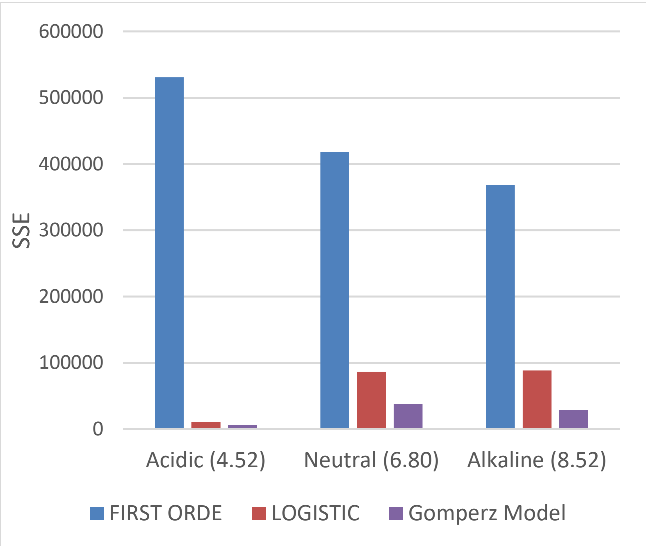

Fig 3. Comparison of SSE Values in Each First Order, Logistic, and Gompertz Modeling

Based on Figure 3, a calculation was performed as a parameter using SSE (Sum of Squared Errors), which is used to evaluate the accuracy of the model in predicting experimental results. The smaller the SSE value, the better the model reflects reality. Based on the results of the three models, the Gompertz model showed the smallest SSE value across all pH conditions, indicating that this model is the most accurate in representing the actual biogas production process.

At acidic pH (4.52), the SSE value of the First Order model was very large at 530,784.12, while the Logistic model was 10,442.52, and Gompertz was only 5,475.56. A similar pattern was observed at neutral pH (6.80), with the First Order model yielding 418,304.00, the Logistic model 86,370.65, and the Gompertz model 37,637.90. Even at basic pH (8.52), despite the highest gas production, the First Order model remains significantly off (368,542.54), compared to Gompertz, which is only 28,960.17.

The reason why the First Order model has the largest error is because it only considers a single-stage reaction without lag or saturation phases, whereas in reality, the biogas system consists of multiple stages such as hydrolysis, acidogenesis, and methanogenesis. The Logistic model is better because it accounts for saturation, but it does not accommodate the lag phase, which is particularly important at low pH levels. Meanwhile, the Gompertz model has the best performance because it explicitly accounts for the lag phase (λ), maximum growth rate (μ), and maximum system capacity (Ym). Therefore, both theoretically and empirically, the Gompertz model is the most suitable for biogas systems based on organic waste such as cow manure (Moharir *et al.,* 2020).

4. CONCLUSION

Based on the results and discussions that have been conducted, it can be concluded that:

a. Effect of pH on Biogas Production

The highest biogas production occurred at pH 8.52 (2,850 mL), because mildly alkaline conditions support optimal activity of methanogenic microorganisms. Conversely, acidic pH inhibits the process, resulting in much less gas production.

b. Gompertz Modeling

The Gompertz model is the most accurate because it considers maximum potential (Ym), production rate (μ), and lag phase (λ). At pH 8.52, this model shows the best results with more gas, faster formation, and a stable process.

c. First-Order Modeling

First-Order modeling is not suitable for biogas systems because it is too simple and does not account for important phases. Its error is very large, especially at low pH, making it less accurate in representing complex biological processes.

d. Logistic Modeling

The Logistic model is better than the First Order model because it accounts for saturation, but it still does not accommodate the lag phase. Its accuracy is still below that of the Gompertz model, especially under extreme or unstable pH conditions.

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