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Submission date: 26-Jul-2022 05:32PM (UTC+0700)
Submission ID: 1875401790
File name: Kusumaningtyas_2021_J._Phys.__Conf._Ser._1918_032022.pdf (662.77K)
Word count: 2872
Character count: 13127

Journal of Physics: Conference Series

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Experimental and kinetic study of free fatty acid esterification derived from *Ceiba pentandra* seed oil with ethanol

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Abstract. Indonesia has an abundant feedstock of *Ceiba Pentandra* which is very potential as a source for biodiesel production. However, it contains very high free fatty acid and can not be directly converted into biodiesel through transesterification process. One of the solution is by reacting *Ceiba pentandra* oil with ethanol under acid catalyst called esterification process. In this study, the operating conditions used for esterification reaction was *Ceiba pentandra* oil to methanol molar ratio of 1:12; with reaction time of 120 minutes. The reaction temperature was varied into 40°C, 50°C, 60°C and 70°C. The results show that, highest conversion achieved was 93.5% at reaction temperature of 70°C. Based on the experimental data, pseudo-Homogeneous model was used to model the kinetic of esterification reaction. Based on this model, the activation energy was 21.319kJ/mol and the kinetic factor was 14,264.08/minutes with R^2 of 0.9675 and SSE of 0.0004.

1. Introduction

Biodiesel is a promising alternative fuel which can be produced from various renewable feed stocks such as oil from plants and animal fats[1]. Several studies have been utilized castor oil [2], used cooking oil[3], *Ceiba Pentandra* oil [4–6] and nyamplung oil [7] through trans-esterification process. However, these natural resources contain high free fatty acid (FFA) which leads to side reactions like saponification that have a negative effect on biodiesel production. Prior to this condition, reduction of FFA on non-edible oils should be performed through esterification process by using low molecular weight alcohol such as ethanol and methanol [8].

Several researchers have studied the conversion of *Ceiba Pentandra* oil into biodiesel [6,9–12]. Previous studies on the esterification of *Ceiba pentandra* oil also had been performed by Kusumaningtyas [13] by using methanol, the highest conversion obtained was 95.14%. However, kinetic study on the esterification of *Ceiba pentandra* oil with ethanol on the presence of H_2SO_4 has not been reported yet.

This work is going to provide experimental data and the mathematical modeling of FFA from *Ceiba Pentandra* oil esterification with ethanol took place. Effect of the esterification parameters such as reaction time and temperature were studied towards the FFA conversion.

2. Materials and Methods

2.1. Materials

Materials used in this research were crude *Ceiba Pentandra* oil from Pati, Jawa Tengah, Indonesia, Ethanol (99.9% p.a. from Merck), H_3PO_4 (Merck), KOH (Merck) and Oxalic acid (Merck).

2.2. Methods and Analysis

In this research, the degumming process, *Ceiba pentandra* oil and esterification process were following the same steps such as the previous studies[13]. However, in the esterification process the methanol was replaced by using an ethanol as a reactant.

2.3. Kinetic Model

In this research, three different pseudo-homogeneous kinetic models were introduced i.e. irreversible 1st order, irreversible second order and reversible second order kinetic model. The esterification of FFA can be written as shown in equation (1).

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C + D \tag{1}$$

where, A is the FFA (RCOOH), B is the ethanol (CH_3OH), C is the methyl ester (R'COOR), D is the water (H_2O), k_1 is the reaction rate constant of forward reaction and k_2 is the reaction rate constant of backward reaction. According to equation 1, the reaction rate of esterification reaction is shown in equation 2.

$$(-r_A) = -\frac{dC_A}{dt} = k_1[A][B] - k_2[C][D] \tag{2}$$

where, $-r_A$ is the reaction rate of A (FFA), [A] is the concentration of FFA, [B] is the concentration of the ethanol, [C] the methyl ester concentration, [D] is the concentration of water and t is the reaction time. Based on equation 2, general equation for irreversible reaction kinetic model is shown in equation 3.

$$\frac{dX_A}{dt} = kC_{A_0}^{\alpha-1}(1 - X_A)^{\alpha} \tag{3}$$

where, k is the reaction rate constant (1/minute), C_{A0} is the initial concentration of FFA (mol/L), X_A is the conversion of FFA and α is the order of reaction.

2.3.1. Model 1: Irreversible 1st Order Kinetic Model. In this model, the value of $\alpha = 1$. By substituting the α into equation 3 and integrating the equation, the kinetic model for irreversible 1st order reaction is shown in equation 4.

$$-ln(1 - X_A) = kt \tag{4}$$

2.3.2. Model 2: Irreversible 2nd Oder Kinetic Model. In this model, the value of $\alpha = 2$. By substituting the α into equation 3, the kinetic model for irreversible 2nd order reaction is shown in equation 5.

$$\frac{dX_A}{dt} = kC_{A_0}(1 - X_A)^2 \tag{5}$$

The differential equation of FFA conversion can be solved by using polymath 6.1 software.

