Potential of SO_4^{2-}/ ZnO Acid Catalyst for Heterogeneous Transesterification of Vegetable Oil to Biodiesel

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Abstract:

Among the possible renewable energy resources, diesel fuels derived from triglycerides of vegetable oils and animal fats have shown potential as substitutes for petroleum-based diesel fuels. The biodiesel could be produced from vegetable oils over homogeneous catalyst, heterogeneous catalyst, or enzymatic catalyst. In this study, the synthesized SO_4^{2-}/ZnO catalyst was explored to be used in the heterogeneous biodiesel production by using the vegetable oils and methanol. The study began with the preparation of SO_4^{2-}/ZnO catalyst followed by the transesterification reaction between vegetable oil with methanol. The independent variables (reaction time and the weight ratio of catalyst/oil) were optimized to obtain the optimum biodiesel (fatty acid methyl ester) yield. The results of this study showed that the acid catalyst SO_4^{2-}/ZnO is potential to be used as catalyst for biodiesel production through heterogeneous transesterification of vegetable oils. Optimum operating condition for this catalytic reaction is the weight ratio of catalyst/oil of 8:1 and reaction time of 2.6 h with respect to 75.5% yield of methyl ester products. The biodiesel product was also characterized to identify the respected fatty acid methyl ester components.

Keywords: biodiesel; super acid catalyst; palm oil; SO_4^{2-}/ZnO; fatty acid methyl ester

1. Introduction

Traditional fossil fuels are limited and causes greenhouse gas emissions. Therefore, greater efforts in research are now being directed towards the use of alternative renewable energies. Among the different possible resources, diesel fuels derived from triglycerides of vegetable oils and animal fats have shown potential as substitutes for petroleum-based diesel fuels. However, the direct use of vegetable oils in diesel engine can lead to a number of problems such as poor fuel atomization, poor cold engine start-up, oil ring stickening, and the formation of gum and other deposits. Consequently, considerable efforts have been made to develop alternative diesel fuels that have the same properties and performance as the petroleum-based fuels [1]. In addition, biodiesel is better than diesel fuel in terms of sulfur content, flash point, aromatic content and biodegradability.

Among the many ways to produce diesel-like fuel from triglyceride vegetable oils, transesterification has been found to be the most viable process [2]. The advantages of biodiesel form transesterification used are [3]: (1) lower dependence on fossil fuels/oil; (2) renewable resources; (3) greenhouse gas emissions friendly because of the closed CO_2 cycle; (4) lower combustion emission profile [4]; (5) biodegradability; (6) improved combustion due to being an oxygenate; (7) low toxicity; and (8) it can be blended in any proportion with regular petroleum-based diesel fuel. In the transesterification, triglycerides in vegetable oil react with alcohol to form a mixture of glycerol and fatty acid alkyl esters, called biodiesel. If methanol is used, the resulting biodiesel is fatty acid methyl ester (FAME), which has proper viscosity, boiling point, and high cetane number. Methanol is the commonly used alcohol in this process, due to its low cost.

The transesterification reaction can be catalyzed by both acidic- and basic-catalysts. Currently from the literature review, most of the biodiesel are synthesized homogeneously using alkaline catalysts because the base catalysis is more active than acid catalyzed [5]. However, in the alkaline metal hydroxide-catalyzed transesterification, even if a water-free vegetable oil and alcohol are used, a certain amount of water is produced from the reaction of the hydroxide with alcohol. The presence of water leads to the hydrolysis of the esters and forms a lot of soap. The formation of soap reduces the biodiesel yield and causes significant difficulty in product separation (ester and glycerol). To avoid the problem, it has been proposed to replace the homogeneous catalysts by a heterogeneous catalysts.

