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Optimization of Biodiesel Production via Esterification of Sludge Palm Oil (SPO) Over Montmorillonite Sulfonated Carbon Catalyst from Glucose

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Abstract. SPO contains high fatty acids with a palmitic acid content of 87.26 % and potentially can be converted into biodiesel. Optimization of SPO esterification using a sulfonated carbon montmorillonite catalyst from glucose has been conducted using Response Surface Methodology (RSM) with Central Composite Design (CCD) to produce biodiesel. The input parameters observed were temperature of 63.18 – 96.82 °C, catalyst weight of 0.3 – 3.7 g, and reaction time of 69.54 – 170.46 minutes and the output parameter were free fatty acid conversion percentage. The optimum conversion percentage was 88.02% at a temperature of 80.51 °C, catalyst weight of 2.25 g, and reaction time of 170.45 minutes. The value of the coefficient of determination (R^2 = 0.895) indicates that the quadratic model is relatively accurate enough to estimate the optimal input parameters. FTIR analysis showed that the esterification product's functional groups C=O and C-O were shown at 1713 cm^{-1} and 1088 cm^{-1}, respectively. Determination of the density and viscosity indicates that the biodiesel product have been qualified according to SNI-04-7182-2006.

INTRODUCTION

Global energy demand has increased sharply due to rapid industrialization and improved quality of life. The price of petroleum products and environmental problems emanating from transport exhaust is also increasing rapidly [1-2]. The most feasible way to solve this problem is to use alternative fuels. From various renewable energy sources, biodiesel or fatty acid methyl ester (FAME), has attracted more attention because it is non-toxic, biodegradable, and environmentally friendly [3-5]. In addition, biodiesel has a higher cetane number and flash point [6-7] and can be used directly or mixed with fossil diesel for use in engines [6, 8].

The main challenges for biodiesel production are related to the raw materials and production methods. Generally, biodiesel production can use raw materials from vegetable oils or animal fats with alcohol and catalyst. Sludge Palm Oil (SPO) is one of the raw materials in Indonesia developed for biodiesel production because of its high free fatty acid content [9-11]. In contrast to crude palm oil (CPO), SPO is not edible, therefore SPO for fuel needs is relatively not triggering competition and disrupting food needs. On the other hand, the CPO price continues to rise, so it is not economical to be processed in the long term [5, 12-13].

Generally, biodiesel could be produced through transesterification using an alkaline catalyst. However, this reaction requires feedstock with a low free fatty acid (FFA), and if this condition is not achieved, FFA could react with an alkaline catalyst, cause the formation of soap, which makes the catalyst inactive, and the purification process

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becomes difficult [14-15]. Esterification using a homogeneous catalyst is one of the potential pathways to overcome the shortcomings of transesterification because of its low costs and high efficiency [16]. However, that catalyst has disadvantages, such as difficulty to separate, cause significant equipment corrosion, and environmental pollution [17].

The use of solid acid catalysts to overcome the lack of homogeneous acid catalysts in esterification reactions has attracted the attention of various researchers. One of the solid acid catalysts that potentially can be used in biodiesel production is sulfonated carbon. Ogino et al. [18] reported that sulfonated carbon showed a higher active site than other solid acid catalysts such as a macroporous resin containing a sulfonic acid group and zeolite, in the esterification reaction levulinic acid with ethanol. Iryanti et al. [19] reported that the sulfonated carbon catalyst of glucose yields conversions of up to 93.4%, which is active, stable, and reusable. The raw materials for sulfonated carbon catalysts can be derived from renewable and low-cost materials such as a piece of wood waste, carbohydrates, orange peel waste, and others [20].

The catalytic activity of sulfonated carbon will be much more effective if placed on a supporting material. Montmorillonite is potentially used as a supporting material catalyst for biodiesel production because it has Lewis and Bronsted acid sites that can catalyze esterification. Montmorillonite was also reported to have good catalytic activity and high conversion in biodiesel production [21-22]. Furthermore, Authority [23] reported that the sulfonated carbon montmorillonite catalyst from glucose has an acidity of 9.4 mmol/g with a conversion percentage of 82.81% in the acetic acid esterification. However, the report has not obtained optimal values and only involves the influence of one independent variable, while the amount of catalyst, reaction time, and temperature also affect the percentage of biodiesel conversion simultaneously. Therefore, it is essential to optimize the parameters of the esterification reaction. Response surface methodology (RSM) is a statistical tool based on experimental design (DoE) and regression analysis. RSM can examine the impact of input variables on the output and determine the process's optimum conditions [24]. Central composite design (CCD) as an optimization tool in RSM has a better optimization advantage than Box-Behnken and Doehlert [25].

