International Conference on Environment 2008 (ICENV 2008)

PALM OIL AS FEEDSTOCKS FOR BIODIESEL PRODUCTION VIA HETEROGENEOUS TRANSESTERIFICATION: OPTIMIZATION STUDY

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ABSTRACT

Fatty acid methyl ester (FAME) prepared by transesterification process using heterogeneous catalyst has receive a lot of interest lately as a sustainable and reliable source of biofuel. Apart from that, palm oil, being the worlds' cheapest edible oil has the economical potential to become the source of FAME. Therefore, in this study, the use of sulphated zirconia alumina as a heterogeneous catalyst to catalyze the transesterification of palm oil with methanol to FAME is studied. This study was carried out using design of experiment (DOE), specifically response surface methodology (RSM) based on four-variables central composite design (CCD) with $\alpha = 2$. The transesterification process variables are reaction temperature (60-180 °C), reaction period (1-5 hours), methanol to oil ratio (4-12 mol mol^{-1}) and amount of catalyst (2-10 wt%). In this study involving many multiple process variables, design of experiment approach was found to be more superior than the conventional one variable at one time approach. Interaction between variables was found to have significant effect on the yield of FAME. At the following conditions; 3 hours of reaction period, 127 °C of reaction temperature, methanol to palm oil ratio of 8 and 6 wt% of catalyst, an optimum FAME yield of 83.3% can be obtained, indicating that sulphated zirconia alumina has the potential as a heterogeneous catalyst for the production of FAME from palm oil.

Keywords: Fatty acid methyl ester; Heterogeneous catalyst; Palm oil; Sulphated zirconia alumina

INTRODUCTION

Depleting non-renewable natural resources such as mineral petroleum has raised the concern for the need of renewable sources to overcome the shortage of transportation fuel in the coming era and at the same time to protect the environment from pollutants. Lately, biodiesel or more accurately, fatty acid methyl ester (FAME) derived from various renewable oil sources has been hailed as the potential substitute to replace petroleum-derived diesel oil. This is due to the similarity of cetane number, energy content, viscosity and phase changes of FAME to those of petroleum-derived diesel fuel. On top of that, the usage of FAME from renewable oil sources have the benefits of lower sulfur content, lower aromatic content, higher heat content (about 88% of no. 2 diesel fuel), biodegradability, renewability, ready availability and liquid nature-portability. [1]

In the literature, various edible and non-edible oils such as soybean, palm, rapeseed, sunflower seed, peanut, cottonseed, coconut, palm kernel, olive, jatropha, castor and rubber has

been reported for the production of FAME. Comparing between edible to non-edible oils, the former has the added advantage due to its abundant availability from the current agricultural industry. Currently, soybean and rapeseed are the common feedstocks for FAME production in USA and Europe, respectively. On the other hand, Asian countries are exploring crude palm kernel oil and crude coconut oil as FAME feedstocks [2]. However, since palm oil is the world's cheapest vegetable oil, therefore crude palm oil itself presents a promising alternative as a feedstock for FAME. Nevertheless, the study on converting palm oil to FAME using heterogeneous reaction is still very limited and only being explored in Asian countries, most probably due to its availability. Table 1 shows the properties of palm oil.

Table 1 - Properties of Palm Oil.

Fatty acids	Percentage (%)
Lauric, C-12:0	0.1
Myristic, C-14:0	1.0
Palmitic, C-16:0	42.8
Stearic, C-18:0	4.5
Oleic, C-18:1	40.5
Linoleic, C-18:2	10.1
Linolenic, C-18:3	0.2
Other/Unknown	0.8

Current commercial production of biodiesel (FAME) is via homogeneous transesterification that have a lot of limitations, making the cost of biodiesel not economical as compared to petroleum-derived diesel. One of the most significant limitations is the formations of soap in the product mixture leading to additional cost required for the separation of soap from the biodiesel. Apart from that, the formation of soap has also led to the loss of triglycerides molecules that can be used to form biodiesel. Besides that, since the catalyst and the reactants/products are in similar phase, the separation of products (FAME) from the catalyst becomes complex. On the other hand, heterogeneous transesterification can overcome all these limitations in which solid based catalyst is used instead of homogeneous catalyst, making it a more efficient process for FAME production with lower cost and minimal environmental impact.