The use of heterogeneous catalyst simplifies greatly the technological process by facilitating the separation of the post-rection mixture. Efforts have been made to improve the mutual oil-methanol solubility for the synthesis of biodiesel by introducing co-solvents such as hexane. Methanol-to-oil ratios, reaction temperature, and the

catalyst amount are variables that affect the activity of heterogeneous basic catalysts. In some researches **[1, 6]**, a high reaction temperature and a high pressure are usually needed to obtain a high conversion for solid acid-catalyzed transesterification. On the other hand, the high reaction temperature and the high pressure are not preferable in the operation cost point of view. Suppes et al. **[6]** achieved enhanced conversion using elevated temperatures of 240-260 ^{o}C with CaCO$_3$ as catalyst whereas Verziu et al. **[7]** investigated low temperatures with use of microwave and ultrasonic conditions. Solid acid catalysts have broadened their applications in biodiesel production recently as the effort was made to replace homogeneous catalysts in conventional biodiesel production processes with heterogeneous catalysts. Previous studies on the transesterification of triglycerides using heterogeneous base catalysts were MgO **[8]**, Ba(OH)$_2$ **[9]**, CaO **[9]**, zeolites **[10]**, mixed of zinc and aluminium **[11]**, KF/ZnO **[12]**, Li/CaO **[13]**, LiNO$_3$/Al$_2$O$_3$ **[14]**, while for acid catalysts were SO$_4^{2-}$/ZrO$_2$ **[15]**, SO$_4^{2-}$/SnO$_2$ **[16]**. Results of the heterogeneous transesterification catalytic reaction researches showed promising yield of fatty acid methyl ester, but the reaction time is still long (more than 2 h). However, in this research the application of zinc oxide based - solid catalysts, particularly solid acid sulphated metal oxide, was investigated in order to find the most suitable acid catalysts, supports, and the most effective parameters on the catalyst activity. Another way to promote mass transfer problems associated with heterogeneous catalysts is using structure promoters or catalyst supports which can provide more specific surface area and pores for active species where they can anchor and react with large triglyceride molecules. The research was designed for investigating the potentiability, catalyst and process performance, and the relation with catalyst characterization.

This paper focuses on the transesterification of palm oil into biodiesel using suphated-zinc oxide (SO$_4^{2-}$/ZnO) catalyst. This preliminary study was purposed for investigating the potential of zinc oxide based-catalysts which focused on optimization of process parameters to obtain the promising yield of biodiesel product using response surface methodology.

2. Experimentals

2.1. Materials

Palm oil (Bimoli brand, acid value: 1.614) and methanol (Merck, 99.9%) were used as feedstocks for transesterification reactions. Zinc sulphate (Merck, 99.5%) was used as zinc precursor in the synthesis of zinc-based catalyst, while sulphuric acid (Merck, 95-97%) was used as sulphated agent material.

2.2. Catalyst Preparation

The ZnO catalyst was obtained after decomposition of zinc sulphate in a box furnace (Ney Vulcan 3-550) at 727 ^{o}C for 5 hours at atmospheric environment. The sulphated-zinc oxide (SO$_4^{2-}$/ZnO) was prepared by incipient wetness impregnation method. The required amount of ZnO powder was immersed into sulphuric acid solution (2 M) and was aged for 6 hours. The mixed materials were then filtered and dried in an oven (Memmert) at 110 ^{o}C for overnight. The dried material was then calcined in a box furnace at 300 ^{o}C for 3 hours. The resulted catalyst (SO$_4^{2-}$/ZnO) was then crushed to a powder material.

2.3. Transesterification Reaction

The transesterification of palm oil with methanol was carried out in the liquid phase using a 500 ml flask as reactor. This reactor was equipped with reflux condenser, stirrer, temperature measurement, electric heater, and thermal controller. The catalyst was dispersed in methanol under agitation for 10 minutes at room temperature. The palm oil was then added into the mixture and sealed. The reactor was subsequently heated under vigorous stirring at a fixed speed of about 1500 rpm during each reaction test. Unless otherwise noted, all of the tests were carried out in a methanol/oil molar ratio of 6:1 and a reaction temperature of 65 ^{o}C. After the reaction was completed, the mixture was collected, aged, and filtered. The solid catalyst was collected. The liquid phase was separated between layers, where the upper layer was collected as biodiesel feedstock and the lower layer was separated as gliserol+methanol phases. The collected biodiesel products were analyzed using a Gas Chromatography – Mass Spectrometry (GC-MS) to identify the presence and composition of resulted fatty acid methyl ester (FAME). In the analysis, a Shimadzu GC-MS QP2010S was used equipped with Rastek RXi-5 MS column (30 m length), while helium was used as a gas carrier.