This study was focused on optimizing the SPO esterification using sulfonated carbon montmorillonite as a catalyst from glucose with input variables such as temperature, catalyst weight, reaction time, and the percentage of conversion of free fatty acids into biodiesel as output variable. The composition of free fatty acids in SPO would be analyzed using Gas Chromatography (GC), the esterification product would be analyzed using FTIR, also the viscosity and density of the product would be compared with SNI-04-7182-2006.

METHODOLOGY RESEARCH

Preparation of Catalyst and Sample

Montmorillonite sulfonated carbon catalyst from glucose was obtained from Authority [23] with the highest acidity of 9.4 mmol/g. SPO waste samples were taken at the anaerobic waste storage 1, PT Citra Koprasindo Tani (CKT), Tanjung Jabung Barat, Jambi Province. Samples of mud were taken with a bailer and put in a bucket. Fatty acid composition analysis of SPO using gas chromatography (GC) according to AOAC [26].

Esterification of SPO and Analysis of FFA Content

The esterification was carried out using a 250 mL boiling flask equipped with a reflux apparatus. An amount of 25 g of liquefied SPO was added with 100 mL of p.a ethanol, followed by a montmorillonite sulfonated carbon catalyst. The esterification reaction was carried out according to three variables: the ratio of temperature, reaction time, and the amount of catalyst shown in Table 1.

TABLE 1. Experimental range and levels coded of independent variables

Variables	Range and Levels					
	Code	-1.68	-1	0	1	1.68
Reaction temperature (°C)	X_1	63.18	70	80	90	96.82
Catalyst weight (g)	X_2	0.3	1	2	3	3,7
Reaction time (min)	X_3	69.54	90	120	150	170.46

Analysis of the free fatty acid content of SPO was carried out according to SNI-01-2901-2006 by preparing 2.5 g of SPO added with 10 mL ethanol, heated at 60°C, and stirred until completely dissolved. Then, the free fatty acids

are titrated with phenolphthalein indicator using NaOH titrant until produced a pink color. Free fatty acid content was calculated according to equation (1):

$$\text{Percentage of FFA (\%)} = \frac{V \times N \times 25.6}{W} \times 100 \quad (1)$$

W, V, N, and 25.6 are the weight of the sample (g), the volume of the titrant solution used (mL), the normality of the titrant solution, and the constant value of free fatty acid content as palmitic acid, respectively. The percentage of conversion of free fatty acids into biodiesel was calculated according to equation (2):

$$\text{Percentage conversion of FFA (\%)} = \left(\frac{FFA_o - FFA_p}{FFA_o}\right) \times 100 \quad (2)$$

FFA_o and FFA_p are the SPO free fatty acid and the free fatty acid after the esterification, respectively. The density (ASTM D-1298-99), viscosity (ASTM D 455), and the functional groups of the esterification product were determined and analyzed using FT-IR as well as the SPO was also analyzed.

Design of Experiment and RSM

RSM with central composite design (RSM-CCD) is used to determine interaction parameters and optimize the esterification biodiesel products. RSM is a statistical technique that has been used in many studies to find and optimize input parameters [27]. The input parameters observed in this study were reaction temperature (X_1), catalyst weight (X_2), and reaction time (X_3), while the percentage of free fatty acid conversion (Y) was observed as an output parameter. Thus, the CCD in this study was carried out with three levels and three factors in 17 experimental sets, with nine factorial points, six axial points, three midpoints, and a rotatability value of ±1.68. The list of Factors and levels can be seen in Table. 1

Each output parameter that is correlated to the input parameter is studied according to the second-order polynomial equation (3):

$$Y = b_o + \sum_{j=1}^{3} b_j x_j + \sum_{ij=1}^{3} b_{ij} x_i x_j + \sum_{ij=1}^{3} b_{jj} x_j^2 \quad (3)$$

Y is the predicted result of SPO conversion percentage, x_i and x_j represent variable, b_o is offset variable, b_j is a linear effect, b_{ij} is the first-order interaction effect, and b_{jj} is the quadratic effect [22]. The use of second-order polynomial equations as a model in RSM-CCD is very suitable and helps optimize input parameters with a minimum number of experiments and can adequately analyze interactions between parameters [28].

