Kinetic Study of Biogas Production from Animal Manure and Organic Waste in Semarang City by Using Anaerobic Digestion Method

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Abstract: The biogas fermentation from animal manure and organic waste was investigated with a comparison percentage of raw material used inside the digester with the anaerobic digestion process. Animal manure consists of cow dung and chicken manure, while organic waste consists of tofu liquid waste and cabbage waste. This study used a batch process that was operated at 55 °C incubator temperature for 90 days. The results of experimental data were predicted with a modified Gompertz model and first-order kinetic model. The equation of the modified Gompertz model to predict biogas production was

\[ P = P_\infty \cdot e^{-e^{-\frac{R_m \cdot e^{A(\lambda - t)}}{\lambda}}} + 1 \]

with

\( P \) is cumulative production of methane;
\( P_\infty \) = methane production potential;
\( R_m \) = maximum specific speed methane production;
\( \lambda \) = lag phase period or minimum time to produce biogas;
\( e \) = math constant (2.7182) and
\( t \) = biogas production cumulative time.

The first-order kinetic model was

\[ Y = Y_m \cdot (1 - \exp(-k \cdot t)) \]

The highest biogas yield was obtained by variable 3 in both kinetic studies compared to 70% cow dung, 15% chicken manure, and 15% tofu liquid waste. Gompertz’s kinetic study predicted variable three would produce 3273.20 mL/g of total solid (TS). In comparison, the first-order kinetic model predicted that variable three would produce 3517.95 mL/(g TS).

Keywords: biogas; kinetic model; Gompertz

INTRODUCTION

Today, there are many ways to overcome the world’s energy crisis, such as wind, hydro, geothermal, tidal, and biomass energy. Biogas is one of the renewable derivative energy from biomass developed by many countries worldwide [1]. The production of biogas depends on its substrate and operating condition. Many biogas production studies have been applied to find optimum conditions and produce the best results in biogas quality and quantity [2]. The potential of biogas production may overcome the world crisis in energy because biogas contains methane (CH₄) which can be used as an energy resource and reduce the use of fossil energy [3].

Based on previous work, one of the best ways to produce biogas is using the anaerobic digestion method [4]. Anaerobic digestion is commonly used as a method to treat organic waste [5-6]. While anaerobic digestion can reduce pollution, it can also provide an energy source in the form of biogas. In addition, anaerobic digestion destroys disease inside bacteria of the organic waste, so it is no longer harmful to the human environment [7].

Anaerobic digestion is a natural biogas formation process that occurs in the absence of oxygen levels. It is usually used to process raw materials from industrial waste, household waste, vegetable waste, and food waste [8-9]. Anaerobic digestion is a natural biological process that can convert organic material into biogas products consisting of methane and carbon dioxide. Thus, anaerobic digestion provides a breakthrough in the processing of organic material, which is usually processed through the composting process into a biodegradation
process of organic matter without the presence of oxygen [10]. Besides, anaerobic digestion allows waste containing high organic matter levels to reduce the load on its organic content. Simultaneously, producing biogas can generate heat, electricity, and biofuel for vehicles [11].

Anaerobic digestion processes involve complex dynamic systems of microbiological, biochemical, and physicochemical processes. Among the possible methods for processing biowaste, anaerobic digestion has been identified as environmentally friendly because it allows bioenergy and potential by-products [12]. Biogas has been developed into kinetic modeling to predict bacterial growth rate using the first-order kinetic model and modified Gompertz equation. The first-order kinetic model is the oldest in modeling the substrate utilization of complex waste [13].

Bacterial growth is often exponential, and therefore, graphs plotting the logarithms of relative population size in Gompertz equation \( y = \ln \left( \frac{N_\infty}{N_0} \right) \) to represent the growth. Three parameters can describe three-phase curves growth: the specific growth maximum rate, \( \mu_m \) which is the tangent to the inflection point; lag time \( [\lambda] \) defined as the x-axis intercept; and the asymptote \( [A] \), the maximum value of \( y \). Then, the previous research conducted by [14] showed a re-parameter to the Gompertz model by including biological parameters such as the R-max and lag time \( [\lambda] \) through \( \ln \left( \frac{N_\infty}{N_0} \right) = P_\infty \cdot \exp \left\{ - \exp \left[ \frac{R_{\text{m}} \cdot e}{A} (\lambda - t) + 1 \right] \right\} \). Moreover, the Gompertz growth curve can be seen in Fig. 1.