2.4. Design of Experiments

A central composite orthogonal design in the response surface methodology was employed for designing experimental works. In this research, two independent variables or process parameters, namely reaction time and weight ratio of catalyst/oil, were used as controlled factors. Meanwhile, other parameters, i.e. methanol/oil ratio

(higher than 6:1) and reaction temperature (65-70 $^{\circ}$C), were fixed and set from literatures. Ranges of independent variables (Table 1) were chosen based on conditions obtained from the exploratory tests prior to this optimization. The response (biodiesel yield) and the controlling factors were modeled and optimized using the response surface methodology (RSM).

The value of star point, α, for orthogonality depends on the number of points in the factorial portion of the design which is given in Equation (1):

$$\alpha = \left\{ \left[\left(n_c + n_s + n_0 \right)^{1/2} - n_c^{1/2} \right]^2 * n_c / 4 \right\}^{1/4} \tag{1}$$

where n_c is the number of points in the cube portion of the design, n_s is the number of star points, and n_0 is the number of center points. Two independent variables or factors, namely, reaction time (X_1) and weight ratio of catalyst/oil (X_2), were selected as controlled factors. The ranges of independent variables were chosen based on the conditions from the variables screened prior to optimization. The ranges and levels used in the experimental work are given in Table 1. In the experimental design, all variables are coded for statistical calculation according to Equation (2) below:

$$x_i = \frac{\alpha \left[2X_i - \left(X_{max} + X_{min} \right) \right]}{X_{max} - X_{min}} \tag{2}$$

where x_i is the dimensionless coded value of the ith variable, X_i is the natural value of the ith variable, X_{max} and X_{min} are the highest and the lowest limit of the ith variable, respectively. The responses and the corresponding factors are modeled and optimized using the response surface methodology (RSM).

A quadratic polynomial equation was developed to predict the response as a function of independent variables and their interactions. In general, response for the quadratic polynomials is described in Eq. (3):

$$Y = \beta_0 + \sum_{j=1}^{2} \beta_j X_j + \sum_{j=1}^{2} \beta_{jj} X_j^2 + \sum_{i<j} \beta_{ij} X_i X_j \tag{3}$$

In this equation, Y is the predicted response, β_o is the intercept coefficient, β_j are the linear terms, β_{jj} are the squared terms, β_{ij} are the interaction terms, and X_i and X_j represent the independent variables. For each experimental factor the variance was partitioned into components, linear, quadratic and interaction, in order to assess adequacy of the second order polynomial function and significance of the terms.

Table 1. Ranges and levels of independent variables

Independent Variables	Range and Levels				
	$-\alpha$	Low level (-1)	Center level (0)	High level (+1)	$+\alpha$
Reaction Time (h) (X_1)	0.9	1	2.5	4	3.8
Weight Ratio of Catalyst/Oil (X_2)	4.1	4	6	8	8.2

Three-dimensional response surfaces and contour plots were used for facilitating a straightforward examination of the influence of experimental variables on the responses. Coefficients of the models were estimated using multiple regression analysis. Fit quality of the model was judged from their coefficients of correlation and determination. The adequacy of each model was also checked with the analysis of variance (ANOVA) using Fisher F-test and p-value. The significance test is purposed to determine relationship between the response and a subset of the independent variables.

3. Results and Discussion

3.1. Modelling and Optimization of Process Parameters

The experimental design matrix including the experimental results which is designed using central composite design of response surface methodology are presented in Table 2. The result consists of 12 sets of coded conditions expressed in the natural values. The design consists of a two-level full factorial design (2^2=4), 4 star

points and 4 center points. The sequence of experiment was randomized in order to minimize the effects of uncontrolled factors.

