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Kinetic Study on the Esterification of Palm Fatty Acid Distillate (PFAD) Using Heterogeneous Catalyst

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Abstract. Esterification with heterogeneous catalysts is believed to have advantages compared to homogeneous catalysts. Palm Fatty Acid Distillate (PFAD) was esterified by $ZrO_2-SO_4^{2-}$ /natural zeolite at temperature variation of 55°C, 60°C, and 65°C to produce biodiesel. Determination of reaction kinetics was done by experiment and modeling. Kinetic study was approached using pseudo-homogeneous model of first order. For experiment, reaction kinetics were 0.0031 s⁻¹, 0.0054 s⁻¹, and 0.00937 s⁻¹ for a temperature of 55 °C, 60 °C and 65 °C, respectively. For modelling, reaction kinetics were 0.0030 s⁻¹, 0.0055 s⁻¹, and 0.0090 s⁻¹ for a temperature of 55°C, 60°C and 65°C, respectively. Rate and conversion of reaction are getting increased by increasing temperature.

1. Introduction

Biodiesel is a renewable and environmentally friendly fuel for diesel engines. It was produced by transesterification or esterification of vegetable oils or animal fats with short chain alcohols in the presence of catalyst [1]. PFAD (Palm Fatty Acid Distillate) is a by-product of the palm oil industry and is considered as low grade oil with high free fatty acids [2]. Esterification is conventionally performed using homogeneous acid catalyst such as sulfuric acid or hydrochloric acid. However, it has a number of drawbacks such as need further processing in the separation of the catalyst from the product and may generate hazardous waste [3-5]. To overcome these problems, researchers have focused on using heterogeneous catalysts for biodiesel production. In this research, the esterification of free fatty acids (FFA) in PFAD with methanol, using $ZrO_2-SO_4^{2-}$ /natural zeolite, was studied. The effects of the mass ratio of catalyst to oil (1 – 10%), the molar ratio of oil to methanol (1:6 – 1:12), and the reaction temperature (55 – 65°C) were studied for the conversion of FFA on PFAD to optimize the reaction conditions. The kinetics of FFA esterification (in PFAD) in the presence of $ZrO_2-SO_4^{2-}$ /natural zeolite also has been investigated. Determination of kinetics of FFA esterification was conducted by using a first order pseudo-homogeneous kinetic model.

2. Materials and Methods

2.1 Materials

Raw materials used in this study was PFAD from Palm Oil Processing Industry Public Company Limited consisting of 93% (wt) of free fatty acids (45.6% of palmitic, oleic of 33.3%, 7.7% of linoleic, 3.8% of stearic, 1.0% myristic, 0.6% of tetracosenoic, 0.3% of linolenic acid, 0.3% of eicosanoic, 0.2% of eosenoic, and 0.2% of palmitoleic acid) and the rest were triglyceride (TG), diglycerides (DG), and monoglycerides (MG). Esterification was done using $ZrO_2-SO_4^{2-}$ /natural zeolite. Other materials used were distilled water, Ba(OH)₂, nitrogen gas and oxygen gas.



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2.2 Method

2.2.1 Activation of natural zeolite

Natural zeolite of 200 g with the size of 200 mesh was dissolved in 500 ml of H₂SO₄ 0.5 M. The solution was stirred for 4 hours at room temperature. Then it was cooled and filtered using Whatman 42 paper. The filtrate was discarded, while the solids were washed with distilled water to neutral. Washing is terminated if it were neutral to the test by using Ba(OH)₂. Then the solids were dried in an oven at 130°C for 24 hours.

2.2.2 The catalyst synthesis of Zirconia

Activated Zeolite soaked in a solution of Zirconium (IV) oxide chloride hexahydrate (ZrOCl₂ · 8H₂O). It was refluxed at 90°C for 3 hours. Samples were filtered and washed with distilled water until the filtrate was clear then dried. Dried sample were calcined by flowing N₂ gas and oxidized by O₂ gas to make ZrO₂/natural zeolite catalyst. 10 g of ZrO₂/zeolite and 20 g of Ammonium Sulphate ((NH₄)₂SO₄) solids were mixed and crushed in a porcelain mortar until homogeneous. It calcined by flowing N₂ gas at 200°C for 4 hours. Heating rate is set at 5 °C/min. ZrO₂-SO₄²⁻/natural zeolite was characterized by crystallinity measurements using X-Ray Diffraction (XRD). Determination of surface area and pore size distribution were done using BET Surface Area Analyzer, the analysis of mineral content by X-ray Fluorescence Spectroscopy (XRF), and analysis of functional groups with Fourier Transform Infrared (FT-IR) spectrometry.

