

# Reduction of FFA in Kapok Randu (*Ceiba pentandra*) Seed Oil via Esterification Reaction Using Sulfuric Acid Catalyst: Experimental and Kinetics Study

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Article Info	Abstract
Article history: Received May 2019 Accepted August 2019 Published December 2019 Keywords : Biodiesel; Methanol; Kapok randu seed oil; Free fatty acid	The rapid growth of the population and economy has boosted up the necessity of fuel and energy source. Until now, the world's dependency on fossil fuel as the primary energy supply is still high. On the other hand, it has been known that the fossil-based oil and gas reserves are shrunk. Hence, it is urgent to develop alternative energy sources, which are renewable and environmentally friendly, to anticipate the energy insufficiency. Biodiesel is among the prospective renewable energy due to its advantages. Biodiesel (fatty acid methyl esters) is a type of biofuel which is derived from vegetable oil or animal fat. There are various vegetable oils that can be used as raw material for biodiesel production. However, non-edible oils are usually preferred to be selected as a biodiesel feedstock to evade the conflict between food and energy needs. Kapok Randu ( <i>Ceiba pentandra</i> ) seed oil is a type of non-edible oil which is cheap and can be employed as biodiesel feedstock. However, this oil has high free fatty acid (FFA) content (8.89%). Thus, it cannot directly undergo transesterification reaction to produce biodiesel since the FFA will react with alkaline catalyst to produce soap. The FFA content in Kapok Randu seed oil needs to be decreased until it is lower than 2%. Hence, prior to transesterification reaction of Kapok Randu seed oil with methanol in the presence of acid catalyst should be conducted to decrease the FFA content. In this work, esterification reaction was performed in the presence of sulfuric acid catalyst. The reactions were conducted at the molar ratio of oil to methanol of 1:12 at the temperature of 40, 50, and 60 °C for 120 minutes. The optimum reaction conversion was 95.14%, achieved at the reaction temperature of 60 °C. Kinetics study using homogeneous models was also performed. It was revealed that the reaction was appropriate with the irreversible second order reaction model. The reaction rate constant (k), activation energy (Ea), and frequency factor (A) were 4.95 L / mole.min, 30,799.21 J/

## INTRODUCTION

The energy need for transportation, industries, and daily life in most countries in the world are mainly supplied by the fossil fuel at this time. However, fossil fuel is a type of nonrenewable energy which is indicated to diminish before long. Besides, the fossil fuel combustion also significantly contributes to the carbon dioxide emission to the atmosphere, causing global warming and climate change. As alternative, biodiesel is an attractive substitute to fossil fuel since it is renewable, harmless, safe, and biodegradable. In addition, it has high energy content, high cetane number, and its properties are similar to petro-diesel (Ong et al., 2013).

Biodiesel can be simply synthesized through several technologies. The most applied

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method is the alkaline transesterification of vegetable oil to produce methyl ester (biodiesel). However, biodiesel production faces a challenge related to production cost which is considerably higher than that of the petro-diesel. In addition, the most usual vegetable oil utilized as raw material for biodiesel production in Indonesia is crude palm oil, which is also important edible oil for food needs. As a response to those issues, it is crucial to employ non-edible oils as biodiesel feedstock, which are more economical than edible oil and undesirable for food.

There are various Indonesian non-edible oils which are potential to be used as biodiesel raw material such as nyamplung (Calophyllum inophyllum) seed oil, used frying oil, rubber seed oil, castor oil, rice bran, and kapok (Ceiba pentandra) seed oil (Handayani et al., 2018; Folaranmi, 2013; Demirbas et al., 2016; Ulfah et al., 2018; Suryanto et al., 2018). Kapok (Ceiba pentandra) seed oil is among the prospective non edible oil for biodiesel synthesis. The area of kapok plantation in Indonesia is 250.500 hectare (Pratiwi, 2014). The main product of kapok plantation is cotton fiber and among the main waste is kapok seed. Kapok seed waste was found abundantly since each kapok fruit log contains 26% seed. Hence, 100 kg kapok fruit will result in 26 kg kapok seed waste. Kapok seed has high content of oil, i.e. 24-40%, which has not been optimally used for industrial purpose (Pertanian, 2015). Kapok seed oil is a type of non-edible oil. This oil contains unsaturated fatty acid of 71.95%, which is considered very high and causes rancidity (Nurlis et al., 2017). It also has high free fatty acid (FFA) which makes this oil unsuitable for fulfilling the food necessity. Thus, kapok seed oil can be processed to produce biodiesel (Ong et al., 2013).