Table 2. Experimental design matrix in their natural values and experimental results

| Run No.	Independent Variables		Dependent Variable
	Time (h)	Weight Ratio of Catalyst/Oil	Biodiesel Yield (%)
1	1.0	4.0	71.1
2	1.0	8.0	72.7
3	4.0	4.0	75.1
4	4.0	8.0	73.1
5	0.7	6.0	68.7
6	4.3	6.0	71.7
7	2.5	3.6	72.5
8	2.5	8.4	75.4
9	2.5	6.0	75.3
10	2.5	6.0	76.7
11	2.5	6.0	74.8
12	2.5	6.0	75.2

The objective of the present study is to determine the optimal values of reaction time (X_1) and weight ratio of catalyst/oil (X_2) such that the maximum biodiesel yield is achieved. The coefficients of the models developed in Eq. (3) are estimated using multiple regression analysis technique. Therefore, the empirical mathematical model of the biodiesel product yield (Y) is presented in Eq. (4).

$$Y = -1.22704 X_1^2 + 8.70791 X_1 - 0.04989 X_2^2 + 1.57303 X_2 - 0.3 X_1 X_2 + 57.99125 \qquad (4)$$

The three-dimensional surface plot of the biodiesel product yield model shown in Figure 1 represents an estimated response (yield) over the process parameters (reaction time and weight ratio of catalyst/oil) over the SO_4^{2-}/ZnO catalyst. Meanwhile, Figure 2 reveals the contour plot of the same empirical model simulation. The results of this study showed that the acid catalyst SO_4^{2-}/ZnO is potential to be used as catalyst for biodiesel production through transesterification of vegetable oils. Optimum operating condition for this catalytic reaction is the weight ratio of catalyst/oil 8:1 and reaction time 2.6 hours with respect to 75.5% yield of methyl ester product.

The appropriateness of the models is judged from the determination coefficient, R^2, which reveals a total variation of the observed values of activity about its mean. In this study, the regression coefficients are estimated with a satisfactory determination coefficient of $R^2=0.81$. The R^2 value means a good agreement between the experimental and the predicted values of the fitted model. It implies that 81% of the total variation in the response is justified by the model. In addition, the correlation coefficient (R =0.90) for the fitted model signifies an acceptable correlation between the experimental and the predicted values. The good fitting is also implied by relation of predicted and observed biodiesel yield as shown in Figure 4.