2.2.3 Esterification of PFAD

PFAD was reacted with methanol in a stirred batch reactor. The catalyst used was ZrO₂-SO₄²⁻/natural zeolite with concentration of 1%, 2.5%, 5% and 10%. Ratio of PFAD to methanol was 1: 6, 1: 8, 1:10, and 1:12. Esterification carried out at a temperature variation of 55°C, 60°C and 65°C.

2.2.4 Reaction kinetics of Pseudo-Homogeneous model

Kinetic of esterification of free fatty acid in PFAD with methanol can be approximated by pseudo-homogeneous second order with assumption that the mass transfer of the liquid as a reactant into the solid as a catalyst is very rapid. Mathematically pseudo-homogeneous model of first order can be described in equation (1) as follows:

$$-r_A = -\frac{dC_A}{dt} = k C_A^\alpha C_B^\beta - k' C_C^\gamma C_D^\lambda \quad (1)$$

Which (-r_A) is reaction rate of free fatty acids, C_A is concentration of free fatty acid; C_B is concentration of methanol; C_C and C_D are concentration of methyl ester and concentration of water formed during the reaction, respectively; k is reaction rate constant and k' is equilibrium constant. In the experiment, C_B was excess so that the concentration is assumed to be fixed and kC_B^β can be symbolized as k₁ and the reaction rate is considered toward the product. The reaction rate can be expressed as pseudo first order.

$$(-r_A) = k_1 C_A \quad (2)$$

Esterification of free fatty acids with the solid catalyst zeolite-sulfated zirconia run in batch.

$$(-r_A) = -\frac{dC_A}{dt} \quad (3)$$

Substitution of Equation (3) to Equation (2) thus obtained:

$$-\frac{dC_A}{dt} = k_1 C_A$$

$$\frac{dC_A}{C_A} = -k_1 dt$$

$$\ln C_A - \ln C_{A_0} = -k_1 dt \quad (4)$$

The parameters of the reaction kinetics (k_1) are through non-linear regression which gives the Sum of Square Quake Error (SSE) between the experimental data and the minimum calculation data using Matlab.

$$SSE(k_1) = \sum (X_{A_{experiment}} - X_{A_{calculation}})^2 \quad (5)$$

Which $X_{A_{experiment}}$ is conversion value of the experimental data and $X_{A_{calculation}}$ is a conversion value calculated from the kinetic equation proposed. Values of parameters obtained at each temperature is then plotted by the Arrhenius equation to obtain the activation energy data.

$$k_1 = A_r \text{Exp} \left(-\frac{E_a}{RT} \right) \quad (6)$$

3. Result and Discussion

3.1 Effect of the amount of methanol to FFA conversion

Esterification is a reversible reaction. The equilibrium is shifted toward the product by making the number of moles of reactant becomes excessive. The influence of the amount of methanol to FFA conversion can be seen in Figure 1.

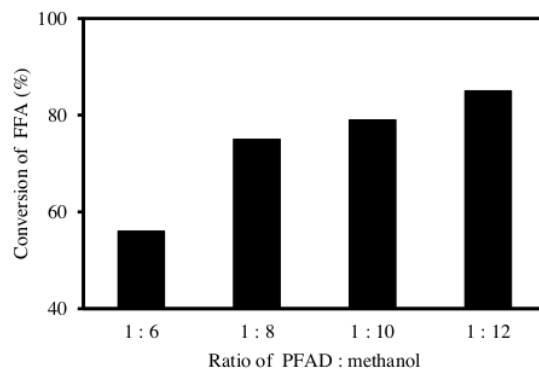


Figure 1. Effect ratio of PFAD to methanol on conversion of FFA (%).

Increasing the amount of methanol will increase FFA conversion. This happens because the larger reactants collide so that the conversion of the FFA even greater. The conversion occurs in processes that use ratio PFAD: methanol 1:12 was 83% of FFA conversion. From Figure 1 it is known that a significant increase in conversions that occur in reactions using the mole ratio PFAD with methanol = 1:10 and 1:12, but not as significant as ratio of 6 to 10. This is because the ratio of reactants 1:12 has begun to reach the maximum conversion.

