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Determination of Kinetic Models in Acidogenesis Process of Palm Oil Mill Effluent

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ABSTRACT

Palm oil mill effluent (POME) can be transformed into biogas. Acidogenesis, as a fermentation process, involves decomposition of hydrolysis products into simpler organic products in the form of acetate, hydrogen and carbon dioxide. Intermediate products from acidogenesis form of volatile fatty acids (VFA), such as propionate, butyrate, valerate, and their isoforms, which require further metabolic processes to produce biogas. The aim of the research was to determine the suitable kinetics model that describes microbial growth (from volatile suspended solid (VSS) values) and production in the acidogenesis process. The reactor used in this acidogenesis process was a stirred tank reactor with a volume of 6 L and operates in a batch system. This research was conducted with a variable agitation rate variation (200; 250; and 300 rpm) at a temperature of 30 °C and 55 °C. The pH was varied, including 5; 5.5; and 6. The kinetic models used in this study were Modified Gompertz, Monod, and Logistic. The best effect of pH on VSS was obtained at pH 5.5, agitation rate on VSS was obtained at agitation rate of 250 rpm and operating conditions for acidogenesis process was achieved under thermophilic conditions (55 °C). Logistic kinetic model is the best kinetic model that can describe VSS and VFA in this study.

Keywords: acidogenesis, agitation, kinetic, palm oil mill effluent, volatile fatty acids.

INTRODUCTION

Indonesia is the largest producer and exporter of palm oil in the world and simultaneously produces large amounts of palm oil waste, including such types of waste as palm stems and leaves, empty fruit bunches, palm kernel shells, and palm oil waste [Chew et al., 2022]. POME is an assemblage of waste sourced through the discharge of three main sources like clarifier wastewater (60%), condensate sterilizer (36%), and wastewater from hydro cyclones (4%) [Ahmed et al., 2015]. Utilization of POME into biogas using a stirred tank reactor (CSTR) with thermophilic microbes, produces active liquid organic fertilizer from waste disposal sourced biogas digesters [Irvan et al., 2018].

The anaerobic digestion (AD) process is divided into four stages, namely hydrolysis, acidogenesis, acetogenesis, and methanogenesis [Da Silva et al., 2023]. The second stage is the process of acidogenesis (also referred to as fermentation), in which the products of hydrolysis are further degraded into simpler organic products in the form of acetate, hydrogen (H_2), and carbon dioxide (CO_2) [Lam and Lee, 2011]. Acidogenesis of the palm oil mill wastewater in order to generate biogas is carried out based on an oxygen-free procedure [Trisakti et al., 2015]. The research studied the effect of the hydraulic retention time (HRT) and pH to variations in the concentration of organic molecules and solids content of POME to the microbial development in the acidogenesis stage. At HRT 4.0 days with microbe concentration, the maximum development of microorganisms was attained as VSS of 20.62 mg/L and chemical oxygen demand (COD) decrease of 15.7%. At pH 6.0, maximum amount of overall VFA produced was 5622.72 mg/L, with acetic, propionic, and butyric acid concentrations of 2257.34, 975.49, and 2389.90 mg/L, respectively. Volatile solids (VS) and COD degradation rates amounted to 11% and 23%, respectively. An experiment was conducted regarding the impact of agitation on acidogenesis step of POME anaerobic breakdown in two-stage process to produce biogas [Trisakti et al., 2017]. At HRT 4.0 days, the maximum growth of microorganisms was recorded, with a COD reduction of 15.7% and a microbe concentration of 20.62 mg VSS/L. At an agitation rate of 200 rpm, the maximum generation of total VFA was attained, with concentrations of acetic acid, propionic acid, and butyric acid being 1,889.23, 1,161.43, and 2,725.95 mg/L, respectively. In turn, COD and VS degradation reached 16.61 and 38.79 % respectively. Intermediate compounds formed in acidogenesis, including volatile fatty acids, such as propionate, butyrate, valerate, and their isoforms, must be further degraded before methanogens can metabolize them to produce biogas [Ezebuiro et al., 2022]. Modeling needs to be done to compare the best kinetics model that will be used to obtain a better bioreactor design model.