Due to the advantages of heterogeneous transesterification process, many different types of heterogeneous catalysts have been developed and reported for the transesterification of various oils to FAME. Among the various types of catalyst reported are alkaline earth metal oxides, anion exchange resins, various alkali metal compounds supported on alumina and zeolite such as potassium-loaded alumina, ETS-10 zeolite, calcium methoxide, calcium oxide and strontium oxide. Xie et al. [3] studied the transesterification of soybean oil to methyl ester using potassium-loaded alumina catalyst. Besides that, Suppes et al. [4] studied the transesterification reaction of soybean oil with zeolite and metal catalysts for the production of biodiesel, while Jitputti et al. [2] studied the transesterification of crude palm kernel oil and crude coconut oil using several acidic and basic solids. There are also many other reports on heterogeneous catalysts in the literature [5-9]. In short, all these study indicated that different oils would require different solid catalyst for optimum conversion to FAME.

Thus, in this study, the production of FAME from palm oil using sulphated zirconia alumina as the heterogeneous catalyst will be presented. Statistical design of experiments will be

used to accumulate and analyze information on the effect of process variables on the yield of FAME from palm oil, rapidly and efficiently using minimum number of experiments. As illustrated in the later section, this method was found superior than the conventional method of studying one variable at one time while keeping the rest constant. Optimization was then carried out to obtain the process variables that could lead to optimum yield of FAME.

MATERIALS AND METHODS

Materials. Purified palm oil was purchased from Yee Lee Edible Oils Sdn Bhd, Malaysia. Methanol and n-Hexane were purchased from R & M Chemicals, UK. and Merck KGaA., respectively. Methyl heptadecanoate (internal standard) and standard references for methyl esters analysis; methyl myristate, methyl palmitate, methyl stearate, methyl oleate, methyl linoleate were obtained from Fluka Chemie, Germany. The catalyst was self-synthesized by using Zirconium Oxide, Aluminium Oxide (purchased from R & M Chemicals, UK) and sulphuric acid (purchased from Sigma-Aldrich Chemie GmbH). The properties of palm oil are given in Table 1 [10].

Design of Experiments. The experimental design selected for this study is Central Composite Design (CCD) and the response measured is the yield of fatty acid methyl esters (FAME). The four transesterification process variables studied are reaction temperature, reaction period, ratio of oil to methanol and weight percentage of catalyst. Atmospheric pressure is used for all the runs.

Table 2 list the range and levels of the four independent variables studied. The levels of the variables investigated are chosen by considering the operating limits of the experimental apparatus. The upper temperature level, 180 °C, is determined by the maximum allowable operating temperature for the batch reactor that is at 200 °C. The lower level is at 60 °C. Reaction period is from 1 to 5 hours. Methanol to oil ratio is at 4 to 12 with methanol in excess to drive the reaction forward. Weight percentage of catalyst is from 2 wt% to 10 wt%. The value of α for this CCD is fixed at 2. Table 3 shows the complete experimental matrix of CCD for the 2^n factorial design (n factors, each at two-levels). The first 8 runs correspond to half of the 2^4 design. The combination of each of the variables at either its lowest (-2.0) level or highest (+2.0) level with the other variables at zero constitute the axial points. 5 additional runs (last 5 rows of the matrix) were carried out at the center points to estimate the overall curvature effect. The order in which the runs were made was randomized to avoid systematic errors.

Table 2 - Levels of the Transesterification Process Variables Chosen for This Study.

Variable	Factor Coding	Unit	Levels				
			-2	-1	0	+1	+2
Reaction Temperature	x_1	°C	60	90	120	150	180
Reaction Period	x_2	hour	1	2	3	4	5
Methanol to oil ratio	x_3	-	4	6	8	10	12
Amount of catalyst	x_4	wt%	2	4	6	8	10

The response of the transesterification process was used to develop a mathematical model that correlates the yield of FAME to the transesterification process variables studied through first

order, second order and interaction terms, according to the following second order polynomial equation,

$$\frac{1}{Y} = b_o + \sum_{j=1}^{4} b_j x_j + \sum_{ij=1}^{4} b_{ij} x_i x_j + \sum_{j=1}^{4} b_{jj} x_j^2 \qquad (1)$$

where $\frac{1}{Y}$ is the inverse yield of FAME, x_i and x_j represent the variables, b_o is the offset term, b_j is the linear effect, b_{ij} is the first order interaction effect and b_{jj} is the squared effect.