Data Analysis

Data from the study were analyzed using Minitab 18. Four main steps were taken to determine the optimum conditions. The steps begin with an analysis of variance (ANOVA), followed by regression analysis, visualizing data using contour plots, and end with the validation of the data [29].

RESULTS AND DISCUSSION

FT-IR Characterization of SPO and Esterification Product

FTIR analysis was carried out in order to identify the functional groups in SPO and esterification products and can be seen in Fig. 1. The spectra of SPO and the esterification product were relatively similar considering that this reaction did not cause a significant change in chemical or functional bonds. It can be seen that the absorption spectra of C=O in SPO appeared at 1705 cm^{-1}, the absorption of the C-O group appeared at 1095 cm^{-1} and the absorption of the C-H group at 2854 cm^{-1} [30-31]. It also can be seen that the C=O absorption band in the esterification product appeared at 1713 cm^{-1}, while C-O functional group appeared at 1088 cm^{-1}. These found were relatively consistent according to previous reports. Abdullah et al. [5] reported that the presence of ester compounds in the esterification product of SPO through FTIR analysis showed a carbonyl group (C=O) appeared at 1744 cm^{-1}, and ester group (C-O) appeared at 1234, 1119, and 1026 cm^{-1}. The FTIR spectrum revealed some significant variation in the 1750-1690 cm^{-1} region [32]. Shah et al. [33] and Mahesa et al. [34] reported that the area at 1708^{-1} and 1746 cm^{-1} were obtained from the absorption

of C=O of free fatty acids and triglyceride carbonyl esters, respectively. Furthermore, the esterification product showed a new peak of OH group at 3394 cm^{-1}. The appearance of the OH group in the spectra indicates the presence of a water and alcohol remaining from the separation [35].

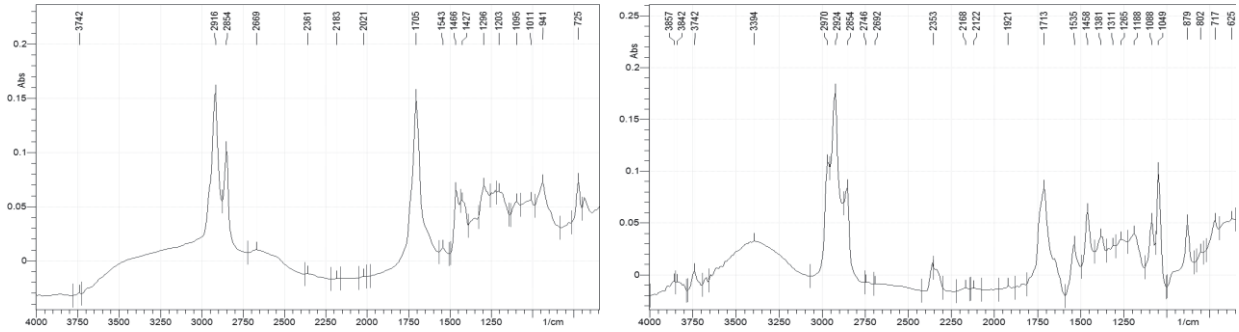


FIGURE 1. FTIR spectrums of (a) SPO and (b) esterification product

GC analysis showed that SPO contains various types of fatty acids. The SPO chromatogram was shown in Fig. 2. The highest fatty acid compositions were palmitic acid and oleic acid around of 66.60 and 19.78 %, respectively. The fatty acids contained in the SPO were saturated fatty acids which caused SPO in the solid form.

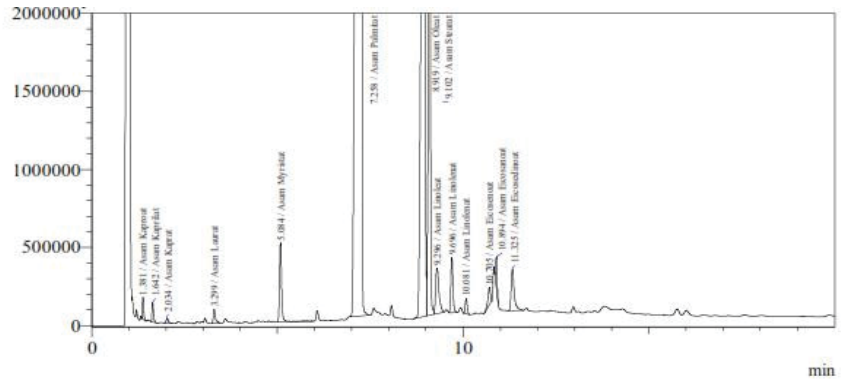


FIGURE 2. The chromatogram of SPO

Similar found also reported by Manurung [10], the highest fatty acid content was oleic acid followed by palmitic acid with percentages of 41.89 and 34.50%, respectively. The analysis of SPO free fatty acids (SNI-01-2901-2006) acquired approximately 87.26 %. The high content of free fatty acids could be potentially converted as biodiesel via esterification using an acid catalyst.

