Esterification of Waste Cooking Oil Using Ultrasonic: Kinetic Study

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Abstract
Waste cooking oil (WCO) have great potential as an alternative raw material for producing biodiesel. The literature on the kinetics of the ultrasonic-assisted esterification of WCO in the presence of a phosphoric acid catalyst are rare, and most literature used conventional method. This study aims to determine the optimum condition and the parameters of first and second order kinetics of the WCO esterification which was assisted by an ultrasonic bath. Variables that were used in this study are methanol/oil mole ratio, acid catalyst concentration, and reaction temperature. The highest conversion was 42.08% on the methanol/oil mole ratio of 15:1, a catalyst (phosphoric acid) concentration of 9% wt, and temperature of 50°C within 90 minutes. The reaction time was reduced to three times (minute) compared to the conventional method, and fatty acid was reduced by 42%. Kinetic parameters were calculated with the assumption that the esterification was an irreversible reaction. The reaction rate constant was increasing with temperature. The activation energy of WCO esterification is 42.94 kJ/mol for first order reaction and 35.30 kJ/mol for second order reaction.

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1. INTRODUCTION
Waste cooking oil (WCO) is a household waste which is a significant problem and difficult to manage. WCO in the Jabodetabek area in the year 2006 was as much as 850.3 tons which pollute the water and soil every week [1]. Therefore, it is necessary to process waste as not to pollute in the environment. WCO has an excellent potential as an alternative raw material for producing biodiesel. Biodiesel is an alternative fuel that is environmentally friendly and can reduce emissions when compared to diesel fuel [2].

Biodiesel is produced through a transesterification reaction in which the reaction between ester compounds (palm oil/CPO) and alcohol (methanol/ethanol) compounds produces methyl esters (biodiesel) and glycerol. However, if the content of free fatty acids (FFA) is high, it requires an esterification process because the high content of free fatty acids may results in the formation of soap (saponification) and makes it difficult to separate glycerol, which reduce the biodiesel quality. The chemical reaction in this study was an esterification reaction between carboxylic acid and alcohol with the help of an acid catalyst. It produced methyl esters and water as shown in Fig. 1. WCO has a free fatty acid content of > 1%, so that waste cooking oil needs to go through the esterification process first to decrease the free fatty acids content [2].
Fig. 1. Mechanism of an esterification reaction

Many researchers are exploring for an alternative methods to replace conventional methods [1-6]. The alternative method for biodiesel process are ultrasonic, and microwave [2]. These methods can both decrease reaction time and increase product purity [3]. In case of ultrasonic method that was utilized in this study, it can accelerates the FFA esterification by increasing mass transfer due to acoustic cavitation [4]. Ultrasonic has been reported to be beneficial to a pseudo-homogeneous system [5]. The ultrasonic process has been known and applied in various chemical processes in several industries, and some new industries have even used it as an alternative to a very useful new process [6]. The production of biodiesel using ultrasonic have three types of transducer that are ultrasonic horn transducer, a push-pull ultrasonic transducer, and multiple transducers coupled with a water bath. The type of transducer that are used in this study is multiple transducers that are coupled with a water bath [2]. Therefore the ultrasonic method has great potential to be commercialized in biodiesel production.

According to Munns & Sullivan, phosphoric acid can be recovered. The recovery of phosphoric acid from wastewater produced by the separation can be reused for the fertilizer industry [15]. So this will be an advantage of phosphoric acid as sulphuric acid cannot be recovered.

Ultrasonic has three types of transducer that were ultrasonic horn transducer, a push-pull ultrasonic transducer, multiple transducers coupled with a water bath. The type of transducer used in this study is multiple transducers that are coupled with a water bath [2]. The production of biodiesel from WCO using ultrasonic tubular reactor compared to a conventional ultrasonic cleaner, and mechanical stirring was done. The reaction time was reduced to 12-24 times (minute) compare to mechanical stirring and the ester contents can be obtained at 96.54% wt [7]. The esterification process were investigated at the effect of molar ratio,
catalyst concentration, and temperature to fatty acid in the feed on the super phosphoric acid catalyzed the esterification of palm fatty acid distillate (PFAD) [8]. Phosphoric acid-catalyzed esterification by ultrasonic was rare because of many of them that used phosphoric acid as a catalyst using the conventional method. The objective of this study was to study the rate order of phosphoric acid-catalyzed esterification by ultrasonic and compare that with a conventional method.