Model Fitting and Statistical Analysis. Design Expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, USA) was used for the regression analysis of the experimental data to fit the second order polynomial equation and also for evaluation of the statistical significance of the equation developed.

Activity Study. Transesterification reactions were carried out in a low pressure batch reactor with a magnetic stirrer, as shown in Figure. 1. Mixture of palm oil, catalyst and methanol was charged into the reactor. The mixing intensity of the magnetic stirrer was set at 350-400 rpm. The reaction temperature, duration, ratio of oil to methanol and weight percentage of catalyst were set according to the values proposed in the DOE shown in Table 3. The excess methanol from the samples was removed using rotary evaporator. The upper layer of the sample was separated from the bottom layer and was analyzed to detect FAME content.

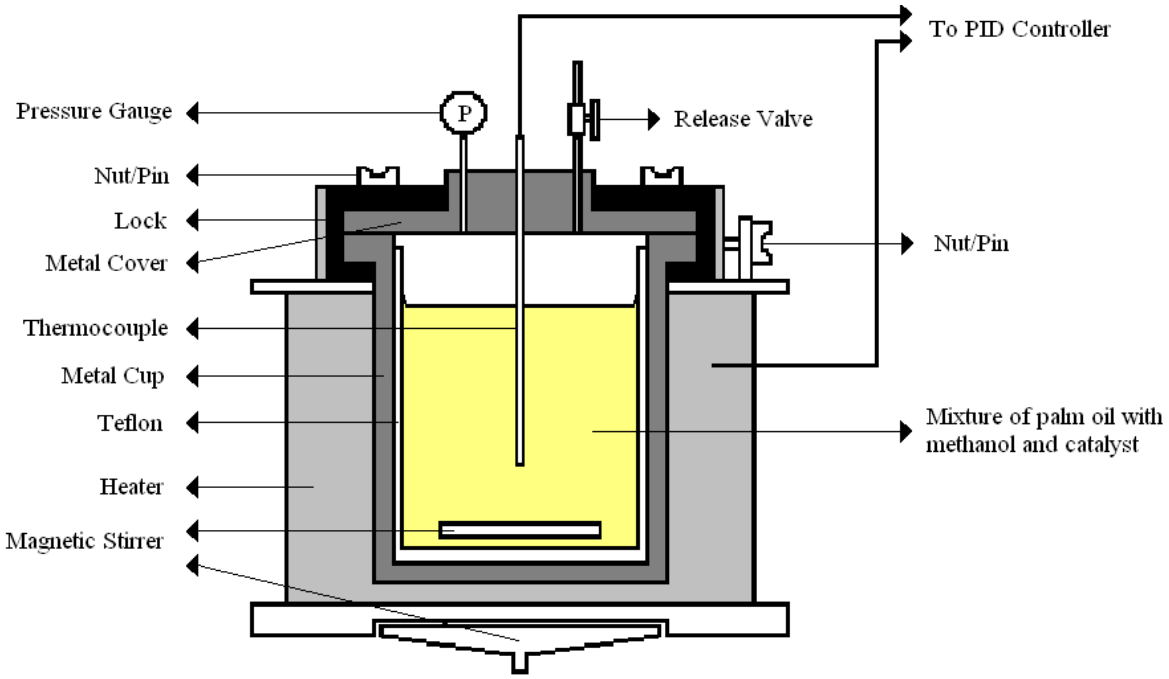

Figure 1 - Schematic Diagram of the Experimental Set-up for the Transesterification Process.

Table 3 - Experimental Design Matrix and Results.