3.2 Effect of catalyst concentration on the conversion of FFA

The influence of the amount of catalyst to the FFA is presented in Figure 2. The increasing amount of catalysts will increase FFA conversion. A significant rise in FFA conversion occurs when the amount

of catalyst was increased from 1% to 2.5%. Its increasing is more significant than 5% to 10%. This happens the total number of active sites has begun to approach the maximum number of reactants needed. At a catalyst concentration of 10% it appears that the conversion slightly increased compared to the catalyst concentration of 2.5%.

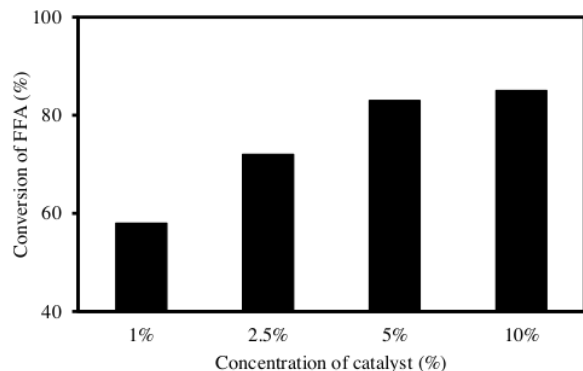


Figure 2. Effect of concentration of catalyst (%) on conversion of FFA (%).

3.3 Effect of reaction temperature on the conversion of FFA

With increasing temperature, FFA conversion will increase as illustrated in Figure 3.

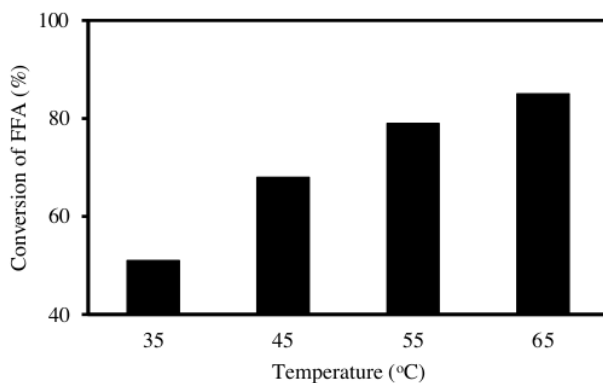


Figure 3. Effect of temperature (°C) on conversion of FFA (%).

The higher conversion was obtained from the reaction at temperature of 65°C. By raising the reaction temperature will raise FFA conversion. Rising temperature will cause the viscosity of the reaction down. That makes the mixing process will be more perfect and mass transfer of reactants to the catalyst surface will be better so the reaction runs perfectly.

3.4 Kinetics model

In this experiment it was seen that the conversion increased sharply after the catalyst was added to the reactor, and increased gradually over time. Something similar to the one delivered by Rattanaphra et al. [6], Alenezi et al. [7], and Park et al. [8]. This is due to several things: At the moment the catalyst is added the solution in the reactor is only the reactant (FFA and Methanol) so that diffusing to the active surface of the catalyst is only the reactant. Diffusion of the reactants to the active surface of the catalyst will accelerate the formation of FAME. After FAME formed and became a co-solvent in the solution, barriers to mass transfer of reactants to the catalytically active surface is greater so that the reaction speed becomes slower [8]. FFA conversion will increase the water that its existence can be deactivated catalyst [9] and the conversion of high FFA produce FAME make the formation

equilibrium of the reaction [7]. Spontaneous conversion occurred at the beginning of the reaction indicates that the rate of formation of FAME at the start of the reaction was controlled by the speed of chemical reactions. Yadav [10] said that the conversion increases with increasing temperature indicates that the reaction rate was controlled by the speed of chemical reactions. Effect of reaction temperature was used to determine the reaction kinetics. Reaction rate constant can be calculated by a pseudo-first-order reaction equation to generate minimum SSE. Data conversion and conversion count of each 10-minute interval is shown in Table 1 and Figure 4. The value of k at various reaction temperatures and SSE values are presented in Table 1.

