Kinetic study of free fatty acid in Palm Fatty Acid Distillate (PFAD) over sugarcane bagasse catalyst

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Abstract. Biodiesel production is made by using edible or vegetable oils; however, their high prices and use as food resource are great limiting factors to their application. During the refining of palm oil, a lower-value by-product known as palm fatty acid distillate (PFAD) is generated in the fatty acid stripping and deodorization stages. PFAD is potentially a valuable, low-cost feedstock for the production of biodiesel. In this work, the esterification reactions of free fatty acid (FFA) in PFAD over sugarcane bagasse catalysts were studied. The effects of catalyst concentration (1 to 10 wt%), reaction temperature (30 to 60°C), and molar ratio of oil/methanol (1:6 to 1:12) on the conversion of FFA was studied to optimize the conditions for maximum conversion of FFA in PFAD and to observe the appropriate kinetic model for the experimental data. A kinetic model was developed on the basis of the Eley–Rideal mechanism according to the experimental data. The esterification reaction occurred between methanol adsorbed on solid base active sites and FFA from the liquid phase. The surface reaction of FFA with adsorbed methanol was assumed to be rate-determining. The collision factor value and activation energy for P-H model were found to be 1217.7985 L/mol.min and 24.2950 kJ/mol, then for E-R model were 1492.6375 L/mol.min and 19.5391 kJ/mol, respectively.

1. Introduction
Increased demand for energy, global warming due to emission of greenhouse gases, environmental pollution, and fast diminishing supply of fossil fuels are the major key factors leading to search for alternative sources of energy [1]. Currently, biodiesel production is made by using edible or vegetable oils (e.g. palm oil, rapeseed, soybean and sunflower oil); however, their high prices and use as food resource are great limiting factors to their application. Therefore, nowadays lots of research done on the production of biodiesel with this material. Biodiesel has attracted lots of attention recently due to its benefits and alternative renewable energy.

Biodiesel is a product of esterification with triglyceride (vegetable oil or animal fat) and alcohol as raw materials. The products are methyl and ethyl esters [1]. During the refining of palm oil, a lower-value by-product known as palm fatty acid distillate (PFAD) is generated in the fatty acid stripping, deodorization stages, and low-cost feedstock for the production of biodiesel [18].

Esterification produces fatty acid methyl or ethyl esters by using some type of catalysts, those are homogeneous acid-catalyzed process, enzymatic process, supercritical process, and heterogeneous catalyst process [2–13, 20]. Heterogeneously catalysed esterification is very important and used in
many applications due to its ease of purification products, reduction of water waste, and economic factor [6, 17].

Kusumaningtyas et al. (2013) in their paper examined the kinetics study of fatty acid esterification with sulphated zirconia/zeolite catalyst for producing biodiesel [12]. In this work, the esterification of PFAD was investigated, and the effects of catalyst concentration, reaction temperature, and molar ratio of oil/methanol on the conversion of FFA were studied to optimize the conditions for maximum conversion of FFA in PFAD and to observe the appropriate kinetic model for the experimental data. Moreover, a kinetic model was proposed on the basis of the Eley-Rideal mechanism and the kinetic parameters were determined by fitting model with the experimental data.

2. Experimental

2.1. Catalyst Synthesis
Sugarcane Bagasse Biochar (SCB) catalyst samples were prepared via concentrated sulfuric acid. The SCB were sulfonated according to the method of Toda et al. [9]. Two hundred mL of concentrated sulfuric acid was added to 20 g of biochar in a 500 mL round bottom flask and heated to 150°C. The SCB catalyst was washed with 80°C distilled water until the wash water was neutral and free from sulfate ions and dried in an oven at 70°C for 1h.

2.2. Catalytic activity
The reaction procedure is mixture of catalyst and methanol was heated up to 60°C under continuous stirring at 500 rpm. Ninety ml of PFAD was heated separately to reach the reaction temperature. Esterification experiment was carried out at reaction time of 2 to 4 h. Biodiesel product was then repeatedly washed using warm distilled water (60°C). The variables affecting the acid-catalyzed esterification such as methanol-to-oil molar ratio (6:1–12:1), catalyst amount (1–10 wt. % of oil), reaction time (15–120 min) and temperature (30–60°C) were studied.

The acid value was calculated using the below equation:

\[ AV = \frac{56.1 \times C \times V}{m} \]  

(1)

where AV is the acid value of the sample (mg KOH.g⁻¹), V is volume of KOH for titration (mL), C is concentration of the KOH for titration (mol/L), m is the weight of the sample (g), and 56.1 is the molecular weight of KOH. The conversion of free fatty acid was calculated using equation (2):

\[ X_F = \left(1 - \frac{AV_2}{AV_1}\right) \times 100 \]  

(2)

where XF is the FFA conversion, AV₁ is the initial acid value of the mixture and AV₂ is the acid value of mixture after reaction.

2.3. Reaction kinetics model
The esterification of PFAD and methanol using SCB as a catalyst is represented as follows:

\[ RCOOH + CH₃OH \rightarrow RCOOCH₃ + H₂O \]  

(3)

Reaction mechanisms of the esterification processes, the following reaction steps were proposed:

2.3.1. Pseudo-Homogeneous model. The P-H model was developed based on the following assumptions: (1) The rate of the esterification reaction under the operating conditions is kinetically controlled; and (2) The entire reaction system is considered to be an ideal solution in which internal and external mass transfer resistance does not exist. Therefore, the reaction mechanism can be given as follows

\[ \frac{dC_F}{dt} = k_1.C_F.C_A \]  

(3)
the concentration of FFAs can be expressed as: \( C_F = C_{F0}(1 - X_F) \); while the amount of alcohol is excessive, thus the concentration of alcohol is constant. The \( X_F \) and \( C_{F0} \) refer to FFAs conversion and the initial concentration of FFAs. Where \( C_{A0} \) are the initial concentration of alcohol, respectively.