Catalyst Code	Experimental variables				Yield (%)
	Temperature (°C)	Period (hour)	Ratio Methanol/Oil (mol mol^{-1})	Catalyst (wt%)	
SZA01	+1	+1	+1	-1	75.39
SZA02	+1	+1	-1	-1	71.25
SZA03	+1	-1	+1	+1	76.20
SZA04	-1	+1	-1	+1	21.54
SZA05	+1	-1	-1	+1	68.63
SZA06	-1	-1	+1	-1	7.82
SZA07	-1	+1	+1	+1	22.91
SZA08	-1	-1	-1	-1	2.32
SZA09	-2	0	0	0	1.49
SZA10	+2	0	0	0	82.81
SZA11	0	-2	0	0	65.32
SZA12	0	+2	0	0	75.46
SZA13	0	0	-2	0	53.91
SZA14	0	0	+2	0	74.96
SZA15	0	0	0	-2	67.33
SZA16	0	0	0	+2	74.64
SZA17	0	0	0	0	72.57
SZA18	0	0	0	0	72.85
SZA19	0	0	0	0	72.48
SZA20	0	0	0	0	72.06
SZA21	0	0	0	0	71.99

Analysis. The resulting products from the transesterification processes were analyzed using Gas Chromatography (GC) which was equipped with Nukol™ column (15 m x 0.53 mm, 0.5 μm film) to identify the presence of fatty acid methyl esters (biodiesel) in the sample. Helium was used as the carrier gas. Oven temperature at 110 °C was initially hold for 0.5 minute and then increased to 220 °C (hold for 8 minutes) at a rate of 10 °C min^{-1}. The temperatures of the injector and detector were set at 220 °C and 250 °C respectively. A quantity of 1 μl from each sample was injected into the column. Methyl heptadecanoate was used as internal standard for the calculation of the yield. The yield of the transesterification processes were calculated as sum of weight of FAME produced to weight of palm oil used, multiplied by 100. The formula is given as:

$$\text{Yield of FAME} = \frac{\sum \text{Weight of Fatty Acid Methyl Esters (g)}}{\text{Weight of Palm Oil Used (g)}} \times 100\% \qquad (2)$$

RESULTS AND DISCUSSION

Development of Regression Model Equation. The model equation that correlates the response (yield of palm oil to FAME) to the transesterification process variables in terms of actual value after excluding the insignificant terms is:

$$\frac{1}{Y} = +0.012 - 0.16x_1 - 0.020x_3 + 0.081x_1^2 + 0.059x_1x_2 + 0.038x_1x_3 + 0.059x_1x_4 + 0.038x_2x_3 - 0.091x_2x_4 + 0.037x_3x_4 \quad (3)$$

Note that inverse transformation of the yield was selected by the software as it was found to give a better fitting. Positive sign in front of the terms indicates synergistic effect, while negative sign indicates antagonistic effect.

Model Adequacy Check. The quality of the model developed could be evaluated from their coefficients of correlation. The value of R-squared for the developed correlation is 0.9892. It implies that 98.92% of the total variation in the yield of FAME is attributed to the experimental variables studied. The graph of the predicted values obtained using the developed correlation versus actual values is shown in Figure. 2. A line of unit slope, i.e. the line of perfect fit with points corresponding to zero error between predicted values and actual values is also shown in Figure. 2. This plot therefore visualizes the performance of the correlation in an obvious way. The results in Figure. 2 demonstrated that the regression model equation provided a very accurate description of the experimental data, which all the points are very close to the line of perfect fit. This result indicates that it was successful in capturing the correlation between the four transesterification process variables to the yield of FAME. The adequacy of the model was further checked with analysis of variance (ANOVA) as shown in Table 4. Based on a 95% confidence level, the model was tested to be significant as the computed F value (112.47) is much higher than the theoretical $F_{0.05\ (9,11)}$ value (2.91) and the p value less than 0.05. Besides that, each term in the model was also tested to be significant at a 95% confidence level as the computed F values for the respective terms are higher than the theoretical $F_{0.05\ (1,\ 11)}$ value (4.84) and the p values were all less than 0.05. Values of p greater than 0.05 indicates that the model terms are not significant. Thus, from these statistical tests, it was found that the model is adequate for predicting the yield of FAME within the range of variables studied.