Table 1. FFA conversion by experiment and model (mol PFAD: methanol = 1:10, catalyst concentration = 10% of PFAD)

Time (minute)	T = 55°C		T = 60°C		T = 65°C	
	X _A experiment	X _A calculation	X _A experiment	X _A calculation	X _A experiment	X _A calculation
0	43,9554	43,9554	42,6150	44,8239	43,8298	43,8297
10	46,3783	45,3391	50,0305	47,2518	48,7786	48,4069
20	48,2605	46,6887	48,6616	49,5728	51,3678	52,6111
30	47,2241	48,0050	51,4416	51,7918	60,7201	56,4727
40	48,8007	49,2887	54,0710	53,9130	61,8794	60,0197
50	51,3480	50,5408	56,5581	55,9410	62,0061	63,2776
50	52,4297	51,7619	58,9105	57,8797	66,0904	66,2700
70	56,5467	52,9529	61,1355	59,7331	67,6226	69,0186
80	56,4099	54,1145	63,2400	61,5049	75,6839	71,5432
	k = 0,0030		k = 0,0055		k = 0,0090	

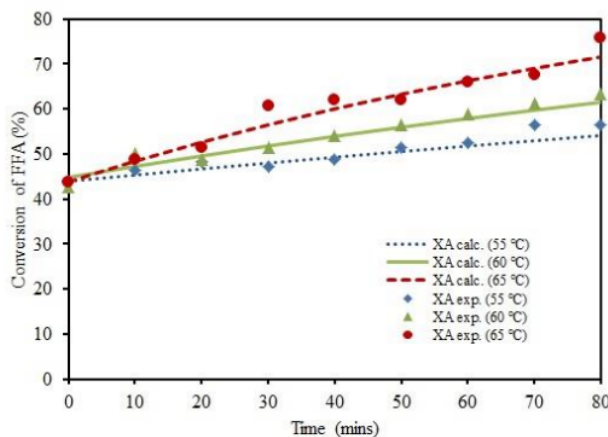


Figure 4. Calculation and experiment conversion of FFA (%) in variation of temperature (°C).

From Table 2 it can be seen that the value of SSE for each variation of the reaction temperature is quite small. The results show that the proposed kinetic model correcting ie homogeneous pseudo first order of the FFA is acceptable, this trend can also be seen from Figure 5.

Table 2. Value of k at different temperature

Temperature (°C)	k ₁ (s ⁻¹)	k ₁ Arrhenius (s ⁻¹)	Rel.Err (%)
55	0.0030	0.0031	4,0046
60	0.0060	0.0054	2,6281
65	0.0090	0.00937	4,4186

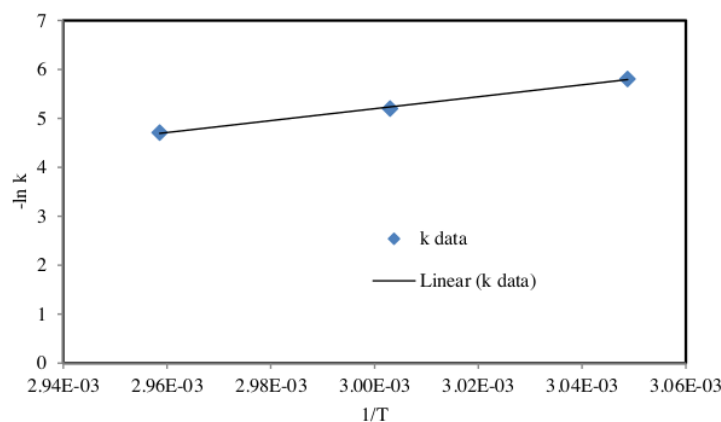


Figure 5. Arrhenius equation of k in difference temperature

From data of reaction rate constant (k) in Table 2 shows that increasing temperatures will increase the value of k . The value of k was used to calculate the value of the collision frequency factor (A_r) and the activation energy (E_a) with the Arrhenius equation. It was obtained by linear regression A_r of $4.3771 \times 10^{13} \text{ s}^{-1}$ and E_a of 999.99 kJ/mol .

4. Conclusion

$\text{ZrO}_2\text{-SO}_4^{2-}$ /natural zeolite can be used to esterification reaction of free fatty acids. Increasing the mole ratio of PFAD to methanol, the amount of catalyst, and the temperature rises has been successful in increasing the conversion of free fatty acids. Correcting kinetic model of homogeneous pseudo first order can be used in determining the value of the reaction kinetics of PFAD esterification to become methyl ester. For experiment, reaction kinetics were 0.0031 s^{-1} , 0.0054 s^{-1} , and 0.00937 s^{-1} for a temperature of 55°C , 60°C and 65°C , respectively. For modelling, reaction kinetics were 0.0030 s^{-1} , 0.0055 s^{-1} , and 0.0090 s^{-1} for a temperature of 55°C , 60°C and 65°C , respectively.

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