In general, there are two approaches to modeling the dynamic behavior of a process, one is based on a mathematical model using differential equations that describe the structure and characteristics of the process, and another is the transient response approach which utilizes output data in response to changes in system inputs, such as impulses or step functions [Horiuchi et al., 2001]. The kinetic and stoichiometric parameters of the fermentation process are usually determined by achieving a certain steady state in a continuously stirred tank reactor, where the conditions are set at each dilution rate. The parameters obtained using this method are compared with the parameters from the more usual steady state [Dominguez et al., 1993]. Combining simple or complex models can represent phenomena more precisely and thereby increase our understanding [González-Figueredo et al., 2018]. Through kinetic analysis, determining several different parameters, including hydrolysis rate constant, lag phase period, and maximum specific methane production rate can be obtained and helps evaluate anaerobic digestion processes. Thus, a correct kinetic model that produces reliable predictive results is essential for process design and operation [Andriamanohiarisoamanana et al., 2020].

First-order and Monod-type kinetics are the most commonly used models to estimate the substrate degradation rates [Wang et al., 2018]. The first-order kinetics model is a model based on the hypothesis that hydrolysis controls the entire process and substrate availability is the limiting factor [Pramanik et al., 2019]. Monod kinetics is known as a basic model that explains microbial growth that is dependent on substrate assuming an impact of the substrate or its products that is not inhibitive. Substrate consumption and formation of growth-related products can additionally be described by employing quantitative models of development as a basis because growth as the outcome of the catabolic and anabolic enzymatic activity of the substrate. The Gompertz model is one of the most widely used models that explain microbial proliferation because to their straightforward creation [Majeed et al., 2016]. The modified Gompertz model (MGM) is suitable for inhibited anaerobic digestion processes, which have methane yields comparable to bacterial growth. MGM has been adopted for most of the kinetic studies in solid-state anaerobic digestion [Ajayi-Banji et al., 2021]. The logistic function model describes microbial population growth as a function of initial population density, time, growth rate, and final population density [Wachenheim et al., 2003].

The aim of the research was to determine the suitable kinetics model that describe microbial growth (from VSS values) and production in the acidogenesis process. The findings of this study hold significant implications for various fields within chemical engineering, environmental science, and biotechnology. This can result in more efficient and cost-effective waste management practices, with potential benefits for both municipal and industrial sectors.

MATERIALS AND METHOD

POME was obtained from PT. Perkebunan Nusantara (PTPN) III, Rambutan palm oil mill (POM), Serdang Bedagai, Sumatera Utara, Indonesia, whereas the starter was obtained from Pilot Plant Biogas Power Plant, Lembaga Penelitian dan Pengabdian kepada Masyarakat (LPPM) Universitas Sumatera Utara (USU), Medan, Indonesia. The equipment used in this study is presented in Figure 1.

The research procedures carried out included POME acidogenesis process and determination of the microbial growth constants. The raw materials used in this study were starter and fresh