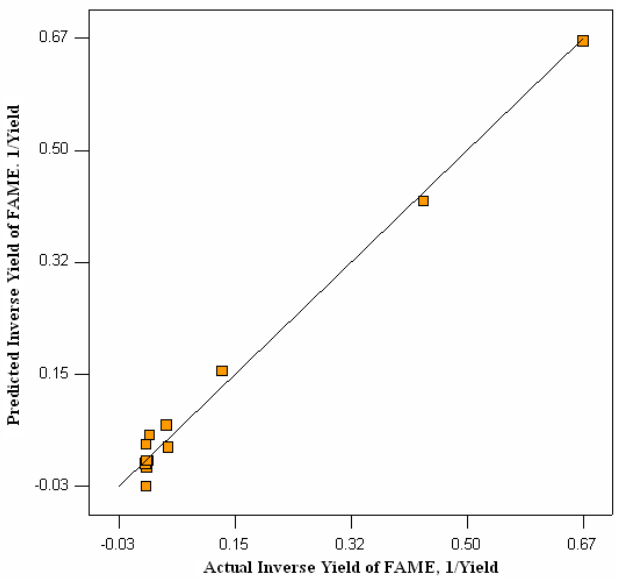

Figure 2 - Predicted Versus Actual Inverse Yield of FAME.

Table 4 - Analysis of Variance (ANOVA) for the Regression Model Equation and Coefficients.

Source	Sum of Squares	Degree of Freedom	Mean of Squares	F-Test	p value
Model	0.540	9	0.060	112.47	<0.0001
x_1	0.220	1	0.220	406.89	<0.0001
x_3	0.006	1	0.006	11.88	0.0055
x_1^2	0.180	1	0.180	344.01	<0.0001
x_1x_2	0.027	1	0.027	51.39	<0.0001
x_1x_3	0.012	1	0.012	21.60	0.0007
x_1x_4	0.028	1	0.028	51.56	<0.0001
x_2x_3	0.011	1	0.011	21.23	0.0008
x_2x_4	0.033	1	0.033	61.40	<0.0001
x_3x_4	0.011	1	0.011	21.04	0.0008
Residual	0.006	11	0.0005		

Effect of Transesterification Process Variables. Based on the analysis of variance, the transesterification reaction was significantly effected by various interactions between the process variables. On the other hand, significant individual process variables that effect the transesterification reaction is only reaction temperature, x_1 and ratio of methanol to palm oil, x_3. This result demonstrated the advantage of using design of experiments in capturing the interaction between variables that effects the transesterification reaction.

Effect of Individual Process Variables. Figure. 3 shows the effect of reaction temperature (90-150 °C) on the yield of the transesterification reaction. It was found that with increasing reaction temperature, the inverse yield decreased (or increase in yield). As seen in Figure. 3, the yield of

fatty acid methyl ester (FAME) increase significantly from 3.6% at 90 °C to 72.8% at 150 °C. The increase in the yield of FAME at higher reaction temperature is due to higher rate of reaction. Is it well reported in the literature that the intrinsic rate constants of the transesterification reaction is strongly influenced by the reaction temperature. Due to higher rate constant at higher temperature, this will lead to higher rate of reaction and eventually higher FAME yield. Another possible cause for the lower yield of FAME at lower reaction temperature could be due to the mixing efficiency of the contents in the reactor involving mainly the various reactants and solid catalyst. Naturally, palm oil and methanol are immiscible, the reactants initially form a three phase system: palm oil-methanol-solid catalyst. Therefore, the transesterification reaction is basically diffusion controlled. At lower reaction temperature, the lower viscosity of palm oil might cause poor diffusion between the phases that will lead to slower rate of reaction.