The adequacy of the empirical model was also checked by analysis of variance (ANOVA) as presented in Table 3. In general, the calculated F-value should be greater than that of tabulated value of the model or lower p-value to be considered as good fitting. In fact, the calculated F-value (in overall) corresponding to the empirical model is 4.98 which is higher than the tabulated F-value (4.38). The F-value shows a statistically significant regression at 5% level of significance especially for reaction time parameter. Therefore, the null hypothesis (H_0) is rejected at 5% level of significance based on the high F-value implies that at least one of the independent variables contributes significantly to the model. In fact, there are two terms that having F-value higher than F-table. This conclusion agrees to lower p-value of the terms. The p-value is defined as the smallest level of significance that would reject the null hypothesis, H_0.
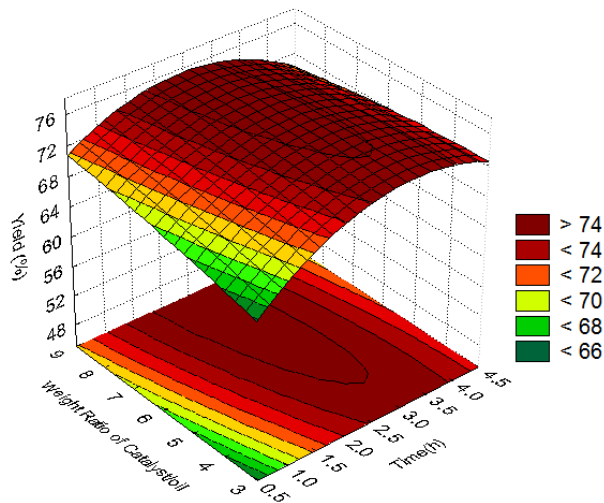
Figure 1. Effect of reaction time and weight ratio of catalyst/oil on the biodiesel product yield in surface plot corresponding to the empirical model in Equation (4).
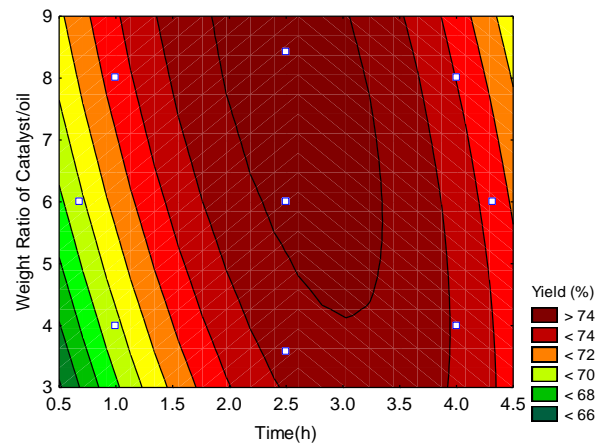
Figure 2. Effect of reaction time and weight ratio of catalyst/oil on the biodiesel product yield in contour plot corresponding to the empirical model in Equation (4).
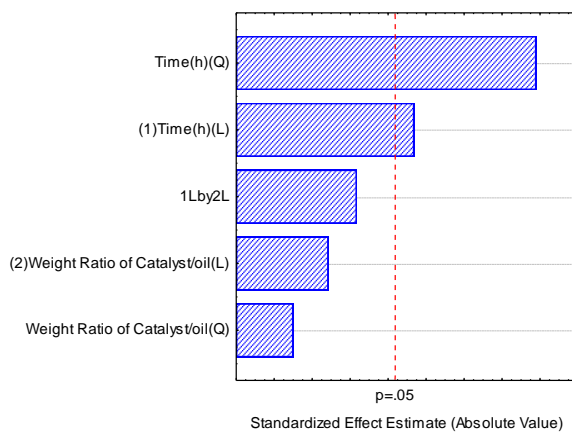
Figure 3. Effect of each term towards the empirical model (Equation 4)
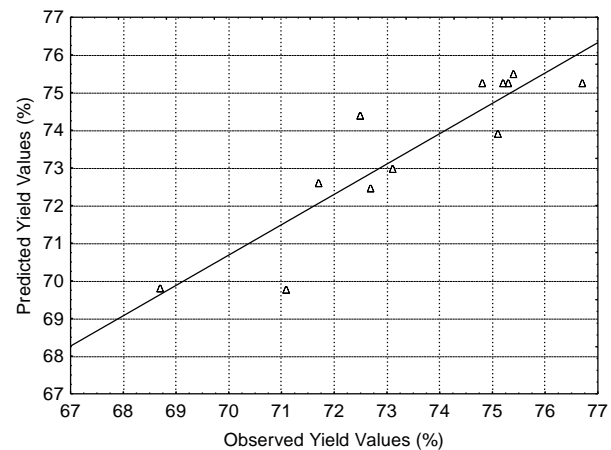
Figure 4. Relation of predicted and observed values of biodiesel yield

Table 3. ANOVA study of the empirical model fitting

Source	Sum of Square	Degree of freedom	Mean Square	F-value	p-value
X_1	9.30702	1	9.30702	4.95430	0.067653
X_1^2	32.67817	1	32.67817	17.39521	0.005874
X_2	1.39515	1	1.39515	0.74267	0.421909
X_2^2	0.17072	1	0.17072	0.09088	0.773240
X_1X_2	3.24000	1	3.24000	1.72471	0.237073
Error	11.27144	6	1.87857		
Total SS	58.06250	11			

Note: Calculated F-value of model = 4.98; F from table ($F_{0.05,5,6}$) = 4.38

3.2. Effect of Process Parameters on Biodiesel Yield

From Figures 1 and 2, it is shown that reaction time has higher effect significantly on the yield of biodiesel than that of weight ratio of catalyst/oil. However, variations of weight ratio of catalyst/oil has lower effect to biodiesel production. The similar trend is also shown in interaction effect between reaction time and weight ratio of catalyst/oil. The trends were also revealed in Figure 3 which respect to effect of each variables. The more

reaction time the more effective contact between the reactants and the catalyst which results in the more effective transesterification process. High yield of fatty acid methyl ester was found at enough reaction (longer than 2 hours) as concluded in recent literatures [1, 3, 15, 17]. According to previous study [17], the reaction time effect is affected by methanol to oil ratio, reaction temperature, and surface area of catalyst. The reaction temperature is crucial for the kinetics of reactions because reaction rates are the temperature-dependent functions according Arrhenius Law. Transesterification of vegetable oils with methanol takes place in the liquid phase, hence the reaction temperature should not be above the boiling point of methanol. Therefore, temperature of 65 ^{o}C is considered the optimal reaction temperature in some literatures [17]. The high temperature may accelerate the diffusion of molecules and adsorption and desorption of molecules on catalysts [1,3]. The optimal methanol/oil molar ratio is to be determined as the tradeoff of energy saving and the complete reaction is considered. Compare to Reddy's work [18], a methanol/oil molar ratio of 27:1 was needed to obtain over 99% conversion in 24 h at room temperature.