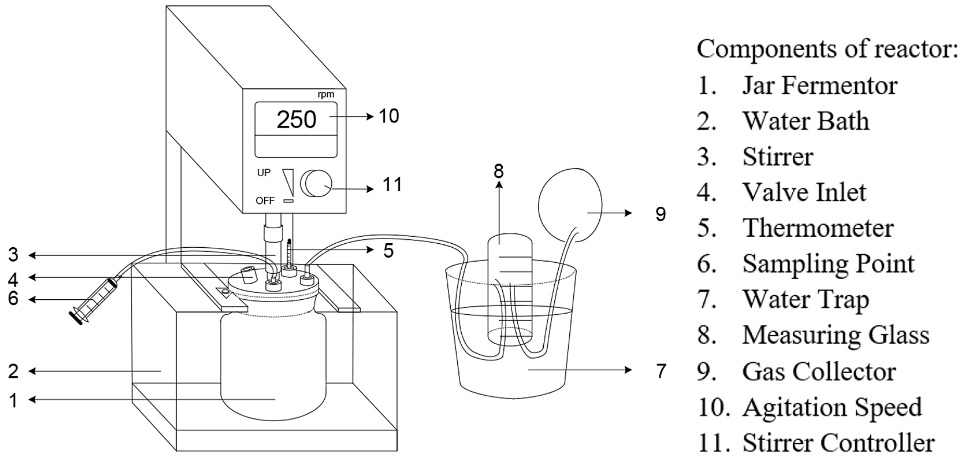

Figure 1. Acidogenic reactor scheme

POME which had been characterized and then put into the 6-liter fermenter with a ratio of 20% and 80% of the total volume. The fermenter was operated using a batch reactor with variations agitation rate of 200; 250; and 300 rpm, the fermenter temperature were 30 °C and 55 °C, and the pH of the fermenter were 5; 5.5; and 6. The measurement parameters studied were the measurement and timing of the initial POME analysis (t_0) as well as the analysis time for each sampling (t_i) and fluid measurement (VSS). Measurement and determination of VSS was carried out every day.

Determination of microbial growth constants was carried out using Modified Gompertz, Monod, and Logistic kinetics. The data needed are time (t; days) and M (VSS; g/L) measured in experiment, where M (VSS; g/L) measured in experiment is used as Mexp value (VSS; g/L), while VSS value of the simulation results is symbolized as M(t) (VSS; g/L). These values were used to determine constant value of microbial growth in each model through trial and error with the non-linear regression method by means of Microsoft Excel 2016 and the Solver add-on program. Through this software, the minimum value of total square of error between Mexp and M(t) as well as growth constant value were obtained from all the kinetic models used. Graphs of M vs t values of experiments and simulations of all models were plotted and compared to all of these graphs. The error value of the kinetic model was calculated using the coefficient of determination (R^2), root-mean-square error (RMSE), and Akaike Information Criterion (AIC) to determine better fit/accuracy in kinetic model used for the experimental results. Then, the same experimental procedure was carried out to determine the volatile fatty acids production constant by analyzing the parameters used, namely the values of potency of daily microbial growth (A), maximum growth rate parameter (R_{max}), lag phase (λ), constant model (k), R^2, RMSE, and AIC in several kinetic models used to obtain the best kinetic model in this study.

RESULTS AND DISCUSSIONS

Effect of agitation rate on volatile suspended solid profile

Agitation rate is one factor that influences microbial growth in acidogenesis. Figure 1 illustrates the impact of the pace of agitation on the VSS profile on each agitation (200, 250, and 300 rpm).

Figure 2 shows the best VSS profile of the variation of agitation rate under ambient and thermophilic conditions. Song et al. [2004] and Trisakti et al. [2017] claimed that mesophilic digesters (30–42 °C) obtained lower VSS. The mesophilic system had a difference of 10.3% compared to thermophilic digesters [Song et al., 2004; Bambang Trisakti et al., 2017]. The higher temperatures in thermophilic conditions can lead to a more rapid and complete degradation of organic matter, resulting in a lower VSS content. In contrast, ambient conditions, with lower temperatures, may not support the same level of microbial activity, leading to slower degradation and higher VSS levels [Zailani et al., 2017]. On the basis of the results, under ambient conditions, the microbial growth profile tends to fluctuate with a VSS concentration of 14.740–23.420 mg/L at an agitation rate of 200 rpm. At the agitation rate of 250 rpm, VSS of 14.740–24.940 mg/L, and at the agitation