Kinetic study on the esterification of FFAs in PFAD was also investigated and found that a methanol/FFA ratio of 9%, a catalyst (phosphoric acid) concentration of 9% and a temperature of 70°C provided a final acid value for the oil lower than 1 mg KOH/g oil within 300 min. They have proposed a model with first and second order irreversible kinetics [8].

The aim of this study were to determine the optimum condition and the parameters of first and second order kinetics of the waste cooking oil esterification which is assisted by ultrasonic wave. The variation used in this study is the molar ratio methanol:oil, catalyst concentration, sonication time and sonication temperature to determine the activation energy value.

2. EXPERIMENTAL SECTION

2.1. Materials

Waste cooking oil (WCO) was purchased from a local fish restaurant, Serpong city, Indonesia. Methanol, Potassium Hydroxide (KOH), Phosphoric Acid (H₃PO₄) 85%, Analytical Ethanol, Hydrochloric Acid (HCl) 25%, Phenolphthalein (PP) Indicator, and aquadest were purchased from E-Merck company, Indonesia.

The initial acid value of WCO was 4.17 mg KOH/g that means the WCO contains 97.9% triglycerides and remaining 2.1% is free fatty acids (FFA).

2.2. Methods

2.2.1. Experiment Procedure

Esterification of WCO was carried out with 100 grams of oil sample. The mixture of methanol and phosphoric acid catalyst for each molar ratio (ratio of methanol to oil samples) was added into WCO in an erlenmeyer flask then assisted by Branson Ultrasonic Cleaner 3510 with the power of 130 Watt and 20 kHz. The initial temperature was measured, and after the esterification process was completed, the final temperature of the sample was measured. The mixture of methyl esters was put into a separating funnel for one hour to obtain three separate layers. The bottom layer of phosphoric acid catalyst was removed and collected, the top layer of methanol is removed. The middle layer that is a mixture of methyl esters and triglyceride (TG) was collected and washed with hot distilled water to remove impurities contained in the product and then separated by a separating funnel. After that the sample was dried in an oven for one hour to ensure removal of the water, and followed by analysis of FFA and acid values. The variation used in this study was the molar ratio of methanol:oil with a variation of 9:1, 12:1, 15:1, catalyst concentration with a variation of 6 wt%, 9 wt%, 12 wt%, and reaction time from 15 to 45 minutes.

2.2.2. Analytical Method

a) Determination of Acid Value

Oil sample was weighed about two grams and mixed with 25 ml of 90 % ethanol in a 250 mL erlenmeyer flask. Then heated until the fatty acids dissolve then the solution is added with 2-3 drops of PP indicator and titrated with 0.1 N KOH until the color is changed to pink and does not change for 15 seconds[9]. The amount of KOH used for the titration is recorded to calculate the level of free fatty acids in eq.(1) and the acid number in eq.(2).

\[
\text{\% FFA} = \frac{V_{\text{KOH}} \times N_{\text{KOH}} \times \text{MR fatty acids}}{\text{mass of sample (gram)}} \times 10^{-1}
\]

\[
\text{Acid value (mgKOH/g)} = \frac{V_{\text{KOH}} \times N_{\text{KOH}} \times 56.1}{\text{mass of sample (g)}}
\]
Where $V$ is the volume of the KOH solution (mL), $N$ is the concentration of KOH solution (mol/L). FFA conversion ($X$) is calculated by eq.(3).

$$X = \frac{\text{initial } \% \text{ FFA} - \text{final } \% \text{ FFA}}{\text{initial } \% \text{ FFA}} \times 100\% \quad (3)$$

b) Determination of Density

An empty 5 ml pycnometer that has been cleaned is weighed, then record the weight of the empty pycnometer, after that the pycnometer is filled with oil samples until full, after that the pycnometer containing the oil sample is closed then wiped with tissue until dry then weighed and recorded the weight of the pycnometer containing the oil sample [9].

c) Determination of Fatty Acid

The fatty acid profile of waste cooking oil was determined by gas chromatography-mass spectrum of GC-MS Agilent/5977A Series with carrier gas: Helium, capillary column: DB 1 (30 mx 250 μm x 0.25 μm), ionizing type: EI (electron impact), gas speed: 40 ml/minute, temperature rise: 10°C/minute, final temperature: 250°C, initial temperature: 70°C, detector temperature: 250°C, injector temperature: 250°C, column pressure: 8.8085 psi, sample volume: 1 μl, and initial time: 1 minute. The FFA in WCO contains 24.72% of palmitic acid, 30.95% of 13-octadecenoic acid (oleic acid), and 8.68% of petroselinic acid (an isomer of oleic acid) [10].