The catalyst to oil weight ratio or the catalyst amount used in reactions affects the reaction rate significantly though it doesn't change the equilibrium conversion for reversible reactions. In general, the more active the catalyst, the less amount of the catalyst is needed. According to Zhao [17], interaction effect between the catalyst surface area and the catalyst amount is significant. In this work, the slight effect of the weight ratio of catalyst/oil towards methyl ester yield is possibly due to lower surface area of the catalyst. However, characterization of this catalyst will be conducted in the next studies. The higher catalyst surface area leads to lower catalyst needed.

3.3. Biodiesel Product Characterization

The composition and some properties of synthesized biodiesel were also investigated. Table 4 shows identification and composition of the biodiesel produced from transesterification of palm oil with methanol using GC-MS. It shows that the biodiesel product is mainly composed of hexadecanoic acid methyl ester, octadecadienoic acid methyl ester, 9-octadecenoic acid methyl ester, and octadecanoic acid methyl ester with percent of each component as listed in Table 4. The composition determines physical properties of synthesized biodiesel. Meanwhile, Table 5 summarizes selected properties of the produced biodiesel compared to that of Indonesian National Standard. The selected properties values are all in biodiesel specification ranges.

Table 4. Identification and Composition of the biodiesel produced from palm oil with methanol using GC-MS

Peak No	Molecular Weight	Component	Identified Compound	Composition (%)
1	16.756	$C_{13}H_{26}O_2$	Dodecanoic Acid Methyl ester	034
2	19.311	$C_{15}H_{30}O_2$	Tetradecanoic Acid Methyl ester	1.59
3	21.385	$C_{17}H_{32}O_2$	9-Hexadecenoic Acid Methyl ester	0.29
4	21.681	$C_{17}H_{34}O_2$	Hexadecanoic Acid Methyl ester	39.44
5	22.632	$C_{18}H_{36}O_2$	Heptadecanoic Acid Methyl ester	0.15
6	23.520	$C_{19}H_{34}O_2$	Octadecadienoic Acid Methyl ester	42.82
7	23.580	$C_{19}H_{36}O_2$	9-Octadecenoic Acid Methyl ester	7.46
8	23.689	$C_{19}H_{38}O_2$	Octadecanoic Acid Methyl ester	6.63
9	24.880	$C_{15}H_{28}O$	2,4,6-trimethyl 11-Dodecen	0.35
10	25.302	$C_{19}H_{36}O_2$	Octadecenoic Acid Methyl ester	0.3
11	25.500	$C_{21}H_{42}O_2$	Eicosanoic Acid Methyl ester	0.64

Table 5. Selected properties of biodiesel product

Properties	This work	Indonesian National Standard
Density (g/ml)	0.887	0.85 – 0.89
Kinematic Viscosity (cSt)	2.62	2.3 – 6.0
Acid Value	0.051	Max 0.8
Cetane Value	58.034	Min 51
Iod Value	62.45	Max 115
Saponification Value	211.67	261.26

4. Conclusions

The synthesized SO_4^{2-}/ZnO (sulphated zinc oxide) catalyst was explored to be used in the heterogeneous biodiesel production from vegetable oil and methanol. The study began with the preparation of SO_4^{2-}/ZnO catalyst followed by the optimization of transesterification process between vegetable oil with methanol. The results of this study showed that the acid catalyst SO_4^{2-}/ZnO is potential to be used as catalyst for biodiesel production through heterogeneous transesterification of palm oil. The optimum operating condition for this catalytic reaction is the weight ratio of catalyst/oil of 8:1 and reaction time of 2.6 h with respect to 75.5% yield of methyl ester products. The biodiesel product was mainly composed of the respected fatty acid methyl ester components. The next research was focused on investigating the different catalyst, the relation between performance and catalyst characterization, and other methods for biodiesel production (like microwave, ultrasonic, and plasma technologies).

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