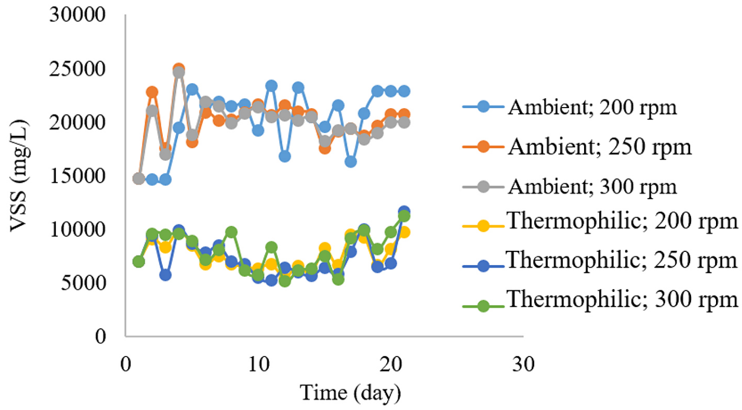

Figure 2. Effect of agitation rate on the VSS profile on ambient and thermophilic conditions

rate of 300 rpm, VSS of 14.740–24.640 mg/L. Under ambient conditions, the highest VSS was 24.940 mg/L, which was obtained at a rate of the agitation of 250 rpm. Meanwhile, under thermophilic operating conditions, it also showed a fluctuating microbial growth profile with a VSS of 5.460–9.720 mg/L at an agitation rate of 200 rpm. At a rate of the agitation of 250 rpm, VSS of 5.240–11.640 mg/L, and at agitation rate of 300 rpm, VSS of 5.140–11.280 mg/L. Under thermophilic conditions, the highest VSS was 11.640 mg/L, obtained at a rate of the agitation of 250 rpm. According to Lindmark et Al., an unstirred digester in the digestion process produces a more stable anaerobic digestion process, but could be more optimal on an industrial scale. An agitation speed that needs to be lowered could be more efficient for microbes in utilizing existing nutrients. As a result, the instability affects the growth of microorganisms slower [Lindmark et al., 2014; Amiri et al., 2022]. The results obtained under ambient and thermophilic conditions with a stirring rate of 250 rpm resulted in a high VSS at the end of the observation.

Determination of kinetic constants of microbial growth rate

The optimum operating conditions for the acidogenesis process in this study were the microbial growth profile based on VSS with an agitation rate of 250 rpm at pH 5.5 and thermophilic operating conditions. The equations or models used describe microbial growth in the acidogenesis process. The kinetic model used is Modified Gompertz, Logistic, and Monod. After matching each model that has been simulated, the model will be evaluated to describe the best level of accuracy in the acidogenesis process. The kinetic model was evaluated based on the coefficient of determination (R^2) and RMSE values for model fit. Then, the effect of pH variations and stirring speed was studied based on the best kinetic modeling.

Figure 3 describes the kinetics modeling of microbial growth based on VSS. The models used were Modified Gompertz, Logistic, and Monod. These models are widely used in reactor systems to understand and predict the growth dynamics of