Several researchers have done many types of research about the kinetic study. Syaichurrozi et al. investigated biogas from vinasse with COD/N variation that predicts the kinetic model using the Gompertz equation [15]. The result shows that 600/7 (COD/N) produces the biggest biogas in 139.17 mL/g COD and gives the best COD removal results until 38.0%. Another research by Mahnert and Linke identified the effect of organic loading rate (OLR) and reactor size while producing biogas from the animal waste slurry. The value of \( y \) at OLR achieves nearly \( y_{max} \) at variable 3 kg volatile solids (VS). The research done by Depanraj et al. (2015) shows the kinetic study on anaerobic digestion of food waste [16]. The results predicted that the highest biogas yield potential shows by a variable with pH 7, 6706 mL in the Gompertz model, and 5482.7 mL in the logistic model. For mathematic modeling, this research will focus on utilizing animal manure and organic waste. Biogas production from animal manure such as cow dung and chicken manure has many advantages in reducing pollution, and the energy generated [17-21].

Furthermore, the presence of cabbage waste and liquid tofu waste as organic waste also needs further handling [22]. The research is necessary because previous research has not optimized raw materials to increase biogas production yield. The kinetic modeling is limited only to one kind of raw material. In contrast, the highest biogas yield potential from the kinetic model can be more optimized by mixing potential raw materials and studying the kinetic model through comparisons of the first-order kinetic model and the Gompertz equation. Through this research, the limitations of the kinetic model of biogas that use variations in mixing raw materials can be resolved to provide maximum results in increasing the yield of biogas production. The research focuses on identifying the effect of various concentrations in raw material and predicting the growth of methanogen bacteria using the first-order kinetic and Gompertz equations. The raw material used in this research is cow dung, chicken manure, tofu liquid waste, and cabbage waste. It will also identify the effect of cabbage waste in biogas results production [23].

**EXPERIMENTAL SECTION**

The research was conducted in the laboratory of livestock products technology at the Faculty of Agriculture and Animal husbandry, Diponegoro University, Semarang, Indonesia.
Materials

The raw material for liquid tofu waste was obtained from the side product of the tofu production process in the Bandungan area, Central Java, Indonesia. Furthermore, livestock manure in chicken and cow dung was obtained from the Faculty of Agriculture and Animal Science, Diponegoro University, Semarang, Indonesia. The toddler bag for biogas yield was obtained from ShilpEnt Kaipa Enterprises.

Procedure

Experimental variables

The raw materials such as tofu liquid waste, cabbage waste, and chicken and cow manure were mixed into a digester, which already contained a starter in the form of fermented cow dung. The mixing was performed according to the variables presented in Table 1.

The variables have seven different percentages in terms of raw materials. Variable 1-4 uses cow dung, chicken manure, and tofu liquid waste as raw materials. Variable one consists of 100% cow dung; variable two consists of 80% cow dung, 10% chicken manure, and 10% tofu liquid waste; variable three consists of 70% cow dung, 15% chicken manure, and 15% tofu liquid waste; variable four consists of 60% cow dung, 20% chicken manure, and 20% tofu liquid waste.

Variable 5-7 uses cow dung, chicken manure, tofu liquid waste, and cabbage waste. Variable five consists of 85% cow dung, 5% chicken manure, 5% tofu liquid waste, and 5% cabbage waste; variable six consists of 70% cow dung, 10% chicken manure, 10% tofu liquid waste, and 10% cabbage waste; variable seven consists of 55% cow dung, 15% chicken manure, 15% tofu liquid waste, and 15% cabbage waste. The target of experimental variables is to determine the effect of tofu liquid waste and cabbage waste in animal manure mixture. Therefore, all seven variables must be appropriately conducted to know the effect of organic waste addition.