Kapok seed oil is a FFA-rich oil, with the FFA content over than 2% (Silitonga et al., 2014). Since this oil contains more than 2% FFA, it cannot directly undergo transesterification reaction since the FFA will react with the base catalyst to produce soap, decreasing the biodiesel yield. Hence, for the high FFA kapok seed oil, the pretreatment process is crucial to lessen the FFA content in advance of the transesterification reaction. Reducing the FFA content can be conducted via several methods such as esterification of acid catalyzed FFA using methanol, neutralization of FFA using sodium carbonate. In this work, the FFA removal in kapok seed oil was conducted through the esterification of FFA with methanol in the presence of sulfuric acid catalyst. In this work, the experimental and kinetics study of FFA esterification were performed.

Many researches related to the conversion of kapok seed oil into biodiesel have been found (Vedharaj et al., 2013; Rashid et al., 2014; Bokhari et al., 2015; Silitonga et al., 2020). However, the kinetics study of the FFA esterification of kapok seed oil in the presence of sulfuric acid catalyst has not been reported yet. Thus, the result of this work will provide information about the kinetic study which is principally required for the industrial process design.

## EXPERIMENTAL

## Materials

Materials used in this research were: crude kapok seed oil from Pati (Central Java, Indonesia), which, after degumming process, has density, viscosity, acid value, acidity, and molecular weight of 0.941 g/mL, 35.36 cSt., 17.82 mg KOH/ g oil, 8.89%, and 854.4037 g/gmol (based on the Gas Chromatography-Mass Spectroscopy analysis on fatty acid composition of kapok seed oil), respectively; methanol (99.99% p.a. form Merck (Germany); potassium hydroxide (analytical grade form Merck (Germany); phenolphthalein from Merck (Germany); and oxalic acid from Merck (Germany).

# Methods

# Esterification Reaction of Free Fatty Acid in Kapok Seed Oil

Prior to the esterification process, crude kapok seed oil was degummed using 0.3% w/w  $H_3PO_4$  at 70°C using batch reactor to remove the gum contained in the feed-stock (Paisan et al., 2017). The degummed kapok seed oil was then heated at 105°C to decrease the water content. After the pre-treatment process, refined kapok seed oil was esterified in stirred batch reactor to reduce the free fatty acid (FFA) content in the oil. Esterification reaction was performed using methanol in the presence of 0.5% w/ w oil sulfuric acid catalyst at the temperature of 40, 50, and 60 °C in 120 minute reaction time. Agitation speed and molar ratio of kapok seed oil to methanol were maintained at 1000 rpm and 1:12, respectively.

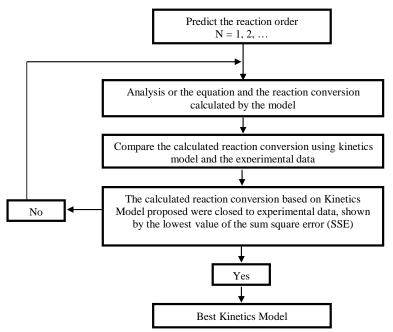


Figure 1. Algorithm to determine the best kinetics model for the reaction.

Samples of the reaction mixture were withdrawn periodically every 10 minutes to determine the acidity by using standard AOCS acid-alkaline titration method. Based on the value of acidity, the reaction conversion can be found out (Banchero & Gozzelino, 2018).

#### **Kinetics Study**

Three homogeneous kinetics models were proposed in this work i.e. Model 1, 2, and 3 as depicted in the Equation 1, 2, and 3, respectively (Kusumaningtyas et al., 2014). Simulation for homogeneous kinetics model determination was performed using Polymath 6.1 software. The best kinetics model of this esterification reaction was selected through the following algorithm (Figure 1).

### **RESULTS AND DISCUSSION**

Crude kapok seed oil was used as raw material for biodiesel production in this work. Fatty acid composition of kapok seed oil after being treated was similar to that of the previous work (Kusumaningtyas et al., 2020). The most dominant fatty acids found were linoleic acid and palmitic acid. This composition is in accordance with the crude kapok seed oil fatty acid composition reported by Silitonga et al. (2020). In advance of the main transesterification reaction, several pre-treatment processes were necessarily carried out, viz. degumming using phosphoric acid to reduce gum, water content removal by heating process, and esterification reaction to reduce the content of FFA (Dharma et al., 2016).

