OPTIMIZATION SYNTHESIS FATTY ACID ETHYL ESTER AS BIODIESEL FROM PALM FATTY ACID DISTILLATE USING $\text{SO}_4^{2-}/\text{TiO}_2$ CATALYST SUPPORTED BY MESOPOROUS SILICA

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ABSTRACT

This research has studied the synthesis of fatty acid ethyl esters for biodiesel production using heterogeneous $\text{SO}_4^{2-}/\text{TiO}_2$ catalysts supported by mesoporous silica. The characterization result of the catalyst using X-Ray of wide-angle powder (WAXRD) and Scanning Electron Microscope (SEM) gives information that the existence of silica as support of $\text{SO}_4^{2-}/\text{TiO}_2$ active site. Observation data were analyzed by Response Surface Design (Composite Central Design). The results of the conversion design analysis, it was observed that the number of catalysts: 5%, Ethanol / PFAD molar ratio: 13 and reaction time: 2.25 hours as a variable for optimization of the esterification process. The physical characterization of ethyl ester as biodiesel is recorded by viscosity and density according to ASTM D-6751. The presence of functional groups which show the formation of ethyl esters indicated by FTIR analysis as C-H (alkanes), C=O, C-O and C-H (alkyl, R). The composition and type of ethyl ester from fatty acids were determined through GC-MS analysis. The highest peaks are indicated as palmitate ethyl ester, stearate ethyl ester and oleate ethyl ester and inform that the esterification reaction carried out has succeeded in producing high-quality biodiesel.

Keywords: Palm Fatty Acid Distillate, Ethyl Ester, Esterification, Heterogeneous catalyst, Biodiesel, Esterification

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INTRODUCTION

Vegetable oils such as palm oil, soybeans, peanuts, and olive oil and animal fats such as beef fat have the opportunity as raw material for biodiesel production. However, the price of oil or fat is relatively high, increasing the cost of biodiesel production. Therefore, it is necessary to evaluate cheaper and easier alternative raw materials for biodiesel production. Substantial efforts have been made to develop non-edible vegetable oils and waste oils such as castor oil and used cooking oil as raw material for biodiesel.^{1,2,3} This type of feedstock was categorized in the second generation biofuel technology, which is sourced from non-food ingredients so that it does not interfere with food crops sustainability (first generation).⁴ The development of other raw materials such as palm fatty acid distillates as non-food raw materials is also very interesting. One of them is palm fatty acid distillate sourced from palm oil-based residual fatty acids which are a by-product of distillation or recovery from desired fatty acids.^{5,6} Also, palm fatty acid distillate constituents consisted of 49.06% palmitic acid, 4.07% linoleic acid, 14.89% palmitoleic acid, 9.24% elaidic acid or 85-95% fatty acids and 5-15% triglycerides.⁷ The high levels of fatty acids in palm fatty acid distillates cause alkaline catalysts to be relatively inefficiently applied.^{6,8} These raw materials which have fatty acids exceeding 0.5% were recommended for biodiesel production through the esterification reaction pathway.⁹ Therefore in this research, the esterification reaction pathway was chosen for synthesis Ethyl ester as biodiesel from palm fatty acid distillates using heterogeneous catalysts. The study of biodiesel production using ethanol as a reagent, because currently, ethanol is also

one of the renewable materials. The biodiesel production study seeks to use ethanol as a reagent because currently, ethanol can be synthesized and is a renewable material. In addition to conventional methanol, the use of ethanol reagents has also been studied even propanol and butanol can be used in biodiesel production.^{4,10} In connection with the focus of this research is the optimization of the process production of ethyl esters as biodiesel using sulfated titanium dioxide solid catalysts to support mesoporous silica. The process was carried out for variations in catalyst quantity (3%, 5%, and 7%), molar ethanol ratio to PFAD (11, 13 and 15), and temperature 80°C. Optimization of the biodiesel (ethyl ester) production process was determined using surface response design (3D surface plot)