2.3.2. Eley-Rideal model. Heterogeneous esterification reaction can be described using Eley-Rideal (E-R) model, where, FFA (F) is not adsorbed on the catalyst surface and remains in the liquid medium and methanol (A) is adsorbed on the catalyst surface because of its polarity. Eley-Rideal model can be developed in the following equation below:

\[
\eta_F = \frac{k \cdot K_E \cdot C_F \cdot C_E}{1 + K_F \cdot C_F + K_E \cdot C_E}
\]  
(4)

In this case the criterion is the minimization of the Sum Squares of Errors (SSE) between the experimental and calculated reaction rates using the equation:

\[
SSE = \sum (X_{F, \text{exp}} - X_{F, \text{calc}})^2
\]  
(5)

3. Result and Discussion

3.1. Effect of methanol amount on the esterification reaction

The esterification is a type of reversible reaction. Therefore, to improve the conversion of this reaction was by adding amount of reactants so that the reaction becomes excessive. The effect of methanol amount added on the esterification reaction was shown in Figure 1. That figure showed that FFA conversion was enhanced while increasing the amount of methanol. Excess methanol (alcohol) added to this reaction made a greater collision among the reactants. Ratio 1:12 of PFAD to methanol gave the highest conversion of FFA, that was 91%. However, there was no significant increase in conversions that occur in this reaction using ratio PFAD to methanol 1:10 and 1:12. These results might be attributed to the maximum conversion and to the saturation of the catalytic surface with methanol or prevention of nucleophilic attack by shielding protonated methanol. That was confirmed by Eley-Rideal mechanism with chemisorption of the methanol [2].

3.2. Effect of catalyst loading on the esterification reaction

The amount of catalyst loading in this reaction was varied as 1%; 2.5%; 5%; and 10%. Figure 2 was the research results. It showed that the conversion of FFA increased with increasing catalyst amounts and the reaction for 10% catalyst loading had the highest conversion. This result might be caused by increasing the number of active sites. Low amount of catalyst loaded in the reaction produced a small number of active sites. Therefore, conversion of FFA became small due to a small number of catalytically active sites occupied by the reactants. Something similar to experiment conducted by Liu et al. (2014). By the experimental data, this reaction was dependent on the catalyst loading on the process and it was found that the conversion of FFA increased with the increasing amount of catalyst in range of 1-10%.

3.3. Effect of temperature on the esterification reaction

The other important variable affecting a conversion reaction is temperature. The effect of different temperature was observed in the range of 30-60°C. The results of conversion of FFA in this research was shown in figure 3. As shown in the figure, increasing esterification temperature caused an increase in conversion of FFA. This was because of higher molecule motion speed and mass transfer rate happened during esterification reaction [1]. By using high temperature might reduce the as-formed water molecules on the catalyst surface bounded to the active sites [1].
Figure 1. Effect ratio of PFAD to methanol (1:6; 1:8; 1:10; and 1:12).

Figure 2. Effect concentration of catalyst on the esterification reaction (1%; 2.5%; 5%; and 10%).

Figure 3. Effect of temperature on the esterification reaction (30°C; 40°C; 50°C; and 60°C).

Figure 4. Comparison of simulation and experimental data (P-H Model).

3.4. Kinetics model
Esterification reaction using heterogeneous catalyst consists of some processes; those are diffusion, adsorption/desorption, and surface reaction. By those processes, various models can be used to approach kinetic of reaction. In this work, two models used to express the models are pseudo-homogeneous model and Eley-Rideal (E-R) model. The differences of these models are in the adsorption and desorption processes. Pseudo-homogeneous model neglect the processes and E-R model take an assumption that one of the adsorbed reactants react with the others [12].

Figure 4 and 5 are the comparison between the simulation and experimental data based on P-H model and E-R model. Furthermore, from those figures, the E-R mechanism shows that this model can lead to the esterification reaction which is better than P-H model. This was conclude that the heterogeneous kinetic model (E-R model) was suitable to correctly describe the reaction kinetics.
From table 1, the data of reaction rate constant (k) shows that increasing temperature will increase the value of k. The value of k will be used to calculate the value of collision factor (Ar) and activation energy (Ea) by using the Arhenius equation. From that equation, the value of Ar and Ea obtained were 1217.7985 L/mol.min and 24.2950 kJ/mol for P-H model, then 1492.6375 L/mol.min and 19.5391 kJ/mol foe E-R model.

| Temperature (°C) | Pseudo-Homogeneous Model | Eley-Rideal Model |
|------------------|--------------------------|-------------------|
|                  | k (L/mol/min) | k Arhenius (L/mol/min) | k (L/mol/min) | k Arhenius (L/mol/min) |
| 30               | 0.0792        | 0.0790              | 0.5558       | 0.6392               |
| 40               | 0.1085        | 0.1075              | 0.9339       | 0.8190               |
| 50               | 0.1392        | 0.1435              | 1.2138       | 1.0333               |
| 60               | 0.1915        | 0.1883              | 1.0934       | 1.256                |

4. Conclusion
The kinetic of esterification reaction was carried out using sugarcane bagasse biochar as catalyst at temperatures from 30 to 60°C. The experimental data from this reaction were fitted to P-H model and E-R model. Increasing the mole ratio of PFAD to methanol, concentration of catalyst, and temperature successfully increases the conversion of FFA. From the simulation results, the value of k increase with increasing reaction temperature. The collision factor value and activation energy for P-H model were found to be 1217.7985 L/mol.min and 24.2950 kJ/mol, then for E-R model were 1492.6375 L/mol.min and 19.5391 kJ/mol for E-R model, respectively.

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