This research focused on determining the effects of main variables on the FFA reduction and kinetics study of the FFA esterification in kapok seed oil using sulfuric acid catalyst. Sulfuric acid is a classical and most common homogeneous catalyst for the esterification reaction which can significantly decrease the amount of FFA in vegetable oils (Marchetti & Errazu, 2008]. The esterification reaction of FFA in kapok seed oil with methanol was operated in the presence of 0.5% w/ w oil sulfuric acid catalyst, agitation speed of 1000 rpm, and molar ratio of kapok seed oil to methanol of 1:12 (Usman et al., 2019). The effect of reaction temperature was evaluated at 40, 50, and 60 °C. The reaction was conducted in 120 minute. To study the influence of reaction time, samples were taken regularly every 10 minutes. Kinetics study of the FFA esterification using homogeneous model was also examined in this work.

### Effects of Reaction Time and Temperature

It is depicted in Figure 2 that the esterification reaction will reduce the FFA content in the oil. The FFA content decreased with the reaction time. However, the rapid reduction happened in the initial reaction until 60 minutes. It

means that the fastest reaction rate occurred in the beginning of the reaction. The highest FFA reduction was obtained at the reaction temperature of 60°C at 120 minute reaction with the final FFA content of 0.44%. This FFA content fulfills the limit of maximum content of FFA in the vegetable oil feed-stock to proceeds transesterification reaction (2%). The result has shown that sulfuric acid is an effective catalyst which brought about high conversion in esterification reaction (Nurhayati et al., 2017). This catalyst acts to speed up the reaction as well as dehydrate the reaction system, shifting the equilibrium toward product formation.

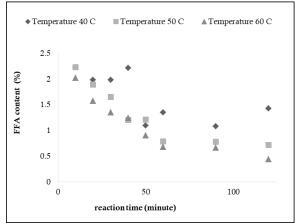


Figure 2. The influence of reaction time and temperature on the free fatty acid (FFA) content.

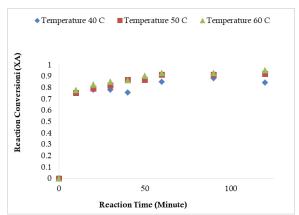


Figure 3. The influence of reaction time and temperature on the free fatty acid (FFA) conversion.

Figure 3 demonstrates that the higher the reaction temperature, the higher rate of the reaction. It came about since the higher reaction temperature will direct to the higher speed of molecular motion, resulting in the increasing of kinetic energy. This condition leads to the higher

reaction conversion (Ofoefule et al., 2019). It also implied that the reaction is endothermic, in which the conversion increased with the rise of the temperature (Marchetti & Errazu, 2008).

The optimum FFA conversion was 95.14%, achieved at the reaction temperature of 60°C in 120 minutes reaction time. This result was in line with the data reported by Mueanmas (2019). It was also described that the reaction rate started faster at the higher reaction temperature as indicated by the Arrhenius Law. The equation demonstrated that the rate constant is a function of the exponent of (- $E_a/RT$ ). It denotes that the higher temperature leads to the higher reaction rate constant, and accordingly accelerates the reaction rate to a great extent. Hence, 60°C was considered as the optimum temperature of the kapok seed oil esterification with methanol employing sulfuric acid catalyst.

## Kinetics of FFA Esterification in Kapok Seed Oil: Model Development

The esterification reaction of FFA can be written as shown in Eq. (1).

$$RCOOH + CH_3OH \stackrel{k_1}{\underset{k_2}{\rightleftharpoons}} R'COOR + H_2O \qquad (1)$$

In which,	
RCOOH	= FFA
CH <sub>3</sub> OH	= Methanol
R'COOR	= Methyl Ester
$H_2O$	= Water

Three types of pseudo-homogeneous kinetics model were proposed in this work, i.e. irreversible first order, irreversible second-order, and reversible second order reactions. To develop the kinetics model, Eq. (1) is simplified to Eq. (2).

$$A + B \stackrel{k_1}{\rightleftharpoons} C + D \qquad (2)$$
$$k_2$$

In which

A = Fatty Acid B = Methanol C = Methyl Ester D = Water

Reaction rate equation can be written as shown in Eq. (3).