2.3. Kinetic of Esterification

2.3.1. Determination of reaction order

Determination of the reaction order in this study uses the most optimum parameter conditions. The model in this study is the first order and second order kinetics that are irreversible. The reaction kinetics used in this reaction are pseudo-homogeneous, that the homogeneous condition of the reactant mixture is not entirely homogeneous. Reactants consisting of oil and alcohol are both immiscible. In the pseudo-homogeneous kinetic model, it is assumed that the oil will form small droplets due to ultrasonic waves so that droplets of oil and alcohol form a homogeneous mixture [2].

The pseudo-homogeneous kinetics model of the esterification reaction uses several assumptions that the reaction occurs begins with heterogeneous followed by pseudo-homogeneous where mass transfer and chemical reaction control the overall process kinetics. This assumption has been recognized by researchers[8]. The chemical reactions only occur in the oil phase and at $t = 0$, there is no FAME (fatty acid methyl ester) or FAME is assumed to be $t = 0$. Due to the excess of methanol and low product concentration can expect the reverse reactions to be negligible [2].

The first order reaction is shown in eq.(4)

$$\ln \frac{1}{(1-Xa)} = kt + C1$$

Where $Xa$ is the conversion of FFA, $k$ is reaction rate constant, $t$ is time, and $C1$ is the integration constant

The second order reaction is shown in eq.(5)

$$\frac{1}{[A0]}(1-Xa) = \frac{1}{[A0]} - kt$$

Where $Xa$ is the conversion of FFA, $k$ is reaction rate constant, $t$ is time, and $A0$ is the initial concentration of oil sample.

The reaction rate constant can be estimated from the slope and intercept of the linear dependence of $1/(1-Xa)$ versus time, respectively.

2.3.2. Estimation of thermodynamic parameters

Activation energy and frequency factor from the most optimum condition of esterification reaction with different temperature can be calculated by Arrhenius equation as shown in eq. (6):

$$k = A_e^{\frac{-Ea}{RT}}$$

where $k$ is reaction rate constant, $A$ is frequency factor, $Ea$ is activation energy
(kJ/mol), R is gas constant (8,314 J/mol.K), T is temperature (K)

Equation (6) is integrated becomes:

\[ \ln k = \ln A - \left( \frac{E_a}{R} \right) \frac{1}{T} \]  

(7)

By plotting \( \ln k \) as a function of \( y \) versus \( 1 / T \) as a function of \( x \) obtained value of \( E_a / R \) as the gradient of the equation graph with \( \ln A \) as an intercept. From the gradient and intercept values, the value of activation energy and frequency factor obtained respectively.

3. RESULT AND DISCUSSION

3.1. Effect of Catalyst Concentration

The effect of phosphoric acid catalyst concentration in this study uses three variations of concentration, namely 6, 9, and 12\%wt to oil. Fig. 2 shows that the higher the time, the greater the conversion of FFA because Ultrasonic accelerates the FFA esterification by increasing mass transfer due to acoustic cavitation[4]. In addition, the conversion of FFA also increased along with an increase in catalyst concentration at the molar ratio methanol to oil is 9:1. However, the increase in catalyst concentration does not increase the reduction of free fatty acids when followed by an increase in the molar ratio of methanol: oil. This is shown in Fig. 2 that FFA conversion at catalyst concentrations from 6\% - 9\% increases even further when compared to catalyst concentrations of 9\% - 12\% even though FFA conversion continues to increase up to 45 minutes. Metre & Nath (2015) examined the esterification reaction of palm fatty acid distillate (PFAD) with conventional methods also showed the effect of phosphoric acid concentration on the esterification reaction similar to the results of this study[8].

The effect of catalyst concentration in an ultrasonic system is related to the cavitation that produces intense local heating and high pressures with very short lifetimes, which have a much higher effect than elevating the temperature of the liquid media[11].