Experimental procedure

The weight of the starter in each digester was 200 g. An anaerobic digestion process was performed to produce biogas in each digester used. The volume of material placed into the digester was 70% × the total volume of the digester [24]. Therefore, the volume of the digester used is 350 mL. Then, the digester was shaken until a homogeneous material was obtained, like in Fig. 2. Then, the digester was placed inside an incubator and kept at a temperature of 55 °C, as in Fig. 3 [25]. The process goes in batch condition without any addition of substrate during the process and being observed in 90 days with the collective data of biogas yield every two days.

![Fig 2. Substrate preparation](image)

![Fig 3. Biogas production under 55 °C](image)

<table>
<thead>
<tr>
<th>Table 1. Experiment variables</th>
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<tr>
<td>Run</td>
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<tr>
<td>1</td>
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<td>5</td>
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<tr>
<td>6</td>
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<td>7</td>
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</tbody>
</table>
**Experimental analysis**

Raw materials were pretreated to determine the C total, N total, C/N ratio, and total solids (TS). The material burned at 550 °C to get ash content percentage to determine total C content. The N total was determined by the Kjeldahl method. The N total number showed by titration number with chloride acid after being distilled with sulphuric acid, NaOH, H$_3$BO$_3$, and BCG-MR. The total solid and volatile solid determination was performed according to the standard method [26].

**Kinetic study**

The biogas obtained by the anaerobic digestion method was calculated using the first-order kinetic model and Gompertz equation for kinetic study. The first-order kinetic model is described by Eq. (1).

\[ y = y_m \left( 1 - e^{-kt} \right) \]  

where, \( y \) = Cumulative biogas yield at digestion time t day (mL/g of volatile solid (VS)), \( y_m \) = Potential for biogas production (mL/g of volatile solid (VS)), \( k \) = Biogas rate constant (1/day), \( t \) = time in days, and \( e \) = mathematical constant (2.718282)

Then for Gompertz equation described by Eq. (2)

\[ P = P_\infty \cdot \exp \left\{ -\exp \left[ \frac{R_m \cdot e}{A}(\lambda - t) + 1 \right] \right\} \]  

where: \( P \) = cumulative production of methane (mL/(g Ts)), \( P_\infty \) = methane production potential (mL/(g Ts)), \( R_m \) = maximum specific speed methane production (mL/(g Ts day)), \( \lambda \) = is lag phase period or minimum time to produce biogas (day), \( e \) = mathematical constant (2.7182), \( t \) = biogas production cumulative time (day).

**RESULTS AND DISCUSSION**

The results focus on the biogas production in each day of variable, cumulative biogas production, and kinetic study by first-order kinetic reaction and Gompertz equation.

**Biogas Production**

The raw material has been analyzed in C/N ratio and total solid content before being produce in biogas. The results are represented in Table 2.

Table 2 shows that the largest total C content was from cabbage waste (42% total C), while the largest N content was from chicken manure (1.27% total N). The biggest number of total solid and volatile solid contained on chicken manure, while the most optimum TS is showed by tofu liquid waste with 8.975%. The optimum solid content obtained for biogas production is in the range of 7–10%. The process for total solid below 7% was unstable, while the total solid above 10% sometimes caused an overloading of the fermenter. The highest result of the C/N ratio was obtained by cabbage waste with 60. This amount of number also will prevent the fermentation process from becoming optimum in biogas production.

Biogas production results in 1-4 which consisted of a mixture of starter, animal manure (dung from cow and chicken), and tofu waste, and also for comparison, biogas production under variable 5-7 consists of a starter, a mixture of animal manure (cow dung and chicken manure) and cabbage vegetable waste as illustrated in Fig. 4. The figure shows the results of biogas production within 90 days. Variable 3 produced the highest amount of biogas, which yielded total biogas of 3251.25 mL in 90 days. The biogas result obtained is the total amount of biogas variable 3 compared to 70% cow dung, 15% chicken manure, and 15% tofu liquid waste, which is added with the starter’s fermentation digester 3.