RSM Analysis

The regression equation for the FFA conversion percentage (%) obtained by regression analysis in code terms was observed through the following equation (4):

$$Y = - 79.14 + 1.33\ X_1 - 2.89\ X_2 + 6.25\ X_3 - 9.76\ X_1^2 - 4.68\ X_2^2 - 0.66\ X_3^2 + 7.03\ X_1\ X_2 - 1.10\ X_1\ X_3 - 0.49\ X_2\ X_3 \quad (4)$$

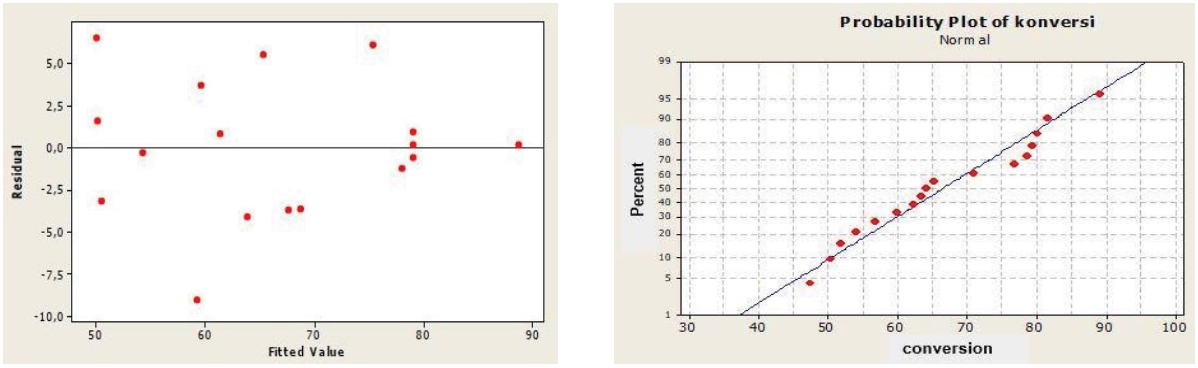
The mathematical model in equation (4) was investigated by the coefficient of determination (R^2). The value of R^2 and R^2_{adj} were 0.895 and 0.765, respectively. The value of R^2 showed that the model can calculate the conversion of 89.5%, which is verified by the equation and indicates an acceptable model accuracy. Thus, there were good agreement between experimental results and predictions for the quadratic model [28]. The positive sign of the term, such as X_1,

X_3, and X_1X_3, indicates a synergistic effect, while other than that term, a negative sign which indicates an antagonistic effect [22]. Analysis of variance (ANOVA) quadratic model can be seen in Table 2.

TABLE 2. ANOVA of quadratic model for conversion of FFA

Source	DF	Adj SS	Adj MS	F	P
Regression	9	2252,67	252.88	4.47	0,030
X_1	1	17,52	17.52	0.31	0.595
X_2	1	114,11	114.11	2.02	0.198
X_3	1	533,28	533,28	9.44	0.018
$X_1.X_2$	1	394.95	394,95	6.99	0.033
$X_1.X_3$	1	9.75	9,75	0.17	0.690
$X_2.X_3$	1	1.93	1,93	0.03	0.859
X_1^2	1	1074.39	1074.65	19.02	0.003
X_2^2	1	246.67	2.46.67	4.36	0.690
X_3^2	1	4.98	4.95	0.09	0.859
Error	7	395.60	56.51		
Lack of Fit	5	394.49	78.90	142.13	0.007
Pure error	2	1,11	0.56		
Total	16	2671.52			

According to ANOVA data, the smaller the probability value (P-value) indicates the significant effect of these variables [36]. P-values were applied to estimate the statistical significance of each model. With a 95% confidence interval, a low P-value (< 0.05) indicates that the parameters in the model are significant and have a good exposition of the true value [37]. Therefore, X_3 X_1X_2 dan X_1^2 are statistically significant. The homogeneity and normality of the conversion residuals are shown in Figure 3.