The use of an excess acid catalyst can cause dehydration of an alcohol to form ether and produce various byproducts. Therefore, acids are used as catalysts in small amounts to avoid various by-products[12]. Sulfuric acid and phosphoric acid can both cause dehydration of alcohol, but sulfuric acid has strong oxidizing properties which can oxidize alcohol to carbon dioxide and simultaneously be reduced by itself to sulfur oxide, sulfuric acid also reacts with alcohol to produce a lot of carbon and other side products [13]. This is an advantage of phosphoric acid which can minimize the formation of unwanted by-products in the esterification reaction process.

The water produced from reactant and dehydration side reactions has an adverse effect on the esterification reaction itself. Water can limit the thermodynamics of the reaction and reduce the performance of the catalyst because it binds strongly to the active ion H\(^{+}\) [2].

The presence of polar compounds due to the dehydration of alcohol from acidic catalysts such as H\(_2\)SO\(_4\) and H\(_3\)PO\(_4\) in large quantities can cause the ester transesterification reaction to being obstructed so it can reduce the reaction rates[14]. The effect to the interference that polar compounds to the reaction by competing for hydrogen ions, hindering the availability of these ions for catalysis. Considering the strong affinity that sulfuric acid has for water, it is likely that the acid will interact more strongly with water molecules than with alcohol molecules. Thus, if water is present in the feedstock or produced during the reaction, the water will preferentially bind to FFA, leading to a reversible type catalyst deactivation[8]. This is the weakness of sulfuric acid.

Optimization of variations in catalyst concentration in this study found is catalyst concentration of 9\% wt.
Fig. 2. The effect of phosphoric acid catalyst concentration on conversion of WCO at 15:1 molar ratio.

3.2. Effect of Molar Ratio of Methanol to Oil

Effect of molar ratio of methanol: oil in this study using three variations, 9:1, 12:1, and 15:1. Fig. 3 shows that the addition of methanol increases the conversion of WCO with the highest FFA conversion in the variation of the molar ratio is 15:1. This can be caused by one factor, namely excessive use of alcohol so that the reaction goes towards the product (methyl ester).

Fig. 3. The effect of molar ratio on the percent conversion of WCO at a catalyst concentration of 9% wt.

The esterification reaction is a reversible reaction so that the highest conversion can be achieved if it can minimize the back reaction. There are two ways to prevent the occurrence of a back reaction that is to remove water continuously and use one of the excess reactants, in this case, using methanol[12]. Continuous removal of water during the esterification reaction is not accessible due to water as a by-product dissolves in excess methanol.

Conversion of WCO depends on the amount of methanol used, in this study using excess methanol to ensure reaction to the product, but also contributing to the formation of 2 layers during the reaction so that it is easy to separate during decantation but if too much methanol can increase water content in commercial methanol and production costs[8]. This can be seen when decantation for 1 hour formed 3 layers, the top layer in the form of a mixture of methyl esters, methanol, and water, the middle layer in the form of a mixture of triglycerides and methyl esters, and the bottom layer in the form of a mixture of water and phosphoric acid.

The effect of the molar ratio in the ultrasonic system is related to the cavitation that produces intense local heating and high pressures with very short lifetimes[11].

An optimum of methanol ratio should be chosen on the foundation of general economics and the equilibrium conversion in the commercial biodiesel industries[16]. Optimization on variations in the molar ratio of methanol: oil by determining the concentration of phosphoric acid catalyst by 9% wt obtained at 15:1. This data is used further to discuss the kinetics of the esterification reaction in the first order and second order.

3.3. Kinetic of Esterification

3.3.1. Determination of reaction order

The esterification reaction kinetics in this study used the most optimum data, the molar ratio of methanol:oil 15:1, 9% wt phosphoric
acid catalyst concentration, reaction time 60 minutes, and temperature of 40-50°C. The kinetics of the esterification reaction in this study uses a pseudo-homogeneous and irreversible assumption, meaning that the homogeneous conditions of the reactant mixture are not entirely homogeneous. Reactants consisting of oil and alcohol are both immiscible.

