Potential of palm fatty acid distillate as a feedstock in the synthesis of ethyl esters using solid SO$_4^{2-}$/TiO$_2$-SiO$_2$ catalysts

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Abstract. Utilization of by-products from the cooking oil industry, such as palm oil fatty acid distillates (PFAD) can reduce the cost of producing ethyl ester/biodiesel. This PFAD is processed into biodiesel using SO$_4^{2-}$/TiO$_2$-SiO$_2$ solid catalyst and ethanol reagent. The central composite design in Response Surface Methodology is applied in optimizing the effect of process variables such as the amount of catalyst, ethanol to PFAD molar ratio and reaction time. The results of the study show that the best-operating conditions with 98.89% ethyl ester conversion were achieved with the catalyst amount of 5% w, a molar ratio of 13 in reaction time of 2.25 hours. The presence of SO$_4^{2-}$/TiO$_2$-SiO$_2$ catalyst components can be characterized using SEM-EDX. A functional group showing the presence of ethyl ester in biodiesel products has been identified using FTIR. Ethyl ester properties related to biodiesel properties can be shown as saponification value: 583.8446 mg/g, iodine value: 8.8714 mg/g and cetane value: 49-54.

1. Introduction
Biodiesel has been known as a good substitute fuel for Petro diesel oil that has renewable properties [1]. The process of biodiesel production has developed from time to time, both in terms of catalyst types and raw materials which are generally related to the environmental issue. In the past, acidic or basic homogeneous catalysts have been used to boost the reaction of biodiesel formation, but now it is no longer desired because it produces toxic waste, thus heterogeneous catalysts are used. In terms of raw material, various types of oils/fats can be transesterified and fatty acids can be esterified using alcohol into biodiesel [2].

Various efforts have been made to develop non-edible vegetable oils and waste oils such as used cooking oil as raw material for biodiesel [3-5]. Meanwhile, the development of other raw materials such as palm oil fatty acid distillate (PFAD) is also interesting. PFAD is a by-product of crude palm oil (CPO) processing into cooking oil, containing various types of fatty acids [6-7]. The use of PFAD, in this case, is very interesting because, in addition to increasing the added value of oil palm plants, it also increases the economic viability of biodiesel in relation to cheap raw material prices and abundant supplies.
This research is related to the production process of ethyl ester type biodiesel through the PFAD esterification reaction using ethanol and solid \( \text{SO}_4^{2-}/\text{TiO}_2-\text{SiO}_2 \) catalyst.

The research variables are ethanol to PFAD molar ratio and catalyst to PFAD weight ratio. The \( \text{SO}_4^{2-}/\text{TiO}_2-\text{SiO}_2 \) catalyst is synthesized by impregnation and calcination while SiO\(_2\) material used is mesoporous material which is synthesized using the modified Ryoo method [8]. The observed variables were the conversion of ethyl ester formation and reaction product composition. The optimal conditions of the PFAD esterification process are determined based on the Surface Response Methodology (RSM), in which the mathematical model can be used to estimate the response to various treatments.

2. Experiment

2.1. Material
KOH (E. Merck), Ethanol (E. Merck), \( \text{H}_2\text{SO}_4 \) (E. Merck), titanium dioxide (E. Merck), palm fatty acid distillate (PFAD) and silica (SiO\(_2\)) derived from the synthesis using the Ryoo method [8].

2.2. Procedures

2.2.1. Catalyst preparation and characterization. Initially, TiO\(_2\) was added with 2 Molar \( \text{H}_2\text{SO}_4 \) solution until completely mixed, then added the synthesized silica using the modified Ryoo method [8]. The weight ratio of TiO\(_2\) to Silica was 5:1 and this mixture continues to be stirred for 6 hours at a speed of 300 rpm. After that, it was put in the oven for 24 hours at 105°C and then calcined in a furnace at 400°C for 4 hours. Morphological characterization of the catalyst that has been synthesized was carried out using scanning electron microscopy (SEM) and the percent of the composition of its constituents EDX.

2.2.2. Esterification of palm fatty acid distillate (PFAD). Firstly, some amount of PFAD is melted and put into a reactor with a temperature of 80°C and the stirring speed of 250 rpm, then ethanol is added and the operating conditions were kept constant.

