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Kinetics Study of Free Fatty Acid Esterification from Sludge Palm Oil Using Zeolite Sulfonated Biochar from Molasses Composite Catalyst

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Abstract. A kinetics study of free fatty acid (FFA) esterification from sludge palm oil (SPO) using zeolite sulfonated biochar from molasses composite catalyst has been conducted. The effect of reaction temperature (60, 70, 80 °C) and the molar ratio of methanol to free fatty acids (17:1, 20:1, 23:1, 26:1, 29:1) on the kinetic parameters such as reaction rate, Arrhenius constant, activation energy, and enthalpy energy were investigated. The study showed that the reaction temperature and the initial free fatty acids concentration were positively correlated with the reaction rate and the reaction rate constant. The forward activation energy and Arrhenius constant for biodiesel formation were 30.6537 kJ/mol and 2.04×10^2, respectively, while the backward activation energy and Arrhenius constant were 15.8714 kJ/mol and 2.502, respectively. The positive enthalpy value was 14.7823 kJ/mol indicates the reaction endothermically occurred. The validation of the kinetic model gives an R^2 value of 0.9612, indicating that the model was acceptable and provided a predicted value close to the actual value.

Introduction

Crude Palm oil (CPO) is an essential commodity for Indonesia, both domestically and internationally. The abundant content of palm oil makes CPO potential as biodiesel feedstock. However, the use of CPO as fuel triggers competition with food needs. In addition, the price of CPO continues to increase; thus, it is not economical to process [1]. On the other hand, CPO processing will produce waste in the form of sludge. If the sludge accumulates in the reservoir, it will disrupt the ecosystem. Interestingly, sludge palm oil is reported to have a high content of free fatty acids, which is potential as biodiesel feedstock [2] and is an ideal way to utilize and reduce sludge waste.

Conversion of free fatty acids from sludge palm oil (SPO) into biodiesel can be carried out through an esterification reaction with alcohol and an acid catalyst. Various acid catalysts have been used to catalyze the esterification of free fatty acids in SPO, such as H_2SO_4 [3] and toluene-4-sulfonic monohydrate acid (PTSA) [4]. Those catalysts produce a large biodiesel yield and show good activity. However, those homogenous catalysts are corrosive, difficult to separate, and can not be recovered [5]. Therefore, heterogeneous acid catalysts are present to overcome these problems.

Materials such as alum [6], sulfated zirconia-rice husk ash [7] have been used as heterogeneous esterification of FFA in SPO catalysts. Furthermore, the literature shows that functionalized biochar is a promising catalyst in the biodiesel production process [8]. Biochar is a material with high carbon content produced by the carbonization of biomass. The material is activated with sulfuric acid and has been widely studied because it has good catalytic activity for esterification reactions. The presence of sulfonic acid groups ($–SO_3H$) with phenolic and carboxylic groups formed on biomass carbonization increases the catalytic activity [9]. Biomass molasse can be used as raw material for making biochar because of its high sugar content [10]. The catalytic activity of sulfonated biochar

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from molasses can be increased by adding a supporting material such as zeolite. Zeolite is one of the potential options because it is porous and has a Brønsted acid site and a Lewis acid site which can catalyze the esterification reaction [11].

Kinetic studies are very important to understanding esterification reactions. Several studies have been reported using various raw materials and catalysts [12-15]. However, based on the literature study, the kinetic study of free fatty acid esterification from sludge palm oil and methanol using a sulfonated zeolite biochar composite catalyst from molasses has not been reported so far. Hence, this research studies methanol's temperature and mol ratio to free fatty acids, considering that those variables affect the reaction kinetics. In addition, kinetic parameters such as reaction rate constant, activation energy, Arrhenius constant, and enthalpy of esterification were investigated. The determination coefficient also validated the match-up between the predicted value from the kinetic model and the observed value.

Methodology Research

Analysis of Sludge Palm Oil FFA. Two and a half grams of sludge palm oil was put into a 250 mL Erlenmeyer, added with 10 mL of methanol, stirred, and heated at a temperature of 60 °C until completely dissolved. The solution was titrated with Phenolphthalein indicator using NaOH titrant. Free fatty acid content as palmitic acid determined according to SNI 01-2901-2006.