Fig. 4 and 5 show the graphs that were obtained to determine first and second order kinetic reaction at 40 and 50°C. The results both of two figure is the same trendline from an integral approach. Base on data, increasing the temperature and also k value rises. These data were used to determine the Arrhenius activation energy and same reported from Budiman et al., higher temperature was increased the reaction rate due to factor heat on esterification reaction[2]. Fig. 4 showed that at first and second order at temperature 40°C it tends to the value of the degree of confidence (R^2) to approach the value of 1 is the first reaction order. Fig. 5 showed that at first and second order at temperature 50°C it tends to the value of the degree of confidence (R^2) to approach the value of 1 in the second reaction order. It can be concluded that WCO esterification reaction follows the homogeneous pseudo model equation of the second reaction order with the highest degree of confidence (R^2) at temperature 50°C.

Fig. 4. First (a) and Second (b) Order Kinetic Reaction at a temperature of 40°C

Fig. 5. First (a) and Second (b) Order Kinetic Reaction at a temperature of 50°C
3.3.2. Estimation of thermodynamic parameters

The equilibrium conversion of WCO into methyl ester via esterification depends on the reaction temperature. Arrhenius equation was used to study the effect of temperature on the specific reaction rate. Rate constant obtained from kinetics study at various temperatures were fitted with the Arrhenius equation. The plot of ln k as a function of a reciprocal temperature (1/T), the values of activation energy and frequency factor were obtained. Fig. 6 shows the variation of the rate constant for the forward desired reaction with temperature.

Based on Fig. 6 the value of frequency factor (A) in the second reaction order was 5,357,457 ml mol⁻¹ min⁻¹, and the activation energy was 35.40 kJ/mol. The frequency factor values of esterification for this study was considerably high indicating that the mass transfer of the reaction increased significantly due to ultrasonic irradiation. Table 1 shown the value of reaction rate constant, and activation energy from the different method of esterification. Metre and Nath reported that the activation energy of the phosphoric acid catalyzed of methyl ester from palm fatty acid distillate was 22384.4 kJ/mol although in the conventional method. The activation energy of the ultrasonic esterification process for WCO was lower than the conventional method which can be attributed to the high catalytic activity of the catalyst used in the present study that can significantly lower the activation energy. Also the effect of the cavitational mainly in terms of the intense levels of turbulence and mixing generated in the reactor contribute to the lowering of this apparent activation energy. The physical effects contribute to the intensification because of the generation of microemulsions between the two phases taking part in the reaction resulted in increasing the available interfacial area enormously and giving faster reaction rates [17].

The value of the collision frequency factor and the activation energy in the second reaction order can be substituted into equation 5 so that the following equation was generated:

\[
k = 5357457 \times \exp \left( \frac{-35.30}{R \cdot T} \right)
\]

**Table 1.** Comparison of the value of reaction rate constant and activation energy with the phosphoric acid catalyzed esterification.

<table>
<thead>
<tr>
<th></th>
<th>Ultrasonic Method (Present Study)</th>
<th>Conventional Method (8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (K)</td>
<td>323</td>
<td>323</td>
</tr>
<tr>
<td>Catalyst Type</td>
<td>H₃PO₄</td>
<td>H₃PO₄</td>
</tr>
<tr>
<td>Catalyst Con.</td>
<td>9%</td>
<td>9%</td>
</tr>
<tr>
<td>Molar Ratio</td>
<td>12:1</td>
<td>12:1</td>
</tr>
<tr>
<td>k (ml mol⁻¹ min⁻¹)</td>
<td>10.47</td>
<td>7.85</td>
</tr>
<tr>
<td>Ea (kJ/mol)</td>
<td>35.30</td>
<td>22384.4</td>
</tr>
</tbody>
</table>

Fig. 6. The Effect of Temperature on the specific reaction rate (Arrhenius equation) at second order.
Equation 6 can be substituted into the equation below to be the following equation:

\[
    r = \frac{-d[A]}{dt} = k [A]^2
\]

\[
    r = \frac{-d[A]}{dt} = 5357457 \times \exp\left(-\frac{35.40}{R \cdot T}\right) [A]^2
\]

3.4. Properties of Methyl Ester

GC-MS analysis was used to prove and determine how much% of the methyl ester content was produced. Fig. 7 showed that the compounds detected produced 15 compounds in which the sample contained methyl esters and other compounds which were already present in the sample before the reaction. Table 2 shown methyl ester compounds contained in the dominant sample containing palmitic acid, methyl ester, and oleic acid, methyl ester.