This PFAD esterification reaction was carried out in 2 variants, namely a reaction using ethanol to PFAD molar ratio of 11, 13, and 15 with catalyst to PFAD weight ratio of 5% and a reaction using catalyst to PFAD weight ratio of 7%, 5%, and 3% with ethanol to PFAD molar ratio of 13%.

Observations were conducted by taking analytical samples every 0.5 hours and the reaction lasted for 4 hours. Unreacted free fatty acid levels were measured by acid-base titration using KOH 0.1 M and the conversions of ethyl ester formation were calculated using the following formula:

\[
\text{Acid value } C = \frac{1000V_{\text{KOH}}M_{\text{W}}N_{\text{KOH}}}{W} \\
\text{Conversion } X = \frac{C_0 - C_1}{C_0} \times 100\%
\]

Where \( V \) is the volume of the KOH solution used for titration (mL), \( M \) is the molecular weight of KOH (56.1 g/gmol), \( N \) is the concentration (gmol/L), \( W \) is the sample weight (g), \( C_0 \) is the acid value before the reaction and \( C_1 \) are the acid values after the reaction.

2.2.3. Statistical analysis of optimization of esterification. Statistical analysis was conducted using Design-Expert® (Stat-Ease, Inc., Minneapolis, USA). Central Composite Design (CCD) was used to study manipulation variables that include the range of (A) the amount of catalyst (3-7wt%), (B) PFAD to ethanol molar ratio (1: 11-1: 15) and (C) reaction time (0.5 to 4 hours).

2.2.4. Characteristics of ethyl ester as biodiesel. Characterization to indicate functional groups that support the presence of ethyl esters was conducted by using Infra-Red Spectroscopy instrument
(Fourier Transform Infra-Red 8400S Shimadzu). Biodiesel quality specification was saponification value (SV), iodine value (IV) and cetane numbers (CN). The SV and IV of the biodiesel products were respectively calculated from equations 3 and 4, while the CN was calculated based on the functional relationship approach with SV and IV according to equation 5. The data used to support these equations were obtained from the results of the ethyl ester characteristics using the GC-MS instrument [8-10].

\[
\begin{align*}
IV &= \sum \frac{(254 \times D \times Ai)}{MWi} \\
SV &= \sum \frac{(560 \times Ai)}{MWi}
\end{align*}
\]

Where \(D\) is the number of the double bond; \(Ai\) and \(MWi\) are the percentage composition and the molecular mass of a particular ester, respectively.

Cetane number was also analyzed by the titrimetric method for saponification values and iodine values which were processed using equation 5

\[
CN = 46.3 + \frac{5458}{SV} - 0.255 \times IV
\]

### 3. Result and discussion

#### 3.1. Characterization of the solid catalyst

The characterization of the \(\text{SO}_4^{2-}/\text{TiO}_2-\text{SiO}_2\) catalyst material is shown in Figure 1. The result of the SEM-EDX analysis in Figure 1 shows the peaks representing elements O, Na, Si, S, and Ti. The Si and Na elements indicate the synthesized silica material, while the Ti elements sourced from TiO\(_2\) and S elements indicate the presence of \(\text{SO}_4^{2-}\). For an element, O has the highest weight % because it is part \(\text{SO}_4^{2-}\), TiO\(_2\), and SiO\(_2\). In addition, the SEM-EDX data informs that \(\text{SO}_4^{2-}/\text{TiO}_2-\text{SiO}_2\) catalysts can be synthesized through the impregnation method. Micrograph material shows that this catalyst is a porous material with a non-uniform pore size. In addition, it appears that the formation of aggregates overlapping between TiO\(_2\) and Silica so that the wall is getting thicker and the pore size is getting smaller. Therefore, the TiO\(_2\) and silica material cannot be observed clearly because the composite has formed and silica has acted as a framework. This also indicates that the impregnation method can be used in catalyst preparation.

