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Kinetic Analysis of Anaerobic Digestion of Rice Husk for Prediction of Methane Yield

Lukhi Mulia Shitophyta^{1,*)}, Nidha Amalia Nurillah¹⁾, Evi Agustina¹⁾, Siwi Purwanti²⁾, and Meilya Suzan Triyastuti³⁾

¹⁾Department of Chemical Engineering, Faculty of Industrial Technology, Universitas Ahmad Dahlan, Yogyakarta, Indonesia

²⁾Department of Primary School Teacher Education, Faculty of Teacher Training and Education, Universitas Ahmad Dahlan, Yogyakarta, Indonesia

³⁾Department of Fishery Product Processing Techniques, Politeknik Kelautan dan Perikanan Bitung, Bitung, Indonesia

*)Penulis korespondensi: <u>lukhi.mulia@che.uad.ac.id</u>

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	Abstract		
Article History	A study of three kinetic models for predicting methane yield was performed. The selected models for predicting methane yield were first-order, modified Gompertz and Monod		
Submitted:	models. Anaerobic digestion of rice husk was simulated using the selected models. A		
September 18, 2023	comparative evaluation of the models was undertaken to determine the best-fit model. All models obtained an accuracy of predicted methane yield of over 0.9. The prediction of methane yield on rice husk has the most accurate model being the modified Gompertz with		
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October 30, 2023	the least deviation of 7.37% and the least accurate model being the Monod model with the		
Published:	highest deviation of 20.39%.		
October 31, 2023	Keywords: anaerobic digestion; kinetic; methane; rice husk		
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	Analisis Kinetika Pencernaan Anaerobik Sekam Padi untuk Prediksi Hasil Metana. Penelitian terhadap tiga model kinetika untuk memprediksi yield metana telah dilakukan. Model yang dipilih untuk memprediksi yield metana adalah model orde pertama, modifikasi Gompertz dan Monod. Digestasi anaerobik dari sekam padi disimulasikan menggunakan model terpilih. Evaluasi kompratif model dilakukan untuk menentukan model yang paling sesuai. Semua model memperoleh akurasi prediksi yield metana lebih dari 0,9. Prediksi yield metana pada sekam padi mempunyai model yang paling akurat adalah modifikasi Gompertz dengan deviasi terkecil sebesar 3,37% dan model yang paling tidak akurat adalah model Monod dengan deviasi tertinggi sebesar 20,39%.		
	Kata kunci: digestasi anaerobic; kinetika; metana; sekam padi		

INTRODUCTION

Energies are a primary resource for all human activities, development in modern civilization and sustainability. Currently, energy need is continually increasing due to the severe consumption of natural resources such as natural gas, oil and coal in industries, houses, etc. [1]. The lessening of natural fuel obedience regarding decreasing greenhouse gases has drawn interest in non-conventional resources from bio-wastes [2]

Biofuel becomes an alternative resource for reducing the consumption of conventional fuels. A biofuel with a widespread choice of developed and described production enhancements is biogas [3]. This biofuel is generated in an Anaerobic Digestion (AD) process, it involves a sequence of processes



including hydrolysis, acidogenesis, acetogenesis, and methanogenesis [4].

The mathematical models can designate digester performance abilities. The terms of the model can be represented in kinetic analysis. There are numerous kinetic expressions used for expressing anaerobic digestion focusing on various variables. The modified Gompertz and first-order kinetics models are extensively employed for predicting biogas yield. The modified Gompertz model is applied to predict the biogas potential relating to the microbes' growth rate in the digester [5]. Several studies have addressed the kinetic model of anaerobic digestion. [2] investigated the kinetic evaluation of the anaerobic digestion of potato peels. [6] used firstorder and Gompertz models for evaluating the kinetic analysis of anaerobic digestion of chicken manure with saw dust. [7] found that modified Gompertz was the best fit for predicting biogas production from food waste. [8] used Gompertz model for determining kinetic model of anaerobic co-digestion of thai rice noodle wastewater with rice husk. However, a study has not been comparing three kinetic models for predicting methane yield for particular rice husk material. Therefore, the present study aimed to compare the predicted biogas yield of three selected models for the anaerobic digestion of rice husk.