2.3.3. Model 3: Reversible 2nd Order Kinetic Model. If the backward reaction is taken into account, then a second order reverse reaction can be applied[2]. The kinetics of the second order reverse esterification reaction can be seen in equation 6 [14].

$$\frac{dX_A}{dt} = k_1\left(\left(\frac{M}{l}\right) - X_A\right)(1 - X_A) - k_2(X_A)(D_o + X_A) \tag{6}$$

where, M/l is the ethanol to FFA molar ratio and Do is the molar ratio of water to FFA in the reactor feed.

2.3.4. Kinetic Parameter. The best Model was then further calculated for the kinetic parameter by using equation 7.

$$\ln k = \ln Ae^{-\frac{Ea}{RT}} \quad (7)$$

Where, Ae is the kinetic factor, Ea is the energy activity, R is gas constant and T is the reaction temperature

3. Results and Discussion

3.1. Properties of Ceiba pentandra Oil

The raw material analysis was carried out on *Ceiba pentandra* oil before and after the degumming process. The raw material was analysed for its fatty acid content by using GC-MS. The density test is carried out to determine the density of the oil. The viscosity of the oil can be determined through the viscosity test, while the acid number test is used to determine the acid number in the oil prior to the esterification process. Density of *Ceiba pentandra* oil before degumming process is 0.942 g/ml, and after degumming process it decreases to 0.941 g/ml. The viscosity of *Ceiba pentandra* oil after degumming process decreases from 35.70 cP to 35.36 cP. While, the acid number drop significantly from 19.6 to 17.82 mg KOH/g oil which also affect the acidity of the oil from 9.78 to 8.89

3.2. Effect of Reaction Time and Temperature on the FFA Content

Figure 1 shows that there is a continuous decline in FFA as a function of reaction time. At the temperature of 70°C, it can be seen that the FFA decreased to 0.782%. These results have met the FFA standard in oil which is 2%. It can be concluded that the esterification of *Ceiba pentandra* oil can be carried out in the presence of 0.5% sulfuric acid catalyst at the temperature of 70°C.

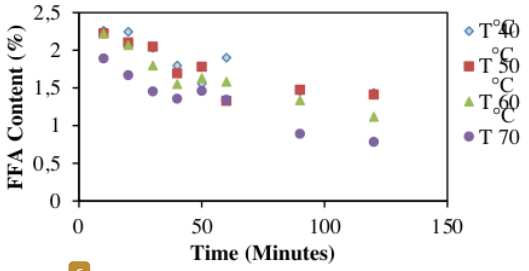

Figure 1. Effect of reaction time and temperature to the FFA content.

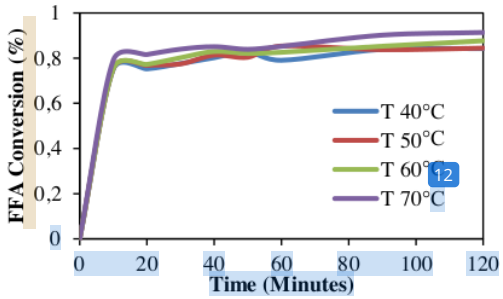

Figure 2. Effect of reaction time and temperature to the FFA conversion.

3.3. *Effect of Reaction Time and Temperature on the FFA Conversion*

Figure 2 shows that the FFA conversion is increasing exponentially at the first 10 minutes of reaction time, and slightly increasing for the rest of reaction time. The highest conversion of FFA was found at the reaction temperature of 70°C and 120 minutes of reaction time with an FFA conversion of 91.37%. Based on these results, the optimum time for the esterification reaction is at a temperature of 70°C for 120 minutes. Higher Temperature and longer time reaction will not affect significantly on the FFA conversion.

At temperature of 40°C the conversion of FFA is lower than the conversion at 70°C. With a higher temperature, the conversion will have a faster rate. In this reaction, the optimum temperature was found to be at 70 ◦C. A positive effect on FFA conversion with temperature is due to the increase in kinetic energy of the reactant molecule[8].

3.4. *Kinetic Parameter of Model 1*

Figure 3 shows the experimental data and the predicted result of FFA Conversion by using Model 1.

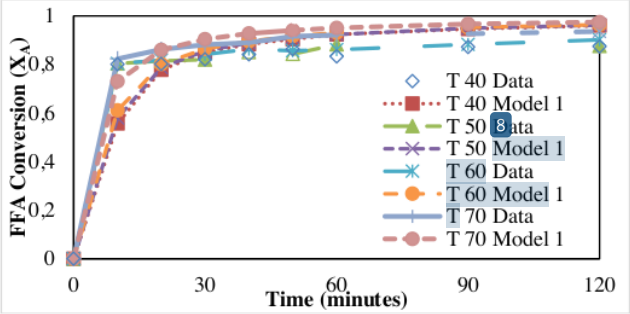

Figure 3. Experimental and calculated conversion of FFA by using Model 1.