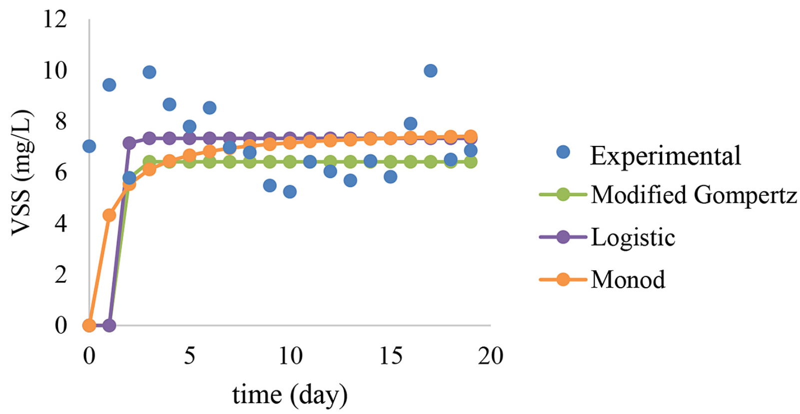

Figure 3. VSS kinetic modeling at the best operating conditions

microorganisms, which is critical to optimizing and improving efficiency [Öktem, 2019]. Each model showed a good fit with the experimental data. The model's fit was evaluated based on the R^2 and RMSE values. After being evaluated, it was concluded that the best kinetic model would be used to see other effects on the kinetic model. According to Pramanik et al. [2019], R^2, RMSE, and AIC are well-established statistical indicators that help determine a better fit for the kinetic model with experimental data. The R^2, AIC, and RMSE values in the Modified Gompertz, Logistics, and Monod models are described in Table 1.

On the basis of Table 1, the evaluation results of each kinetic model were considered to match the experimental data. For the Modified Gompertz, Logistic, and Monod kinetic models, the model provides good kinetics in explaining growth. This is indicated by a reasonably good R^2 value, where R^2 ranges between 0.828–0.885. The coefficient of determination was defined as the sum of the squares of the regression results divided by the total number of squares. In general, R^2 is interpreted as representing the percentage variation of the dependent variable, which is explained by the variation of the independent variable [Silva, 2011]. The Monod model was obtained based on the results obtained by the growth kinetics model with the highest R^2. The R^2 value which is very close to 1 shows that the biogas results obtained can be satisfactorily explained by the model used [Kouame et al., 2023]. Meanwhile, the RMSE values for various kinetic models show a range of 2.461–3.060. RSME measures the error based on the difference between the experimental and model biogas production values. In many model sensitivity studies using only the RMSE, detailed interpretation is unimportant because the same model variation will have a similar distribution of errors [Chai and Draxler, 2014].

Determination of kinetic constants of the formation rate of volatile fatty acids

The product of the acidogenesis reaction is VFA, which consists of three main components acetic acid, propionate, butyrate, and by-products in the form of gas phase (carbon dioxide (CO_2), hydrogen sulfide (H_2S), ammonia (NH_3), and hydrogen (H_2)). After obtaining the optimum conditions for the acidogenesis stage, i.e., pH 5.5, agitation rate of 250 rpm, and thermophilic conditions, the experimental data were matched with the Logistic, Monod, and Modified Gompertz models. This stage aimed to ascertain the maximum rate of growth of VFA products and effect agitation on the reaction rate (Fig. 4).

On the basis of Table 2, the lowest value of Akaike's Indicator Criterion (AIC) was obtained at Logistics model -17.026. The AIC is another method used to compare kinetic models and determine which one is more likely to be correct. The second-order AIC can be positive or negative. A smaller AIC value indicates a better fit and predictive ability of the model [Lim et al., 2021]. The lowest value shows the best AIC. This is consistent with what Nguyen et al. reported, i.e. that lower AIC and Bayesian information criterion (BIC) values indicate a more suitable kinetic model [Nguyen et al., 2019]. From Table 3, it can be seen that the increase of agitation rate from 200 rpm to 250 rpm increased the potential of the formed VFA product by 1.5356 g/L^{-1} to 2.4522 g/L^{-1}, but the increase of agitation rate up to 300 rpm tended to decrease the potential of the VFA product by 1.7069 g/L^{-1}. The maximum growth rate parameter (R_{max}) obtained the greatest value at an agitation rate of 250 rpm of 1.2369 g/L/day. Meanwhile, increasing the agitation rate of 300 rpm reduced the R_{max} of 0.2747 g/L/day.

Table 1. Evaluation value and kinetic constants in model

Kinetic models	Constant		R^2	RMSE	AIC
Modified Gompertz	Rm*	22.916	0.828	3.060	1.924
	λ	1.663			
	A	6.410			
Logistic	Mm	7.330	0.834	2.956	0.777
	λ	1.600			
	Rm**	25.773			
Monod	Mm	7.721	0.885	2.461	0.806
	k	0.788			

Note: Maximum growth rate parameter (Rm*), lag phase (λ), potency of daily microbial growth (A), maximum growth rate parameter (Mm), maximum of biogas rate production (Rm**), and constant model (k).