$$(-r_A) = -\frac{dC_A}{dt} = k_1[A][B] - k_2[C][D]$$
(3)

Where,

- $-r_A = Rate of the reduction of A concentration$
- [A] = Concentration of fatty acid
- [B] = Concentration of methanol
- [C] = Concentration of methyl ester
- [D] = Concentration of water
- k<sub>1</sub> = Reaction rate constant towards product formation
- $k_2$  = Reaction rate constant towards reactant formation

t= reaction time

Basically, esterification reaction is a slow reversible reaction. However, when far excess alcohol is applied, alcohol can be considered constant. Far excess reactant will shift equilibrium towards product formation, means that the reaction to the left side is neglected. This assumption is relevant to the development of irreversible reaction kinetic models (order 1 and 2). Based on this assumption, the reaction rate can be reformulated to Eq. (4). After the reaction takes place for t minute, then it can be written as follows:

$$-r_{\rm A} = -\frac{\mathrm{d}C_{\rm A}}{\mathrm{d}t} = \mathrm{k}C_{\rm A}^{\alpha} \tag{4}$$

In which,  $C_{Ao}$  is the initial concentration,  $X_A$  is the FFA conversion, and  $\alpha$  is the reaction order.

System is taken into account to have constant density. Hence, it is assumed that there is no volume changing in the system. For the kinetics model evaluation, reaction conversion of FFA  $(X_A)$  is often used as the parameter of concentration of FFA. Correlation between reaction conversion and concentration is described in the Eqs. (5) and (6).

$$C_{A} = \frac{N_{A}}{v} = \frac{N_{Ao}(1 - X_{A})}{v} = C_{Ao}(1 - X_{A})$$
 (5)

$$-dC_{A} = C_{Ao}dX_{A}$$
(6)

Correlating Eqs. (5) and (6) with Eq. (4) will result in kinetics equation as shown in Eq. (7).

$$C_{Ao} \frac{dX_{A}}{dt} = kC^{\alpha}_{Ao}(1 - X_{A})^{\alpha}$$
(7)

Rearrangement of Eq. (7) will generate Eq. (8).

$$\frac{\mathrm{dX}_{\mathrm{A}}}{\mathrm{dt}} = \mathrm{kC}_{\mathrm{Ao}}^{\alpha-1} (1 - \mathrm{X}_{\mathrm{A}})^{\alpha} \tag{8}$$

Eq. (8) is applicable for irreversible reaction model, in which  $\alpha$  is the order of reaction. In this study, Eq. (8) was derived into Model 1 and Model 2.

**Model 1** is the irreversible first order reaction kinetic model in which  $\alpha = 1$ . For  $\alpha = 1$ , Eq. (8) can be rearranged to Eq. (9).

$$\frac{\mathrm{dX}_{\mathrm{A}}}{\mathrm{dt}} = \mathbf{k}(1 - \mathbf{X}_{\mathrm{A}}) \tag{9}$$

By using differential solution, Eq. (9) can be changed to Eqs. (10) and (11).

$$\frac{\mathrm{dX}_{\mathrm{A}}}{(1-\mathrm{X}_{\mathrm{A}})} = \mathrm{kdt} \tag{10}$$

$$-\ln(1 - X_A) = kt \tag{11}$$

 $C_A$  is the FFA concentration (mol/L), t is reaction time (minute),  $X_A$  is reaction conversion, and k is reaction rate constant (1/minute). Eq. xx is a linear equation. Thus, the value of k in first order reaction is identical to the value of slope of the linear correlation between  $-ln(1-X_A)$  as y axis and time (minute) as x axis.

**Model 2** is the irreversible second order kinetics model, in which  $\alpha$ = 2. If  $\alpha$ = 2, then Eq. (8) becomes Eq. (12).

$$\frac{dX_{A}}{dt} = kC_{A0}(1 - X_{A})^{2}$$
(12)

By using differential solution, Eq. (12) can be turned into Eqs. (13) and (14).

$$\frac{dX_{A}}{(1-X_{A})^{2}} = kC_{Ao}dt$$
 (13)

$$\frac{X_{A}}{(1-X_{A})} = C_{Ao}kt$$
(14)

 $C_A$  is the FFA concentration (mole/L), t is reaction time (minute),  $X_A$  is reaction conversion, and k is reaction rate constant (L/mol. minute). Eq. 14 is a linear equation with  $\frac{X_A}{1-X_A}$  as y axis and t (minute) as x axis, in which the slope is the result of multiplying FFA initial concentration  $C_{Ao}$  with reaction rate constant (k).