EXPERIMENTAL

Palm fatty acid distillate (PFAD) is used as raw material, the reagent used ethanol (E.Merck) and synthesized catalysts. The catalyst used is the result of synthesis as titanium dioxide sulfate which is supported by mesoporous material.¹¹ This mesoporous material (Silica) was synthesized based on the modified *Ryoo* method.^{11, 12} The synthesized catalyst was characterized by a WAXRD ($\alpha=1.5406 \text{ \AA}$) in a diffractometer Bruker D2 Phaser 2nd Gen. And for morphology characterization of the catalyst was conducted by using a Scanning Electron Microscope (SEM). The focus of this study is to determine the optimum conditions for the production process of biodiesel (ethyl ester)

The esterification process of PFAD begins by liquefying large quantities using a hot plate, after which it is transferred to the reactor. The conditions in the reactor were set at 80 °C with a stirring speed of 250 rpm. Ethanol reagent was added to the reactor with a molar ratio of PFAD to 13 and followed by a certain amount of catalyst recorded in percent by weight against the weight of PFAD (7%, 5%, and 3%). After the desired operating condition of the reaction is reached, the set reaction time lasts up to 4 hours.

The variation of the molar ratio consisted of 11, 13 and 15 at the reaction temperature conditions for each process constant at 80 °C. Observations were made every 30 minutes by sampling. The analysis was carried out on the free fatty acid content which was calculated according to equations 1 and 2.

The results were determined using a formula: Acid Value = $\frac{56.1 \times N \text{ KOH} \times V \text{ KOH}}{\text{sample mass}}$ (1)

Reaction conversion is determined using the formula: Conversion = $\frac{C_0 - C_1}{C_0} \times 100$ (2)

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

RESULTS AND DISCUSSION

The procedure of this study was started by synthesizing heterogeneous catalysts and characterizing them. Catalyst performance was tested in the esterification of palm fatty acid distillate into fatty acid ethyl ester. Silica characterization and catalyst were indicated through the characterization of WAXRD with Bragg angles of $2\theta = 10- 60^\circ$.

Fig- 1: Diffractogram of XRD and SEM of Catalyst

Figure-1 shows the diffraction pattern of X-Ray of wide-angle powder (WAXRD) of synthesized $\text{SO}_4^{2-}/\text{TiO}_2$ catalyst which supported by silica. Sample silica which was characterized shows area of diffusion peak or amorph peak by Bragg corner recorded as around $2\theta = 23.43^\circ$.^{13, 14} These data recorded that this sample is amorph phase silica. The particular for the catalyst of characterization of $\text{SO}_4^{2-}/\text{TiO}_2$ the peak area of diffusion was at $2\theta = 25.19^\circ, 37.67^\circ, 47.90^\circ, 53.75^\circ$ and 54.92° . the indication of this peak supports the existence of the active site of $\text{SO}_4^{2-}/\text{TiO}_2$ and equal to previous studies.^{15, 16} Silica and TiO_2 have fused so that the walls appear thick and the pore size decreases in the micrograph in Fig-1. This treatment also has the effect of pressure and release of water so that the sample structure becomes large aggregates. This can occur as an effect of temperature treatment when drying and calcining the sample. This micrograph also shows that the active site $\text{SO}_4^{2-}/\text{TiO}_2$ has been impregnated in the silica matrix, which acts as the catalyst support site.

Optimal conditions for the synthesis of Fatty acid ethyl ester from PFAD feedstock using the heterogeneous catalyst was analyzed with Response Surface Methodology. The Central Composite (CCD) experimental design was chosen to assess the relationship between reaction conversion, the ratio of ethanol /PFAD reactants and the amount of catalyst to time. Data of observations were 20 of the run according to experimental design.