The measurement of biogas volume started from the second day and was measured every two days [27]. The biogas can be produced when it is also optimum in C/N ratio, percentage comparison in each material, and

<table>
<thead>
<tr>
<th>No</th>
<th>Material</th>
<th>Total C (%)</th>
<th>Total N (%)</th>
<th>C/N ratio</th>
<th>TS (%)</th>
<th>VS (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cow dung</td>
<td>27.31</td>
<td>0.95</td>
<td>28.74</td>
<td>22.73</td>
<td>18.11</td>
</tr>
<tr>
<td>2</td>
<td>Chicken manure</td>
<td>19.51</td>
<td>1.27</td>
<td>15.36</td>
<td>32.00</td>
<td>18.38</td>
</tr>
<tr>
<td>3</td>
<td>Liquid tofu waste</td>
<td>10.28</td>
<td>0.21</td>
<td>48.95</td>
<td>8.98</td>
<td>8.55</td>
</tr>
<tr>
<td>4</td>
<td>Cabbage waste</td>
<td>42.00</td>
<td>0.70</td>
<td>60.00</td>
<td>5.93</td>
<td>5.38</td>
</tr>
</tbody>
</table>

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Fig 4. Biogas cumulative production

TS content [28-29], which means variable 3 has the optimum conditions required to produce the highest biogas yield. Variable A in this research provided a higher yield than that obtained in the experiment by Latinwo and Agarry involving biogas with a mixture of chicken manure and cow dung [30]. For variable 3, the phase corresponding to the highest gas production in the graph is the lag phase from day 2 to 8, followed by an exponential phase from day 10 to 20. Day 8 to 28 is a stationary phase. On day 28, anaerobic bacteria began to die, so that the biogas production began to decline every day. From day 68 to day 90, there was no more gas production. For variables with the addition of cabbage waste (variable 5-7), the results tend to be low caused by the mixture of these variables is not in the optimum C/N ratio, making the fermentation process hampered.

Kinetic Study

The graph in Fig. 4 depicts a sigmoidal growth curve containing mathematical parameters than parameters with biological meaning. It is challenging to estimate initial values for the parameter if the parameter has no biological meaning. Furthermore, it is challenging to calculate 95% confidence intervals for biological parameters if parameters are not estimated directly in the equation but must be calculated from mathematical parameters. Therefore, all growth models were rewritten to replace mathematical parameters with A, μ, and λ. This matter is done by deriving the expression of biological parameters as a function of basic function parameters and then replace them in formulas [22].

The development of the Gompertz equation is:

\[ y = a \cdot \exp[-\exp(b - ct)] \]  
(3)

To get the inflection point of the curve, the second derivative of the function with respect to t calculated

\[ \frac{dy}{dt} = \alpha c e^{-(b - ct)} \cdot e^{-(b - ct)} \]  
(4)

The second derivative of the equation is:

\[ \frac{d^2y}{dt^2} = \alpha c^2 e^{-(b - ct)} + \frac{e^{-(b - ct)}}{c} + (e^{-(b - ct)} - 1) \]

The parameter \( a \) in the Gompertz equation can be replaced by \( P_{\infty} \), yielding Modified Gompertz equation:

\[ P = P_{\infty} \cdot \exp\left[-\exp\left(\frac{R_{\max} \cdot e^{-(\lambda - t) + 1}}{A}\right)\right] \]  
(5)

This equation can be used as a model approach to producing biogas in a batch system. According to the specific growth rate of methanogenic bacteria in a biodigester, the rate of biogas production in batch conditions is predicted to comply with the Gompertz equation modified [23]. In this equation, \( P \) is the cumulative specific biogas production, L/kg of volatile solid; \( A \) is the potential for biogas production, mL; \( R_{\max} \) is the rate of biogas production maximum (L/g of volatile solids in each day); \( \lambda \) period of lag phase (minimum time for produce biogas), day; e is exp \((1) = 2.7183\) and \( t \) the cumulative time for biogas production, day. The constants \( A, \lambda, \) and \( R_{\max} \) can be determined using nonlinear regression [31]. In this research, the cumulative production of biogas has been studied using the modified Gompertz model, and the results are shown in Table 3.