As the comparison to the irreversible reaction model, the reversible reaction kinetics model was also evaluated (Model 3).

**Model 3** is reversible second order reaction kinetics model. This model can be applied when the reaction rates towards product and reactant formation are both taken into account. This model refers to that developed by Alenezi et al. (2010) as written in Eq. (15).

$$\frac{dx}{dt} = k_1 \left( \left( \frac{M}{1} \right) - x \right) (1 - x) - k_2(x) (D_o + x)$$
(15)

Where, M/1 is the molar ratio of methanol to FFA, and Do is the mole water per mole FFA in the feed and t is reaction time.

The appropriate kinetic model will present the highest value of determination coefficient  $(R^2)$ on the graph of each model. The closest value of  $R^2$  to 1 indicates that the kinetic model is the most suitable. Furthermore, the method for determining the kinetics model is the data integralistic method. The data of acidity obtained in the sample analysis was converted to reaction conversion and used for data fitting of each kinetics model. Based on the calculation algorithm, the best kinetics model is the model providing the lowest value of sum square error (SSE). SSE is the quadratic difference of square the value of observation (experimental data) and the calculation value. SSE can be used to measure variation in a group. In determining the reaction kinetics, the reaction kinetics models were tested using the sum square error method to determine the proximity between the calculation value and the experimental data. The lowest SSE value shows the model providing the calculation results which are in accordance with the experimental data. SSE can be formulated as shown in Eq. (16).

$$SSE = \sum_{i=1}^{n} (X_e - X_m)^2$$
 (16)

Where,  $X_e$  is the reaction conversion obtained by experiment (experimental data) and  $X_m$  is the reaction conversion obtained by calculation using the kinetics model proposed

Once the best kinetics model has been determined, the reaction kinetics parameters (activation energy and frequency factor) can be revealed. The value of activation energy (Ea) and frequency factor (A) are determined initially by calculating the value of reaction rate constants (k) at several different temperatures. Correlation of reaction rate constants (k), temperature (T), activation energy (Ea), and frequency factor (A) were demonstrated by the Arrhenius equation as shown in Eq. (17).

$$k = A \exp \frac{-Ea}{RT}$$
(17)

Eq. (17) can be modified to Eq. (18).

$$\ln k = \ln A - \frac{Ea}{RT} \tag{18}$$

Eq. (17) shows the linear correlation between ln(k) as y axis and 1/T as x axis. Slope on the Eq. xx is the division result of activation energy (Ea) and the gas constant (R). On the other hand, the intercept of Eq. xx is the natural logarithm of frequency factor (A).

### **Determination of Best Kinetics Model**

The selection of the appropriate kinetics model was conducted by comparing the calculated reaction conversion of each model with the experimental data as depicted in the algorithm (Figure 1). The selected kinetics model is the model which best fit the experimental data.

### Model 1: Irreversible First Order Reaction

To observe suitability Model 1 to the experimental data of reaction, the value of  $(-\ln(1-X_A))$  and time (minute) resulted from the experiment and model calculation are plotted in Figure 4.

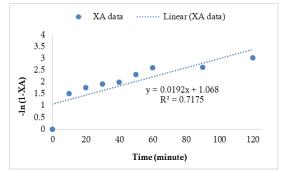


Figure 4. Comparison of Model Calculation and Experimental Data for Irreversible First Order Kinetics Model.

Based on the plotting in Figure 4, it was found that the slope value is 0.0192. In this case,

the value of slope is the value of reaction rate constant (k). Therefore, k value for irreversible first order reaction model was 0.0192/minute. To determine the SSE value of the model, comparison of calculated reaction conversion based on Model 1 and the experimental data is exhibited in Figure 5.

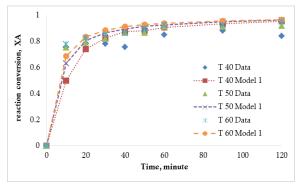


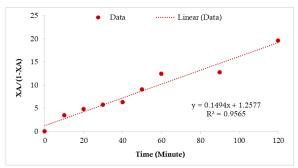
Figure 5. Comparison of Model Calculation and Experimental Data for Irreversible First Order Kinetics Model.