The second-order model equation given by RSM was used to predict process optimization and analysis the interaction between the variable and conversion reaction, which was the response from the experimental design. The quadratic equation model is explained according to the following equation (3).^{17,18}

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \dots + \sum_{i < j} \beta_{ij} x_i x_j + \varepsilon \quad (3)$$

This equation (3) has been widely applied as a group design model from central-composite design (CCD). Where y is the response variable ($y_{\text{Conversion}}$), X_i is the code level of the independent variables of i and X_j is the independent variable of j . The terms β_0 , β_i , β_{ii} and β_{ij} were regression coefficients for each linear term, quadratic conditions for variables i and interaction terms between variables i and j . The independent variable of i is encoded by X_i and X_j for independent variables of j . The total number of variables optimized in the experiment is stated as code. Whereas for code ε , it states a random error. This polynomial equation visualizes the relationship between the response rate and the experimental factors of each and determines the optimal conditions by the response surface. This study uses the type of Design-Expert software.

Fig-2: Effect of Interaction of Catalyst and Ethanol/PFAD on Conversion

Fig-2 expresses the treatment data of the amount of catalyst, molar of Ethanol / PFAD ratio and reaction time to reaction conversion as the response variable. Analysis of surface response design to determine the condition of the ethyl ester as biodiesel production process from the PFAD feedstock with the application of catalyst of heterogeneous $\text{SO}_4^{2-}/\text{TiO}_2\text{-SiO}_2$ (Mesoporous Silica). The response of the surface design is the reaction conversion using second-order models are CCD expressed in a 3-dimensional plot curve and

perturbation chart shown in Fig- 2. Recorded by factor coding: actual prediction of process design for optimum was: A = catalyst (%): 5, B = molar ratio of Ethanol / PFAD: 13 and, C = reaction time (hour): 2.25. Data from the design surface response analysis concluded that the process of producing fatty acid ethyl esters from PFAD feedstock was suggested to take place with the composition. The coefficient of determination (R^2) for the conversion was 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 response variable data were shown in Fig- 3 were interconnected in Fig- 2. The 3D curves shown in Fig.-2 were the results of the Surface Methodology Response analysis derived from the actual data implicit in Fig.-3

Fig.-3: The Relation Between Reaction Time Versus Conversion

The graphs in Fig- 3 indicate the number of efficient ethanol reactants with simultaneously of the catalyst was used. The experiment was designed to vary the molar ratio of ethanol to PFAD by 11, 13 and 15. The amount of catalyst as a fixed variable was 5%, the reaction temperature was 80°C and the reaction time was 4 hours. Whereas of the experimental for the variation of the catalyst was designed at 3%, 5%, and 7% and the molar ratio of ethanol to PFAD was 13, with the reaction temperature and time reaction were running at 80°C and 4 hours. The end of this experiment was very surprising because unexpectedly the amount of ethanol with a 15 molar ratio caused the catalyst activity to decrease. Theoretically, in the esterification reaction using a homogeneous catalyst, the more amount of ethanol is used, the higher the reaction conversion, until finally, the equilibrium condition of the reaction turns constant.

This prediction deviation was caused by a component of water formed, as shown in the reaction. The amount of water formed during the reaction will be more and together with ethanol it will be absorbed to fill the pore cavity of the catalyst so that it can inhibit mass transfer and ultimately reduce the activity of the catalyst. Figure-3 it can be seen that the reaction with a 13 molar ratio is still the best, where the final conversion achieved is 98.9%. The other graph in Fig.-3 is an appreciation of the effect of the number of catalysts at 3% and 7% and the fixed variable molar ethanol/PFAD ratio is 13.