![Figure 1. SEM-EDX analysis of the synthesized catalyst: SEM image of the catalyst and EDX spectrum of the catalyst depicting peaks for O, Ti, Si, and S.](image)
3.2. Statistical analysis
An analysis is recorded in the second-order equation model of the RSM. This quadratic equation model is explained according to the following equation: \[ y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \cdots + \sum_{i<j}^{k} \beta_{ij} x_i x_j + \varepsilon \] (6)

Equation 6 is applied as a group of design models of central-composite design (CCD), where \( y \) is the response variable (conversion), \( x_i \) is the code level of the independent variable \( i \) and \( x_j \) is the independent variable \( j \). The terms \( \beta_0 \), \( \beta_i \), \( \beta_{ii} \) and \( \beta_{ij} \) are the regression coefficients for each of the linear terms, the quadratic terms for the variable \( i \) and the interaction terms between the variables \( i \) and \( j \). The independent variable \( i \) is encoded by \( x_i \) and \( x_j \) for the independent variable \( j \). The total number of variables and optimized in the experiment is stated by code \( k \), while code \( \varepsilon \) represents a random error. This polynomial equation visualizes the relationship between the response and experimental rates of each factor and determines the optimal conditions on the response surface and contour plots.

This study uses observational data from research or actual coding factors that are processed in Design-Expert 11 software.

The optimal conditions of the synthesis process of Fatty acid ethyl ester were analyzed using Response Surface Methodology. An experimental design used by Central Composite Design (CCD) to assess the relationship between reaction conversion, ethanol to PFAD ratio reactants and the amount of catalyst to reaction time. Research observations were set on 20 data in accordance with the experimental design of the conversion response factor.

| Run | Factor 1      | Factor 2       | Factor 3    | Response 1 |
|-----|---------------|----------------|-------------|------------|
|     | A: Catalyst % | B: Ethanol/PFAD Molar ratio | C: Reaction Time hour | Conversion % |
| 1   | 7             | 15             | 4           | 84.569     |
| 2   | 8.363559      | 13             | 2.25        | 74.08      |
| 3   | 3             | 15             | 4           | 60.43      |
| 4   | 5             | 13             | 2.25        | 90.6       |
| 5   | 5             | 16.3636        | 2.25        | 79.96      |
| 6   | 3             | 11             | 4           | 72.74      |
| 7   | 5             | 13             | 5.19314     | 45.88      |
| 8   | 7             | 15             | 0.5         | 81.46      |
| 9   | 3             | 15             | 0.5         | 98.67      |
| 10  | 5             | 13             | 2.25        | 79.8       |
| 11  | 3             | 11             | 0.5         | 96.67      |
| 12  | 1.63641       | 13             | 2.25        | 86.95      |
| 13  | 5             | 9.63641        | 2.25        | 98.9       |
| 14  | 7             | 11             | 0.5         | 75.2       |
| 15  | 5             | 13             | -0.693137   | 37.87      |
| 16  | 5             | 13             | 2.25        | 23.28      |
| 17  | 5             | 13             | 2.25        | 98.89      |
| 18  | 5             | 13             | 2.25        | 96.57      |
| 19  | 7             | 11             | 4           | 20         |
| 20  | 5             | 13             | 2.25        | 98.66      |
In this study, two independent variables were determined, namely molar ethanol and the amount of catalyst $\text{SO}_4^{2-}/\text{TiO}_2-\text{SiO}_2$. On the other hand, the optimum esterification quality variable is the response (conversion) variable. Figure 1 is a 3D Response Surface plot for the interaction of time, amount of catalyst and ethanol to the PFAD molar ratio to the conversion response variable. The conversion value is calculated against changes in the value of free fatty acids in sample samples and recorded every 0.5 hours for 4 hours. The data is processed with surface response design to determine the optimum conditions of the process factors. The results of the surface response design using Design-Expert software with the second-order model is CCD. Predictions from the optimum process design for the amount of catalyst (%): 5, the Ethanol to PFAD molar ratio: 13 and reaction time (hour): 2.25

This surface responsiveness design analysis data can be a clue in the production of fatty acid ethyl ester.
FAEE Conversion (%): \( Y = 81.18 - 6.51A + 2.1B + 7.38C + 10.14AB + 1.26AC + 5.5BC + 0.5158A^2 + 3.67B^2 - 13.15C^2 \)

Where, \( Y \) is the conversion of esterification reaction, \( A \) is the amount of catalyst, \( B \) is ethanol to PFAD molar ratio, and \( C \) is reaction time.

The coefficient of determination \( (R^2) \) for the conversion is 0.4483 or 44.83%. This determination value explains that about 44.83% of research data was the effect of this treatment factor, while for other treatments was around 65.17% or greater effect. The regression parameter test results in Figure 2 states that the amount of catalyst and molar ratio of ethanol / PFAD did not have a significant effect as indicated by the \( p \)-value greater than \( \alpha = 0.05 \).