Effect of Temperature and Methanol to FFA Molar Ratio over the Initial Esterification Rate. The esterification was carried out in a batch reactor by preparing 25 g of SPO collected from PT. Agro Indralaya Mandiri, and 2 g of catalyst. The catalyst of zeolite-biochar sulfonated composite from molasse used according to Ramadhani [16] with a ratio of zeolite to molasses 1:2 (w/w %), which has the highest of acidity value of 22.6 mmol/g. The temperature variables studied were 60 °C, 70 °C, and 80 °C, while the mole ratio methanol to FFA was 17:1, 20:1, 23:1, 26:1, and 29:1. The esterification product was taken as much as 2.5 mL every 10 min with a reaction time of 60 min. FFA reduction (X) was calculated according to the initial and remaining free fatty acid concentration difference. The X value was then used to calculate the reaction rate.

Effect of Temperature on the Reaction Rate Constant. The reaction rate constant was calculated according to the kinetic integration Eq. 1. Then, the slope of the graph was obtained and used to determine the value of the rate constants k_1 and k_2.

$$\ln\left[\frac{(A_o - x(\frac{1}{2}+\beta))}{(A_o - x(\frac{1}{2}-\beta))}\right] = 2k_2\alpha t \quad (1)$$

Determination of Arrhenius Constant, Activation Energy, and Enthalpy of Esterification. The Arrhenius Constant and Activation Energy were calculated using the ln form of the Arrhenius Eq. 2. The enthalpy value of the reaction is obtained from the difference between the reaction activation energy and the activation energy of the reverse reaction.

$$\ln k_n = \ln A - \frac{Ea_n}{R}\frac{1}{T} \quad (2)$$

Arrhenius constant (A) was calculated from anti ln intercept values obtained from graphs 1/T to ln k_1 and 1/T to ln k_2, while the activation energy (Ea_n) was calculated from the slope value.

Kinetic Model Validation. The validation of the kinetic model was carried out to show that there was a match between the experimental and predicted kinetic equation model used in the study that can be calculated according to Eq. 3.

$$X_{\text{kinetic model}} = \frac{A_o(e^{2k_2\alpha t}-1)}{\beta(1+e^{2k_2\alpha t}) + 0.5\,A_o(e^{2k_2\alpha t}-1)} \quad (3)$$

Results and Discussion

Effect of Temperature and Methanol to FFA Molar Ratio over the Initial Esterification Rate. The effect of the initial free fatty acid concentration and temperature on the initial reaction rate at a 20-min reaction was shown in Fig. 1. It can be seen that the initial reaction rate increases with increasing temperature. The higher the temperature causes the molecules to move faster and the kinetic energy of the molecules to increase. Thus, collisions between reactant molecules also increase, resulting in a faster reaction [17]. In addition, the initial free fatty acid concentration also affects the initial reaction rate, which the higher the initial free fatty acid concentration causes the reaction rate to increase [13]. The initial fatty acid concentration was directly affected by the molar ratio of methanol to oil. The less volume of methanol in the system while the amount of catalyst and fatty acids were constant; hence the total volume decreased, and the concentration of free fatty acids and catalysts in the reaction system increased. The increasing concentration of free fatty acids and catalysts causes the probability of collision between fatty acids and the catalyst. As a result, the activated complex catalyst-reactant would be formed faster, increasing the reaction rate.

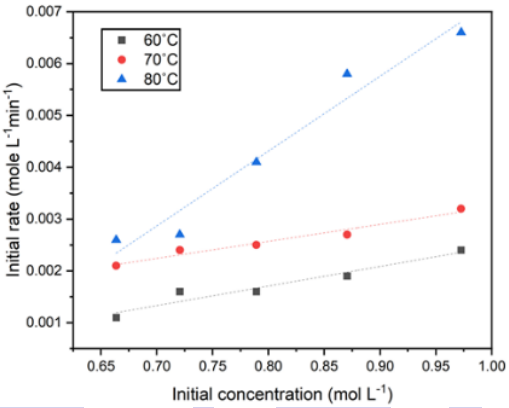

Fig. 1. Effect of temperature and methanol to FFA molar ratio over the initial rate of esterification at catalyst weight of 2 g and SPO weight of 25 g

Effect of Temperature on the Reaction Rate Constant. The effect of temperature on the reaction rate constant with three replicates measurement was shown in Table 1. Table 1 shows that as the temperature increases, the average value of the forward rate constant (k_1) is greater than the backward rate constant (k_2), indicating a tendency to form product more quickly and in large quantities than in the opposite direction. According to Hidayat et al. [13], the reaction temperature is not only positively correlated to the reaction rate of the forward reaction but represses the reverse reaction either. Table 1 also shows that at a temperature of 80 °C, the rate constant value was quite large compared to other temperatures. The higher the reaction temperature, the greater the reaction rate constant. Similar results have been reported by another study [17] associated with the increase in kinetic energy. Thus more collisions between reactant molecules occurred and correlated to the increase of rate constant.