Table-1: Viscosity and Density of the Reaction Product

S. No.	Quantity of Catalyst	Temperature (°C)	Ethanol (Molar)	Viscosity at 40°C (cSt)	Average ρ Ethyl Ester at 15°C (g/cm³)
1	3%	80	13	3.0621	0.8713
2	7%	80	13	3.6903	
3	5%	80	13	4.1198	
4	5%	80	11	3.9111	
5	5%	80	15	3.7596	

Characteristics of biodiesel or ethyl ester have been determined based on the standard method of ASTM D-6751.⁷ The standard quality values for density at 15 °C and Kinematic Viscosity at 40 °C were 860 - 900 kg /m³ and 4-6 mm² / s. The data in Table-1 shows that the physical properties of biodiesel include the best viscosity and product reaction density that meet the requirements of ASTM D-6751-02.^{6,19,20} These physical properties provide information that the esterification reaction pathway has been carried out has succeeded in converting Palm Fatty Acid Distillate into ethyl ester fatty acids as biodiesel.

Fig-4: Spectrum FT-IR of PFAD and Ethyl Ester

The presence of ethyl esters synthesized from PFAD can be proved by the characterization of Fourier Transform-Infra Red (FTIR). This characterization was used to find out the functional groups contained in the sample. From the results of the Fourier Transform-Infra Red (FTIR) analysis which reported the emergence of peaks in Fig.- 4 shows the emergence of peaks at wavelengths of 1035.81 cm⁻¹, 1095.60 cm⁻¹, and 1199.76 cm⁻¹ which indicate the presence of CO groups from esters that usually appear in wavelength 1050 - 1300 cm⁻¹. The functional groups of C-H alkane (CH₂ and CH₃) appeared at wavelengths of 2928.11 cm⁻¹ and 2854.74 cm⁻¹. For alkyl groups found in esters because of the presence of alcohol reactants in this case ethanol (C₂H₅) is shown at a wavelength of 1348 cm⁻¹ and 1471.43 cm⁻¹. For functional groups, C = O indicates esters which usually appear at wavenumbers 1690-1760 and in this Fig-4 appear at a wavelength of 1737.92 cm⁻¹. The peak is formed as a result of FT-IR analysis spectra which can be concluded that the sample from the research results is biodiesel. Indications characteristic FT-IR spectra can be concluded that the sample of the research is biodiesel for alkane functional group (-CH) found according to the type of fatty acid, ester (-COO-) and alkyl alcohol (R) to form a compound ethyl ester^{7,21,22}. The product of the esterification reaction PFAD recorded as the presence of the ethyl ester functional group has been proven through the FT-IR spectrum in Fig.-4. Clarification of the type and composition of esters (FAEE) formed was characterized using Gas Chromatography-Mass Spectrometry (GC-MS).

The identification through GC-MS analysis carried out has recorded the composition of fatty acid components and ethyl ester in the sample. Observations focused on 5 types of ester components which have a role in the quality of biodiesel. The quality is a set number, the higher the value shows that the biodiesel is of high-quality performance. The data in the figure shows the types of ethyl esters which each explain palmitate, stearic, oleic, myristic and linoleic and it is known that 3 components are the largest composition contained in the biodiesel synthesized. These three components represent cetane numbers in the range 55-58 for oleate ester and greater than 80 for palmitate ester and stearate ester²³. Focus on data % peak area some fatty acids were observed in Fig- 5, it can be calculated component formed ethyl ester reached 93.11%. Conclusions from the analysis of GC-MS stated that the fatty acid components contained in PFAD be as feedstock for the synthesis of ethyl esters as biodiesel quality.

Fig.-5: Chromatogram of Palm Fatty Acid Distillate (Before Esterification) and Ethyl Ester/Biodiesel (After Esterification)

CONCLUSION

In this study, we can conclude that the esterification reaction for biodiesel production can be managed using PFAD feedstock, a heterogeneous catalyst that has been synthesized and ethanol reagents. The conditions for the esterification process can be determined through observations from the analysis of the actual data and the Surface Design Response (Composite Central Design analysis model) which recorded that the amount of catalyst needed was 5%, and ethanol / PFAD were 13 molar at the reaction time of 2.25 hours. Observation of the ethyl ester produced recommends that this product is high-quality biodiesel.

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