MATERIALS AND METHODS Feedstock and Inoculum

Rice husk was collected from local mills in Yogyakarta. Then, it was ground and sieved using 250-micron sieves. The ground rice husk was stored in air-tight bags at room temperature. The Rumen fluid of the cow was obtained from a slaughterhouse in Yogyakarta. Rice husk was used as feedstock while rumen fluid of cow was used as an inoculum.

Pretreatment of Rice Husk

The pretreatment was performed by soaking the rice husk in 1 g/L NaOH solution. The substrate was stirred until homogenous. Then, it dried in the oven at 50° C for 120 minutes.

Experimental Set-up

The pretreated substrate was introduced into 1 L batch digesters and mixed with inoculum by feedstock and inoculum ratio of 1.2 and 1. Water was added to adjust the substrate volume of 600 ml. The digester was tight-closed. The experiment was run at room temperature. Biogas volume was measured by the water displacement method every three days.

Kinetic Analysis

Excel Solver was employed to calculate the kinetic parameters of all models, which included the firstorder, modified Gompertz and Monod models. The First-order model assumes a correlation between Volatile Solids (VS) biodegradation and biogas yield at any time [9]. The mathematical equation of firstorder model is written in Equation (1) [10].

$$G_t = G_0 \times \left(1 - exp(-kt)\right) \tag{1}$$

The modified Gompertz model supposes biogas production relates to the growth rate of methanogen in the digester [11]. The modified Gompertz equation is shown as follows [12].

$$G_t = G_0 \times exp\left\{-exp\left[\frac{R_m \cdot e}{G_{0,1}}(\lambda - t) + 1\right]\right\}$$
(2)

Monod model describes the non-linear correlation between substrate concentration and specific growth rate. This model considers substrate concentration as a liming factor [13]. The Monod model is presented as follows [14].

$$G_t = G_0 \quad \times \left(\frac{kt}{1+kt}\right) \tag{3}$$

Where G_t is the cumulative methane yield at time t (L/kg VS), G_0 is the methane potential of the substrate (L/kg VS), k is the rate constant (1/day), R_m is the maximum methane production rate (L/kg VS day), λ is lag phase time (day), t is digestion time (days), and e is equal to exp (1) or 2.7182.

RESULTS AND DISCUSSION Biogas Production of Rice Husk

Biogas production began on day 3 with a biogas yield of 0.3 L/kg VS then it increased regularly until attaining a peak yield of 4.32 L/kg VS on day 21. After day 24, biogas yields drive down slowly until reaching the constant yield on day 30 to day 36. At the initiation of biogas production, the microbes present in the organic matter became active and started rising in population. When biogas production began to increase, microbes were completely established and were acting on more substrate. At the peak of biogas production, microbes were working on the maximum amount of substrate possible. After this stage, biogas production started to drop because the excess matter was being converted to methane. At this stage, there is also a stable decline in the amount of organic matter available to the bacteria to work [15]. Figure 1. shows the daily biogas yield during 36 days.



Figure 1. Daily biogas yield during anaerobic digestion of rice husk

A decrease in biogas production occurred due to the inhibition of fermentation and methanogenesis, leading to the buildup of Volatile Fatty Acids (VFA) [16]. Overproduction of VFA instigates pH reduction, inhibition of methanogen activities, and reactor failure, thus lowering biogas yields [17]. The experimental cumulative biogas yield is presented in **Figure 2.**



Figure 2. Cumulative biogas yield during anaerobic digestion of rice husk

The highest cumulative biogas yield was obtained on day 36 (12.25 L/kg VS). Similar to the daily biogas yield, cumulative biogas yield increased when digestion time increased. This cumulative biogas yield was used to compare and calculate predicted methane yield using three models (first-order, modified Gompertz, and Monod model).