It can be seen that, with the increase in reaction temperature it also increases the reaction rate and reduces the reaction time[15]. At the temperature of 40°C, it requires 90 minutes to obtain ±90% conversion while it only needs 45 minutes to get the same conversion at 70°C. The kinetic reaction rate constants, sum square of errors (SSE) and the coefficients of determination (R^2) are shown in Table 1.

Table 1. Kinetic parameter of Model 1.

Temperature (°C)	k (L/mol.min)	SSE	R^2
40	1.36×10^{-2}	0.1318	0.296
50	1.44×10^{-2}	0.1135	0.325
60	1.56×10^{-2}	0.085	0.398
70	2.00×10^{-2}	0.053	0.666

3.5. *Kinetic Parameter of Model 2*

Figure 4 shows the experimental data and the predicted result of FFA Conversion by using Model 2.

The kinetic reaction rate constants, sum square of errors (SSE) and the coefficients of determination (R^2) are shown in Table 2.

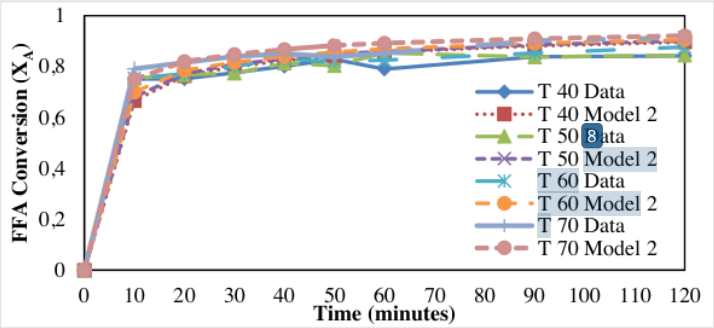

Figure 4. Experimental and calculated conversion of FFA by using Model 2.

Table 2. Kinetic parameter of Model 2.

Temperature (°C)	k (L/mol.min)	SSE	R^2
40	2.2398	0.017	0.5184
50	2.4655	0.014	0.5690
60	2.7877	0.009	0.6975
70	4.2198	0.005	0.7156

The SSE of Model 2 is much lower compared to Model 2. It is in line with the *Le Chatelier* principle where the excess of ethanol cause the concentration of the reactants is higher than the concentration of the products. Due to this condition, the reaction will be shifted towards the product side. [13]

3.6. Kinetic Parameter of Model 3

Figure 5 shows the experimental data and the predicted result of FFA Conversion by using Model 3.

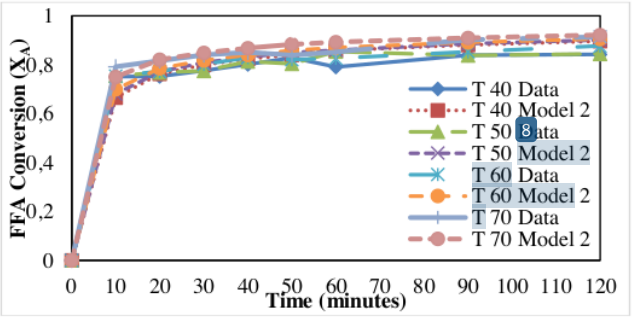

Figure 5. Experimental and calculated conversion of FFA by using Model 3.

The kinetic reaction rate constants, sum square of errors (SSE) and the coefficients of determination (R^2) are shown in Table 3.

Based on Table 1, 2 and 3 the average SSE for Model 1, 2 and 3 were 0.0958, 0.01125 and 0.071 respectively. From Table 3, it can be seen that the kinetic reaction rate of forward and backward reaction have almost the same value. It probably, the backward reaction is also can be considered in

the esterification reaction[5]. However, SSE of Model 2 is much lower compared to the Model 3, it indicates that the model is particularly in a good agreement with the experimental data for FFA esterification process. By using arrhenius equation, it can be obtained that this reaction had an energy activity of 17.74 kJ/mol and kinetic factor of 2,015.85/minute.

Table 3. Kinetic parameter of Model 2.

Temperature (°C)	k_1 (L/mol.min)	k_2 (L/mol.min)	SSE	R^2
40	3.22 x 10-2	7.43 x 10-2	0.099	0.638
50	3.30 x 10-2	7.04 x 10-2	0.0881	0.673
60	3.41 x 10-2	6.58 x 10-2	0.074	0.788
70	3.58 x 10-2	4.47 x 10-2	0.023	0.690

4. Conclusion

The conversion free fatty acid is affected by reaction time and temperature. Higher reaction temperature increases the FFA conversion. Best FFA conversion obtained was 91.37% at reaction temperature of 70°C and 120 minutes reaction time. The best kinetics model to predict FFA conversion in this esterification model was an irreversible second-order model with the reaction rate constant with SSE of 0.01125 and R^2 of 0.625. The kinetics parameter of *Ceiba pentandra* esterification reaction with a 0.5% sulfuric acid catalyst had an energy activity of 17.74 kJ / mol and kinetic factor of 2,015.85/minute.

Acknowledgement

The authors would like to acknowledge Faculty of Engineering Universitas Negeri Semarang for the financial support.

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