From Table 3, the highest results of biogas by experimental data were obtained by variable 3 with total biogas of 3251.25 mL/(g Ts) and then variable 4 with 3046.25. The results of the Gompertz modified model predicted that the highest biogas yield was obtained by variable 3 with 3273.20 mL/(g Ts). The lower results predicted by Gompertz modified model are shown by variable 7 with 1476.45 mL/(g Ts). The highest value of \( A \) (maximum biogas production) showed by variable 3 with 3274.58 mL/(g Ts), suitable for \( P \)-predicted value.
Table 3. Results comparison of modified gompertz model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
<th>R4</th>
<th>R5</th>
<th>R6</th>
<th>R7</th>
</tr>
</thead>
<tbody>
<tr>
<td>P Experimental</td>
<td>2146.25</td>
<td>2690</td>
<td>3251.25</td>
<td>3046.25</td>
<td>1683.75</td>
<td>1682.5</td>
<td>1463.75</td>
</tr>
<tr>
<td>P Predicted</td>
<td>2136.419</td>
<td>2694.361</td>
<td>3273.196</td>
<td>3068.56</td>
<td>1701.17</td>
<td>1700.30</td>
<td>1476.45</td>
</tr>
<tr>
<td>A (mL/g Ts)</td>
<td>2136.566</td>
<td>2694.613</td>
<td>3274.584</td>
<td>3071.204</td>
<td>1701.275</td>
<td>1700.485</td>
<td>1476.607</td>
</tr>
<tr>
<td>Rm (mL/day)</td>
<td>101.106</td>
<td>129.26</td>
<td>130.784</td>
<td>112.6176</td>
<td>82.937</td>
<td>76.9821</td>
<td>67.531</td>
</tr>
<tr>
<td>λ (days)</td>
<td>7.75</td>
<td>11.19</td>
<td>9.25</td>
<td>9.14</td>
<td>8.69</td>
<td>7.4755</td>
<td>8.36</td>
</tr>
<tr>
<td>R²</td>
<td>0.9551</td>
<td>0.9618</td>
<td>0.9754</td>
<td>0.9807</td>
<td>0.955</td>
<td>0.9597</td>
<td>0.9615</td>
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</table>

The predicted value also shows that variable 3 has the highest value. The highest maximum specific speed methane production was also obtained by variable 3 with 3274.584 mL/day, while the lower specific speed methane production was obtained by variable 7 with 67.53 mL/day. Then, for λ value, the best result shows by variable 6. Variable 6 only needs 7.48 days as the minimum time to produce biogas. The variable that needs the longest minimum time to produce biogas is variable 2, with 11.19 days of minimum time. The results in Table 3 shows that variable 3 has the best raw materials comparison percentage to fulfill the requirement of optimum condition to produce biogas [20]. Gompertz’s modified model in every variable in this research is depicted in a graph comparing the observed biogas data and the predicted biogas data through the Gompertz equation. The graph comparing the observed biogas data and the predicted biogas data in variable 1 can be seen in Fig. 5.

Fig. 5 shows that the predicted data in variable 1 using Gompertz modified model go unidirectional, with almost the same values on the graph. It means the Gompertz modified model has already suitable to predict biogas yield in this variable. The same condition goes to variables 2-7, where all the graphs show that experimental data and predicted data go in straight values, so the Gompertz modified model is already suitable to predict biogas yield in all of these variables.

Results in the Gompertz model show that almost all of the variables fit well with the prediction of biogas yield obtained by the Gompertz model. The fitting model of the Gompertz model will later be compared with another kinetic model to predict the biogas yield. The author used first-order kinetic reaction to predict biogas yield production for another comparison, as shown in Table 4.

From Table 4, the highest results of biogas by predicted data using the first-order kinetic model was obtained by variable 3 with total biogas of 3517.95. It shows higher biogas predicted than Gompertz modified model with 3273.20 mL/(g Ts) biogas predicted for variable 3. Then, it is followed by variable 4 with 3310.16 mL/(g Ts), which is also higher than Gompertz modified model with 3068.56 mL/(g Ts) in the biogas yield prediction. Then, the lower results predicted by the first-order kinetic model are shown by variable 7 with 1476.45 mL/(g Ts). Finally, the highest value of Yₘ (maximum biogas production) showed by variable 3 with 3772.25 mL/(g Ts), which is suitable with the P-predicted value.