(a) (b)

FIGURE 3. (a) Plot of relationship between residual conversion vs fitted value and (b) plot of normality of residual conversion

Figure 3 (a) showed the plot between the residual and the fitted value seems to spread randomly around zero, which indicates that the residual variance is homogeneous [36]. The residual test shows that the independent variable affects the conversion of reaction products. On the other hand, the residual normality test in Figure 3 (b) was carried out based on the Kolmogorov-Smirnov test. The calculated KS statistical value was smaller than the table value, indicates that the obtained model was normally distributed [28].

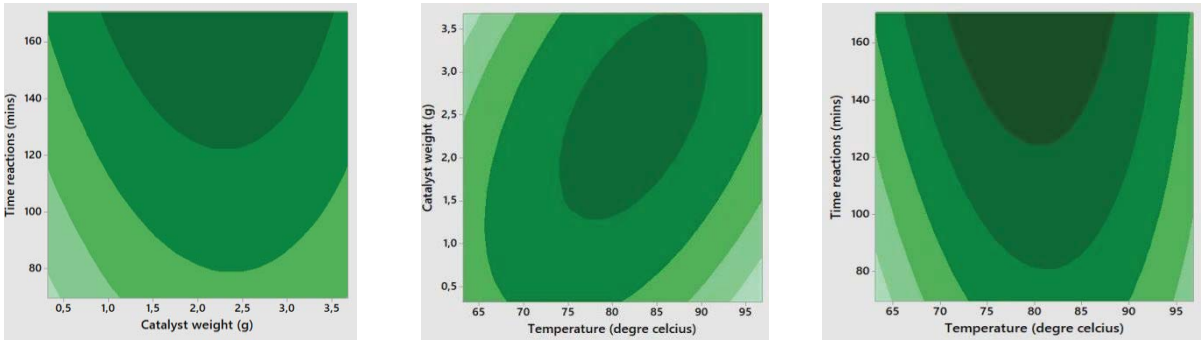
Optimization of FFA conversion using RSM

The results of the conversion of free fatty acids using a montmorillonite sulfonated carbon catalyst are shown in Table 3. Table 3 shows that the FFA conversion ranged from 47.35 to 88.88%. The largest conversion was obtained on the 13th run with a temperature of 80°C, a catalyst weight of 2 g, and a reaction time of 170.46 minutes. This situation shows that the free fatty acids in SPO almost entirely react with ethanol to form biodiesel.

TABLE 3. FFA conversion using montmorillonite sulfonated carbon catalyst

Runs	Temperature (°C)		Catalyst weight (g)		Time reaction (mins)		FFA conversion (%)
	Actual	Coded	Actual	Coded	Actual	Coded	
1	90	+1	3	+1	150	+1	76.78
2	90	+1	3	+1	90	-1	65.06
3	90	+1	1	-1	150	+1	62.20
4	90	+1	1	-1	90	-1	56.62
5	70	-1	3	+1	150	+1	59.82
6	70	-1	3	+1	90	-1	51.79
7	70	-1	1	-1	150	+1	81.45
8	70	-1	1	-1	90	-1	63.35
9	96.82	+1,682	2	0	120	0	54.02
10	63.18	-1,682	2	0	120	0	47.35
11	80	0	3.7	+1.682	120	0	79.83
12	80	0	0.3	-1.682	120	0	50.31
13	80	0	2	0	170.46	+1.682	88.88
14	80	0	2	0	69.54	-1.682	63.96
15	80	0	2	0	120	0	79.25
16	80	0	2	0	120	0	78.49
17	80	0	2	0	120	0	79.98

Contour plot of the percentage of free fatty acid conversion to the interaction of two variables is shown in Figure 4. In each graph, one residual variable is kept constant at the center point. Figure 4 (a) shows the interaction of catalyst weight and reaction time on the free fatty acid conversion percentage. The free fatty acid conversion percentage obtained was more than 80% at the condition of the catalyst weight of 1 – 3.5 g, and the reaction time was more than 120 minutes. The percentage of free fatty acid conversion increased as the catalyst weight increased because it was positively correlated with the increase in the catalyst's active site [37]. However, too much catalyst causes an increase in the mass transfer resistance of the reaction, and as a result, the conversion percentage decreases, the mixture becomes viscous, and mixing becomes more difficult. This trend is consistent with the reported by Karmakar et al. [38] on the conversion of jatropha and Karanja oil using Delonix regia char steam activated doped with H_2SO_4 and KOH also Aslan [39] on the conversion of black mustard seed oil to produce biodiesel using a KOH catalyst.