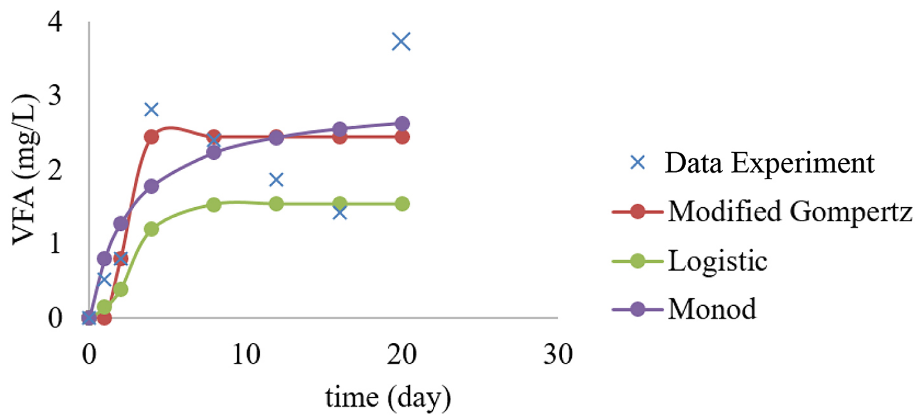

Figure 4. Product kinetic modeling at the best conditions

Table 2. Kinetic model evaluation at the best conditions

Property	Monod	Logistics	Modified Gompertz
A (g/L)	2.988	2.452	2.447
k (1/day)	0.123	–	–
R_{max} (g/L/day)	–	1.237	5.119
λ (day)	–	1.239	1.844
R^2	0.620	0.700	0.690
RMSE	0.841	0.751	0.760
AIC	1.327	-17.026	5.309

Note: Potency of daily microbial growth (A), constant model (k), maximum growth rate parameter (R_{max}), lag phase (λ), coefficient of determination (R^2), RMSE, and AIC.

Table 3. Logistic kinetic model evaluation data at agitation rate variations

Property	200 rpm	250 rpm	300 rpm
A (g/L)	1.536	2.452	1.707
R_{max} (g/L/day)	0.451	1.237	0.275
λ (day)	1.224	1.239	0.699
R^2	0.910	0.700	0.940
RMSE	0.188	0.751	0.189

Note: Potency of daily microbial growth (A), maximum growth rate parameter (R_{max}), lag phase (λ), coefficient of determination (R^2) and Root-Mean-Square Error (RMSE).

CONCLUSIONS

The influence of agitation and pH on the rate constant of microbial growth and VFA formation from POME has been successfully studied using modified Gompertz modeling in this research. This is important to study to produce optimum microbial growth and VFA in terms of agitation and pH that are appropriate in continuous-sustained tank reactor. The study explains of microbial profile growth in the acidogenesis process. This process is essential, because the acidogenesis stage will also affect the methanogenesis process. The study of microbial growth kinetics to determine the best conditions in this process. The best agitation rate on volatile suspended solid was obtained at an agitation rate of 250 rpm. The best kinetic constants potency of daily microbial growth (A), maximum growth rate parameter (R_{max}) and lag phase (λ) for microbial growth were 2.4522 g/L, 1.237 g/L/day, and 1.239 days at an agitation rate of 250 rpm. Kinetic evaluation based on the coefficient determination (R^2) and RMSE were 0.700 and 0.751, respectively. Logistics is the best kinetic model to describe microbial growth and VFA production, because it has the lowest AIC value of -17.026. This shows that the modified Gompertz equation is most suitable for the kinetic study of biogas production and for determining the lag phase of the reaction and the maximum biogas potential. This potential benefits for both municipal and industrial sectors.

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