Fig. 7. The Chromatogram of Methyl Ester Esterification Reaction on 12: 1 Molar Ratio and 9% Catalyst Concentration

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Table 2. The Composition of Methyl Ester of WCO Esterification

<table>
<thead>
<tr>
<th>Time (Minutes)</th>
<th>Methyl Ester</th>
<th>Molecular Formula</th>
<th>% Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.814</td>
<td>Myristic acid, methyl ester</td>
<td>C₁₅H₃₀O₂</td>
<td>0.97</td>
</tr>
<tr>
<td>18.715</td>
<td>Palmitoleic acid, methyl ester</td>
<td>C₁₇H₃₂O₂</td>
<td>1.12</td>
</tr>
<tr>
<td>18.941</td>
<td>Palmitic acid, methyl ester</td>
<td>C₁₇H₃₄O₂</td>
<td>33.92</td>
</tr>
<tr>
<td>20.568</td>
<td>8,11-Octadecadienoic acid, methyl ester</td>
<td>C₁₉H₃₄O₂</td>
<td>8.69</td>
</tr>
<tr>
<td>20.639</td>
<td>Oleic acid, methyl ester</td>
<td>C₁₉H₃₆O₂</td>
<td>34.48</td>
</tr>
<tr>
<td>20.829</td>
<td>Stearic acid, methyl ester</td>
<td>C₁₉H₃₈O₂</td>
<td>3.76</td>
</tr>
</tbody>
</table>

Table 3. Characteristics of Methyl Ester

<table>
<thead>
<tr>
<th>Parameter</th>
<th>WCO Methyl Ester</th>
<th>SNI-04-7182-2006</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (kg/m³)</td>
<td>896.6</td>
<td>850 - 890</td>
</tr>
<tr>
<td>Acid Value (mg KOH/gr)</td>
<td>2.19</td>
<td>0.6 max</td>
</tr>
<tr>
<td>Saponification Value (mg KOH/gr)</td>
<td>162.3</td>
<td>&lt;500</td>
</tr>
<tr>
<td>FFA (%)</td>
<td>1.22</td>
<td>2 max</td>
</tr>
<tr>
<td>Solubility:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Water</td>
<td>Insoluble</td>
<td></td>
</tr>
<tr>
<td>- Methanol</td>
<td>Partially Soluble</td>
<td></td>
</tr>
<tr>
<td>- Ethanol</td>
<td>Soluble</td>
<td></td>
</tr>
</tbody>
</table>

3.5. Characteristics of Methyl Ester

The quality of methyl esters obtained in the esterification reaction was determined by characterizing the physical and chemical properties which include density, acid value, saponification value, FFA content, and solubility. The results of the characterization of methyl ester products from WCO esterification are shown in Table 3.

The measurement of several physical and chemical properties gives results that density and the acid number doesn't meet SNI standards. This was because the product was mixed with triglycerides which have not been converted into methyl ester which means that the product needs further reaction, namely the transesterification reaction.

Solubility test of methyl ester resulting from the esterification reaction of WCO against some polar and non-polar solvents showed that the product of methyl ester resulting from the esterification reaction was nonpolar. This was caused by the polarity of the ester group covered by the length of the carbon chain that was nonpolar so that it does not dissolve in water[18].

4. CONCLUSION

This research has explored the production of biodiesel from WCO by ultrasonic. The results were typical of esterification reaction where the amount of catalyst and the methanol to oil molar ratio are the most critical process parameters. The optimum in this study was obtained at 50°C, 9% catalyst concentration, and 1:15 molar ratio amongst all the combinations. The reaction time was reduced three times (minutes) compare to the conventional method, and fatty acid concentration reduced by 42%. Kinetic and thermodynamic studies were performed to
calculate the rate constants, frequency factor, and activation energy. Kinetic reaction model in this study used irreversible order two reaction with R\(^2\) value 0.9954; the rate constants were found to be 10.47 ml mol\(^{-1}\) min\(^{-1}\), the frequency factor was 5,357,457 ml mol\(^{-1}\) min\(^{-1}\) and the activation energy was 35.40 kJ/mol. The main methyl ester compounds are palmitate ester and oleate ester.

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