3.3. Characteristics of ethyl esters as biodiesel

The existence of synthesized ethyl ester from PFAD can be proven by Fourier Transform Infra-Red (FTIR) characterization. This characterization aimed to determine the functional groups in the sample. From the results of the Fourier Transform-Infra Red (FTIR) analysis, the peak appears in Figure 3 shows that the peaks at wavelengths of 1035.81 cm⁻¹, 1095.60 cm⁻¹ and 1199.76 cm⁻¹ indicating the presence of C-O groups from esters which usually appear at wavelengths of 1050 - 1300 cm⁻¹. The function of C-H alkanes (CH₂ and CH₃) appears at wavelengths of 2928.11 cm⁻¹ and 2854.74 cm⁻¹. For alkyl groups in esters due to alcohol reactants indicated at wavelengths of 1348 cm⁻¹ and 1471.43 cm⁻¹. For the functional group, C = O of the ester it usually appears at the wavenumber of 1690-1760 and in this picture is seen at 1737.92 cm⁻¹. From the results of FT-IR spectra analysis it can be concluded that the sample of the research results is biodiesel because alkane (-CH) functional groups are found according to the types of fatty acids, esters (-COO-) and alkyl from ethanol (R) forming ethyl ester compounds [14-15].

![Figure 3. Spectrum FT-IR of Palm Fatty Acid Distillate and Ethyl Ester](image)

In addition to the FT-IR spectrum which explains the presence of ethyl esters, it can also be noted that the ethyl ester spectrum derived from the palmitic acid feedstock with the process and application of SO₄²⁻/TiO₂-SiO₂ catalysts shows a similar spectrum model for ethyl esters from PFAD.

To prove the type and composition of esters (FAEE) formed, it was characterized by using Gas Chromatography-Mass Spectrometry (GC-MS). The results of the components of the FAEE can be seen in Figure 4. In addition, the GC-MS characterization results are used to calculate iodine value, saponification value, and cetane value. Cetane number (CN) indications are generally used as quality parameters related to ignition delay time and combustion quality. The high value of the cetane number informs the ignition property and the great chance that the ethyl ester can be used as biodiesel [11].
The results of GC-MS have selected 5 types of ethyl ester which has the highest % area as the main component of this biodiesel. The cetane number calculation uses equations 3, 4, and 5, and obtained 49.2 as its result, whereas for the cetane number determined by equation 5 which is a function of the iodine value (titrimetric method) and saponification value (titrimetric method), it was obtained 8.87 mg/g, 583.84 mg/g and 53.65.

![Figure 4. Chromatogram of the product esterification reaction](image)

**Table 2. Fatty acid ethyl ester of PFAD Biodiesel**

| No. | Ethyl Ester                              | Approximate composition (%) |
|-----|------------------------------------------|----------------------------|
| 1   | Palmitate Acid, Ethyl Ester (C₁₆H₃₆O₂)    | 36.69                      |
| 2   | Stearate Acid, Ethyl Ester (C₂₀H₄₀O₂)     | 7.56                       |
| 3   | Oleate Acid, Ethyl Ester (C₂₀H₃₈O₂)      | 38.8                       |
| 4   | Myristic Acid Ethyl Ester (C₁₆H₃₂O₂)     | 1.97                       |
| 5   | Linoleic Acid, Ethyl Ester (C₂₀H₃₆O₂)    | 8.42                       |
| 6   | Others                                   | 6.56                       |

Based on the results of the analysis, ethyl ester as biodiesel from PFAD feedstock had a cetane number that is in accordance with quality standards according to ASTM D6751 which is 48-60 [15].

4. **Conclusions**

The quality parameters tested are conversions as a response to the independent variables indicating that the conversion has a second-order model:

\[ Y = 81.18 - 6.51 A + 2.1 B - 7.38 C + 10.14 AB + 1.26 AC + 5.5 BC + 0.5158 A^2 + 3.67 B^2 - 13.15 C^2 \]

Optimization of the PFAD esterification process into ethyl ester in the maximum surface plot analyzes was obtained at the catalyst load of 5% by weight, the ratio of PFAD and ethanol was 13 Molar and the reaction time was 2.25 hours. Ethyl ester produced from this research was concluded as renewable biodiesel energy that has been indicated based on cetane number ranging from 49-54 and according to ASTM D6751.

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