Kinetic Analysis of Biogas Production from Rice Husk

Table 1.summarizes the kinetic parameterscalculated for the anaerobic digestion of rice huskusing the first-order, modified-Gompertz, andMonod models.The first-order and Monod models

calculated the biogas production rate constant (k). Meanwhile, the modified Gompertz model estimated Rm values. Moreover, **Table 1.** presents RSME, SSE, R², and the difference between predicted and experimental biogas production.

The modified Gompertz model indicated better performance compared to the two other models in terms of predicted methane yield, with the lowest RSME of 0.0007 and the R^2 was greater than 0.9 (0.9360). Additionally, there was the lowest difference between the predicted and experimental biogas production obtained by the modified Gompertz. This was less than 10%.

Table 1. Summary of kinetic analysis

		Model	
Parameter	First- order	Modified Gompertz	Monod
Go (L/kg VS)	385.2744	13.4584	244.3100
Rm (L/kg VS day)	-	0.9701	-
λ (day)	-	10,2909	-
k (day-1)	0.0010	-	0.0019
RMSE	1.7515	0.2079	2.5505
\mathbb{R}^2	1.0000	0.9360	0.9972
SSE	9.0877	2.3051	18.0526
difference between experimental and predicted methane yield	13.93%	7.37%	20.39%

The first-order model provides the highest R^2 value (1) among the two models. The R^2 is the square of the relationship between the actual and predicted values. The R^2 of 1 denotes that the regression model describes all of the predicted variables, which means that the relationship between the predicted and experimental values is flawless [18]. The predicted methane production and using three models is presented in **Figure 3**.

The rate constant (k) was found to be 0.0010 day⁻¹ and 0.0019 day⁻¹ by first-order and Monod models, respectively. The R² value fitted by the first-order model was greater than the R² value matched by the Monod model, pointing out that the first-order model predicted methane yield more applicable than the Monod model. This finding corresponded to a report by Nguyen et al. (2021), who found that the Monod model provided a higher k (2.393/day) and a smaller R² (0.40) than the first-order model (k = 0.9144/day, R² = 0.84).

Though modified Gompertz had the lowest R^2 value compared to the two models, this model is still compatible in predicting methane yield for anaerobic digestion of rice husk since the obtained R^2 value is higher than 0.9.



Figure 3. Kinetic analysis of biogas yield using three models. (a) experimental and predicted methane production using a first-order model; (b) experimental and predicted methane production using a modified Gompertz model; (c) experimental and predicted methane production using the Monod model

The divergence between experimental and predicted biogas production can be calculated using Root Mean Square Error (RMSE). RMSE is 0, denoting perfect prediction. RMSE standard can be biased for the peaks and greater values that will generate the highest error [19]. The least-applicable model for methane prediction from rice husk was logged by the Monod model, which obtained the highest RMSE of 2.5505.

Modified Gompertz is the most applicable model for simulating methane production of anaerobic digestion from rice husk since it had the smallest RMSE and divergence. Additionally, the predicted methane yield by modified Gompertz (13.22 L/kgVS) was nearly comparable and close to the experimental output (12.25 L/kgVS). The result is also in agreement with the discoveries by [10], [20], [21] and [7].

CONCLUSION

A comprehensive study of first-order, modified Gompertz, and Monod models was completed. Correspondingly, all input parameters, such as the methane potential of the substrate (Go), rate constant (k), maximum methane production rate (Rm), and lag phase (λ) were evaluated for the analysis of the models. All models revealed the exactness of the predicted methane potential of over 0.9. In terms of the total methane potential and daily methane yield compared to the experimental data, the modified Gompertz model gained the least deviation of 7.37%. The model which was the least accurate was the Monod model, which has the highest deviation of 20.39%.

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