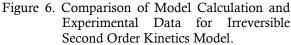
#### Model 2: Irreversible Second Order Reaction

The second model proposed is second order reaction kinetic model. Second order reaction can occur as irreversible or reversible reaction. In this work, far excess methanol was applied on the FFA esterification in kapok seed oil. It can be stated that the reactant concentration was considerably higher that the product concentration. Based on Le Chatelier principle, reaction equilibrium will shift from the high concentration to the low concentration. Therefore, employing great excess of methanol as reactant will lead the higher product formation [cc]. Therefore, Model 2 is the irreversible second order reaction kinetics model.

Recalling Eq. 13, this equation is a linear equation with  $\frac{X_A}{1-X_A}$  as y axis and reaction time as x axis. Plotting this line resulted in slope which the value is identical to the multiplication of C<sub>Ao</sub> with k as revealed in Figure 6

Based on the linear equation in Figure 6, it was found that the value of slope was 0.1494. On the other hand, sample analysis indicated that initial concentration of kapok seed oil was 0.2989 M. Therefore, the value of reaction rate constant (k) was 0.4998 L/mol. minute. Furthermore, comparison of reaction conversion calculated based on the kinetic model 2 with the experimental data is displayed in Figure 7.





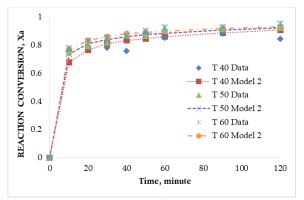


Figure 7. Comparison of Calculated Reaction Conversion Based on Model 2 (Irreversible Second Order Kinetics Model) to the Experimental Data at Different Reaction Temperatures.

### Model 3: Reversible Second Order Reaction

The third model (Model 3) proposed was reversible second order reaction as presented in Eq. 14. To solve the equation, simulation using Polimath 6.1 software has been conducted. The inputed data for the simulation was the reaction conversion (X<sub>A</sub>) and the derivative of reaction conversion (XA) with respect to time (t) or  $(\frac{dX_A}{dt})$ . Data tabulation for Polymath simulation is shown in Table 1.

Table 1.	Data Inpu	itted for	Polymath	Simulation.
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Time (Minute)	Conversion (X <sub>A</sub> )	dx/dt
0	0	0
10	0.7772	0.0777
20	0.8267	0.0413
30	0.8507	0.0283
40	0.8631	0.0215
50	0.9004	0.0180
60	0.9253	0.0154
90	0.9271	0.0103
120	0.9514	0.0079

Table 2.	The Value of SSE and Reaction Constants of Each Model for the Reaction Conducted at 40°C,
	50°C, and 60°C with fixed molar ration of oil and methanol of 1:12 and catalyst concentration of
	0.5%.

Model	Temperature (°C)	<b>k</b> <sub>1</sub>	<b>k</b> <sub>2</sub>	SSE
First Order Model	40	1.50 x 10 <sup>-2</sup>	-	0.10033
(Model 1)	50	2.05 x 10 <sup>-2</sup>	-	0.02367
	60	1.48 x 10 <sup>-2</sup>	-	0.01401
Reversible Second Order Model	40	2.435	-	0.01849
(Model 2)	50	3.651	-	0.00215
	60	4.950	-	0.00183
Reversible Second Order Model	40	2.09 x 10 <sup>-2</sup>	2.57 x 10 <sup>-2</sup>	0.07722
(Model 3)	50	2.57 x 10 <sup>-2</sup>	1.99 x 10 <sup>-2</sup>	0.02710
	60	2.95 x 10 <sup>-2</sup>	1.62 x 10 <sup>-2</sup>	0.01615

Based in the simulation, the value of reaction constant towards the product formation  $(k_1)$  and the reaction constant toward reactant formation  $(k_2)$ . Comparison between the calculated reaction conversion resulted from the simulation of Model 3 and the experimental data is demonstrated in Figure 8.

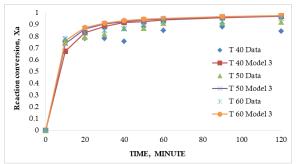


Figure 8. Comparison of Calculated Reaction Conversion Based on Model 3 (Reversible Second Order Kinetics Model) to the Experimental Data at Different Reaction Temperatures.