The predicted value also shows that variable 3 has the highest value. The highest value of K was obtained by variable 6 with 0.039. It was then followed by variable 1, 5, 7, 2, 3, 4 with the value of 0.03876, 0.0386, 0.0369, 0.0303, 0.0299, 0.027, respectively. For comparing the

Table 4. Results comparison of first order kinetic reaction

<table>
<thead>
<tr>
<th>Parameter</th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
<th>R4</th>
<th>R5</th>
<th>R6</th>
<th>R7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y Experimental</td>
<td>2146.25</td>
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<td>3046.25</td>
<td>1683.75</td>
<td>1682.5</td>
<td>1463.75</td>
</tr>
<tr>
<td>Y Predicted</td>
<td>2274.57</td>
<td>2918.70</td>
<td>3517.95</td>
<td>3310.16</td>
<td>1804.16</td>
<td>1795.79</td>
<td>1669.53</td>
</tr>
<tr>
<td>Yₘ (mL/g Ts)</td>
<td>2346.20</td>
<td>3122.70</td>
<td>3772.25</td>
<td>3623.08</td>
<td>1861.83</td>
<td>1848.21</td>
<td>1627.84</td>
</tr>
<tr>
<td>K</td>
<td>0.0388</td>
<td>0.0303</td>
<td>0.0299</td>
<td>0.0270</td>
<td>0.0386</td>
<td>0.0390</td>
<td>0.0369</td>
</tr>
<tr>
<td>R²</td>
<td>0.9501</td>
<td>0.9507</td>
<td>0.969</td>
<td>0.965</td>
<td>0.9473</td>
<td>0.9529</td>
<td>0.9572</td>
</tr>
</tbody>
</table>
Fig 5. Results of Gompertz model for variable 1-7

performance model, the modified Gompertz model has a higher coefficient determination in all variables than the first-order kinetic reaction model. For example, in variable 3, which has higher results of biogas, by using Gompertz modified model, the value of $R^2$ is 0.9754, whereas, by using the first-order kinetic reaction model, the value of $R^2$ is 0.969, which is lower than Gompertz modified model. The first-order kinetic model results in every variable in this research depicted in a graph comparing the observed biogas data and the predicted
biogas data through the first-order equation. The comparison graph of experimental and predicted biogas data in variable 1 using the first-order kinetic model can be seen in Fig. 6.

Fig. 6 shows that the predicted data using the first-order kinetic model goes unidirectional, with almost the same values on the graph, but it does not fit well, and there is a slight difference between the experimental data and the predicted data from the biogas yield. The coefficient of determination from the first-order kinetic reaction is lower than using the Gompertz model. The coefficient of determination in first-order kinetic reaction are 0.9501,
0.9507, 0.969, 0.965, 0.9473, 0.9529, 0.9572, respectively for variable 1-7. Then, the biogas production rate constant (K) was determined as 0.03876, 0.0303, 0.0299, 0.027, 0.0386, 0.039, 0.0369, respectively for variable 1-7. The highest K value is shown by variable 1.

The first-order kinetic model shows a deviation between experimental and predicted data. However, the value of $R^2$ here is still at a good standard and can represent experimental data. The first-order kinetic model also provides checks and comparisons on the results obtained from the Gompertz model. Furthermore, as a result, the comparison of experimental data and expected data from both the Gompertz model and the first-order kinetic model tends to be linear.

**CONCLUSION**

From the data obtained in this research, it can be concluded that the highest biogas yield production was obtained by variable 3 with the comparison of 70% cow dung, 15% chicken manure, and 15% tofu liquid waste. The raw materials affect the results of biogas yield. From the comparison of raw material used, the addition of cabbage waste in variables 5-7 makes the biogas yield results low. It is caused by the C/N ratio in cabbage waste higher than 30:1, reducing the potential biogas produced. The results of the Gompertz modified model predicted that the highest biogas yield was obtained by variable 3 with 3273.20 mL/(g Ts). The lower results predicted by Gompertz modified model are shown by variable 7 with 1476.45 mL/(g Ts). Then, the highest results of biogas by predicted data using first-order kinetic model obtained by variable 3 with total biogas of 3517.95 and followed by variable 4 with 3310.16 mL/(g Ts). For comparing the performance model, the modified Gompertz model has a higher coefficient determination in all variables than the first-order kinetic reaction model. It means the best fit was obtained from the modified Gompertz model.

**REFERENCES**