(a) (b) (c)

FIGURE 4. Contour plots of FFA conversion vs (a) catalyst weight (g) and time reactions (mins), (b) temperature (°C) and catalyst weight (g), and (c) temperature (°C) and time reaction (mins)

Figure 4 (b) shows the interaction of temperature and weight of the catalyst on the percentage of free fatty acid conversion. The free fatty acid conversion obtained is more than 75 % at a catalyst weight of 1.5 – 3.5 g and a reaction temperature of 75 – 90 °C. The percentage of free fatty acid conversion increases with increasing temperature. Very low temperatures cannot provide sufficient energy for the reaction to proceed appropriately, whereas high temperatures cause degradation of products or loss of reactants, resulting in a shift in the equilibrium of the reaction. The reduction in the percentage of free fatty acid conversion may be due to inefficient reflux and vaporization of

ethanol [38]. This found was also consistent according to Yahya [22] in the conversion of waste cooking oil using Fe-montmorillonite K10 catalyst. The interaction of temperature and reaction time on the percentage of free fatty acid conversion is shown in Figure 4 (c). The free fatty acid conversion obtained is more than 80% at a temperature of 70 – 90 °C and a reaction time of more than 120 minutes. The longer the reaction time, the greater the contact between substances, thus the free fatty acids in the SPO will react with ethanol more completely and produce a greater conversion of reaction products [36].

The input optimization variable to the output variable is shown in Fig. 5. The optimum conditions obtained were at a reaction temperature of 80.51 °C, a catalyst weight of 2.25 g, and a reaction time of 170.45 with a conversion percentage of 88.02 %. The obtained desirability function is 0.98 close to 1, which means the developed solution is very good [40]. Data validation shows that the experimental value corresponds to the predicted output.

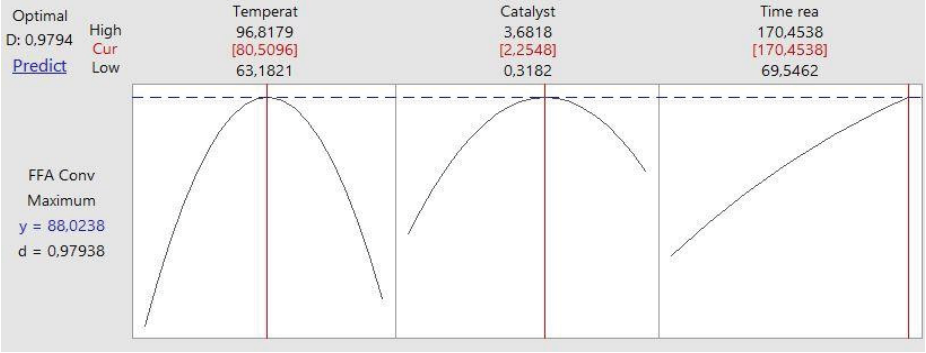


FIGURE 5. Optimization of parameters using minitab 18.

High density and viscosity can cause engine problems, especially during fuel atomization. Therefore, it is important to know the viscosity and density of biodiesel [35]. SNI-04-7182-2008 (0.85-0.90 gr/cm^{-3} for density and 2.3-6.0 for cSt viscosity) were used as a standard to see the quality of biodiesel. The density and viscosity of biodiesel at optimum conditions have been determined and the values obtained are 0.889 g/cm^{-3} and 5.24 cSt, respectively. It could be concluded that these values were within the range and in accordance with SNI-04-7182-2006.

CONCLUSION

SPO contains high fatty acids and is potentially converted into biodiesel with 87.26 % of palmitic acid Optimization of SPO esterification using a montmorillonite sulfonated carbon catalyst from glucose has been conducted using Response Surface Methodology (RSM) with Central Composite Design (CCD) to produce biodiesel. The optimum conversion percentage was 88.02 % at a temperature of 80.51 °C, catalyst weight of 2.25 g, and reaction time of 170.45. The value of the coefficient of determination (R^2 = 0.895) indicates that the quadratic model is relatively accurate enough to estimate the optimal input parameters. FTIR analysis showed that the esterification product's functional groups C=O and C-O were appeared at 1713 cm^{-1} and 1088 cm^{-1}, respectively. Determination of density and viscosity showed that the biodiesel product has been qualified according to SNI-04-7182-2006.

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