The appropriate kinetics model is the model providing the lowest Sum Square of Error (SSE) value. The low SSE value indicates the suitability between the calculation provided by the model simulation and the experimental data. Based on the model calculation, the value of reaction constants and SSE for Model 1, 2, and 3 is revealed in Table 2 for the reaction conducted at 40°C, 50°C and 60°C with fixed molar ration of oil and methanol of 1:12 and catalyst concentration of 0.5%. Comparison of calculated reaction

conversion based on Model 1, 2, and 3 with the experimental data at the reaction temperature of  $60^{\circ}$ C is exhibited in Figure 9.

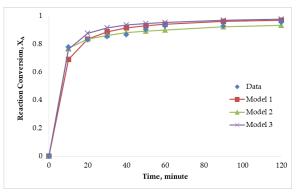


Figure 9. Comparison between the Calculation based on Model 1, 2, 3, and the Experimental Data at the Reaction Temperature of 60°C.

Correlation between the calculated reaction conversion based on Model 1, 2, 3, and experimental data at the reaction temperature of 60°C is demonstrated in Figure 9. Based on the result in Table 2 and Figure 9, it could be concluded that the most appropriate model is Model 2. Model 2 has the lower SSE value and the highest proximity between the calculated result and the experimental data. Therefore, Model 2 was selected for the determination of kinetics constants of this reaction. The other reaction kinetics parameters i.e. activation energy (Ea) and the frequency factor (A) were revealed by using Model Kinetics 2.

## Determination of Frequency Factor and Activation Energy Model

Frequent factor (A) and activation energy (Ea) values were found out using standard Arrhenius equation (Eq. (17)). Furthermore, the values of reaction rate constants at different temperatures based on Kinetics Model 2 are presented in Table 3.

Table 3.	Reaction	Rate	Constants	at	Different
	Temperat	ures Ba	ased on Kin	etic	s Model 2

Temperature	Temperature	k
(°C)	(K)	(L/mole.min)
40	313.15	2.435
50	323.15	3.651
60	333.15	4.950

The initial step to reveal frequent factor (A) and activation energy (Ea) values is modifying Arrhenius equation to linear equation as written in Eq. (18), which represents the linear correlation between ln (k) as y ordinate and I/T as x abcis. Slope in Eq. 18 is the natural logarithmic of A. On the other hand, intercept of Eq. (18) is the result of Ea divided by ideal gas constant (R). Correlation of ln (k) and 1/T is shown in Figure 10.

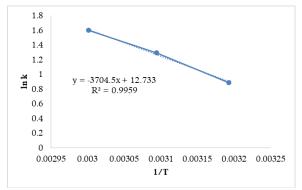


Figure 10. Correlation of ln k and 1/T values for Model 2.

Plotting of ln (k) and 1/T resulted in linear equation as shown in Eq. (19).

 $y = -3704.5x + 12.733 \tag{19}$ 

Eq. (18) was utilized to determine the values of A and Ea. It was found that the esterification of FFA in kapok seed oil with methanol in the presence of 0.5% w/w sulfuric acid catalyst, at molar ratio of oil and methanol of 1:12 has frequent factor (A) and activation energy (Ea) values of 338.744 min<sup>-1</sup> and 30,799.21

J/mole, respectively. The activation energy discovered in this work was in the similar order of magnitude compared to fatty acid esterification employing sulfuric acid catalyst (Neumann et al., 2016; Jansri et al., 2011). However, the Ea obtained in this work was much higher than the fatty acid esterification reaction catalyzed by ionic liquid (Roman et al., 2019).

# CONCLUSION

Based on the experimental work, it can be concluded that the temperature and reaction time were the significant factors influencing the conversion of FFA to methyl esters. The higher temperature and the longer reaction time will enhance the reaction rate and FFA conversion. The best conversion was 95.14%, achieved at the reaction time of 120 minutes at the temperature of 60°C. At this condition, FFA content could be reduced up to 0.44%, which fulfilled the maximum limit of 2%. The kinetics study revealed that the kinetics model that fits the FFA esterification in kapok seed oil using methanol in the presence of sulfuric acid catalyst is homogeneous irreversible second-order kinetic model. Based on the kinetics study, it was found that the esterification of FFA in kapok seed oil with methanol in the presence of 0.5% w/w sulfuric acid catalyst has reaction constant (k) of 4.95 L/mole.min, with the activation energy (Ea) and frequency factor  $(A_1)$  of 30,799.21 J/ mole and 338,744 /min, respectively.

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