Table 1. Effect of temperature on the reaction rate constant

T (°C)	k_1	k_2
60	0.0030	0.0013
70	0.0049	0.0015
80	0.0056	0.0018

Determination of Arrhenius Constant, Activation Energy, and Enthalpy of Esterification. Determining the activation energy for the forward reaction of esterification of free fatty acids from SPO was 30.65 kJ/mol, and the Arrhenius constant was 2.04×10^2. Such a high value of activation

energy indicates that the reaction is sensitive to temperature and confirms that the reaction is kinetically controlled [22]. The value of activation energy was relatively consistent with another study [18]. Meanwhile, the activation energy for the backward reaction was 15.8714 kJ/mol, and the Arrhenius constant was 2.502. The results of this study are accurate because the coefficients of determination for the forward and backward reactions are 0.9114 and 0.9926, respectively. The low activation energy indicates that the reaction rate decreases with increasing reaction temperature. Therefore, it can be stated that the reactant molecules must have a minimum energy value of the respective activation energy for the forward reaction or the activation energy for the reverse reaction to form an ester product. The value of the molecular fraction is shown in Table 2.

Table 2. The molecular fraction at different temperature

T (°C)	T (K)	f ($e^{-Ea/RT}$)
60	333	-5.733
70	343	-5.566
80	353	-5.408

According to Table 2, increasing the temperature increases the molecular fraction. The larger the molecular fraction of a reactant, the greater the probability that molecule interacts to form products. Meanwhile, the value of the enthalpy energy for the esterification reaction was 14.7823 kJ/mol. If the enthalpy energy for the esterification reaction is positive, the reaction between free fatty acids and methanol is endothermic. According to Le Chatelier's principle, if the temperature is increased, the equilibrium will shift to the side of the reaction that absorbs heat (endothermic). Similar results have been reported by another study [19]. According to Jyoti et al. [20], reversible reactions in which the forward reaction was endothermic (absorbs heat to occur), the forward reaction would be preferred. Therefore, increasing the temperature for an endothermic reaction favors product formation.

Kinetic Model Validation. The validation of the kinetic model was carried out to see the suitability between free fatty acids reduction obtained from the experimental results and predicted value from the mathematical model. The data can be considered valid if the determination coefficient value is close to 1.0 [8]. Fig. 2 Shows the correlation between the experimental and predicted value from the mathematical model of FFA reduction.

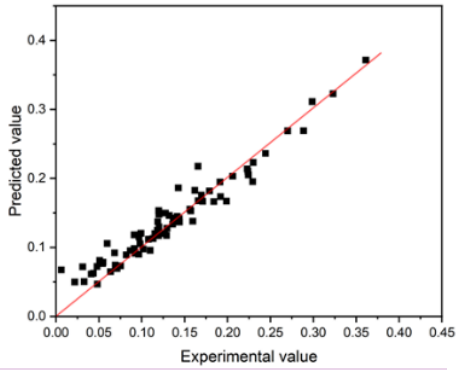

Fig. 2. Correlation between the experimental value and predicted value of FFA reduction

From the regression equation, the determination coefficient obtained was 0.9612. This indicates a match between the decrease in the value of free fatty acids from the experimental results and the mathematical model. Thus, the kinetic model can well predict the reduction of free fatty acids.

Conclusions

From the research, the rate of fatty acid esterification reaction generally increases with increased temperature and initial fatty acid concentration. The forward rate constant (k_1) was relatively greater

than the backward rate constant (k_2), along with the increased temperature rate and methanol to oil mole ratio. Furthermore, the value of activation energy and Arrhenius constant for the reactions in the product were 30.6537 kJ/mol and 2.04×10^2, respectively. Meanwhile, the reactions in the opposite direction were 15.8714 kJ/mol and 2.502, respectively. The esterification reaction of free fatty acids from CPO sludge was endothermic with a reaction enthalpy value of 14.7823 kJ/mol. Validation data shows that the kinetic equation model can be accepted for calculating free fatty acid esterification of SPO kinetic with a determination coefficient of 0.9612.

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