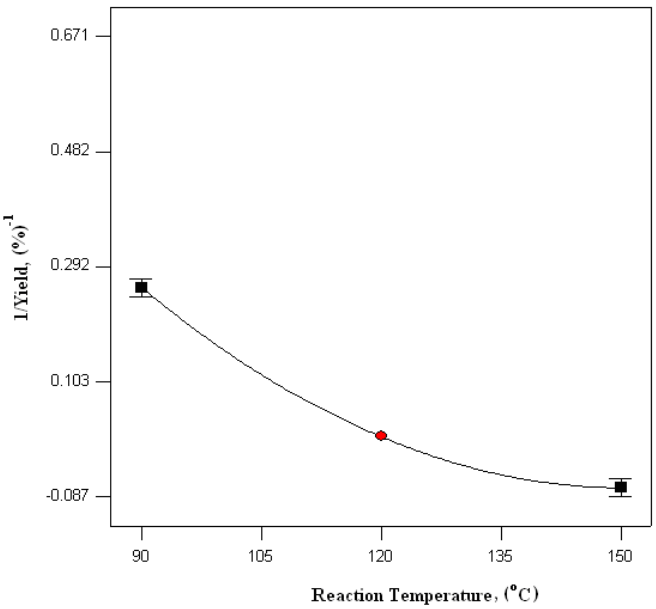

Figure 3 - Inverse Yield Versus Reaction Temperature at 3 hours Reaction Period, Methanol to Oil Ratio of 8 and 6 wt% Catalyst.

The transesterification process consists of a sequence of three consecutive reversible reactions where the triglyceride is successively transformed into diglyceride, monoglyceride and finally into fatty acid methyl esters (FAME) and glycerin. The ratio of methanol to oil is one of the important factors that affect the conversion of triglyceride to FAME. Stoichiometrically, three moles of methanol are required for each mole of triglyceride, but in practice, a higher molar ratio is required in order to drive the reaction towards completion and produce more FAME as products. The results obtained in this study is in agreement with this, as shown in Figure. 4, where at higher methanol to oil ratio, the inverse yield decreased indicating an increase in yield. Higher ratio of methanol used could also minimize the contact of access triglyceride molecules on the catalyst's active sites which could decreases the catalyst activity. Besides that, an increase in the ratio of methanol could also lead to the increase in the purity of the FAME layer which would also be responsible for the observed increased in FAME yield [11].

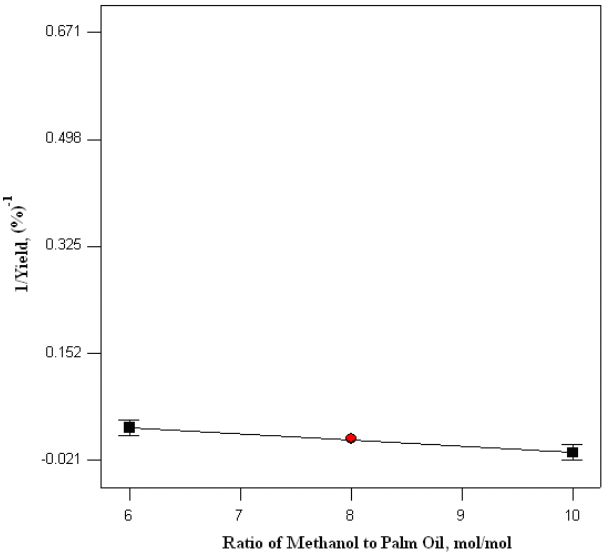

Figure 4 - Inverse Yield Versus Methanol to Oil Ratio at 3 hours of Reaction Period, Reaction Temperature of 120 °C and 6 wt % Catalyst.

Effect of Interaction between Process Variables. Unlike most of the results reported in the literature, the transesterification process variables were found not to have straight forward effect on the FAME yield. Instead, the process variables were found have to have significant interaction effects. Figure. 5, 6 and 7 show the interaction between reaction temperature with reaction period, ratio of methanol to oil and wt% of catalyst used, respectively, on the yield of FAME. Generally, an increase in reaction temperature was found to increase the yield of FAME in all three cases. This is due to similar explanation given in the previous section. Another notable observation is that at lower range of reaction temperature, using higher reaction period, higher ratio of methanol to oil and higher wt% of catalyst, always resulted in FAME yield higher than when using lower reaction period, lower ratio of methanol to oil and lower wt% of catalyst. However, at higher range of reaction temperature, the totally opposite was observed. Reactions carried out using lower reaction period, lower ratio of methanol to oil and lower wt% of catalyst was found to have higher yield as compared to reactions using higher reaction period, higher ratio of methanol to oil and higher wt% of catalyst.

For instance, referring to Figure. 5, the plot shows that at lower range of reaction temperature, 4 hours of reaction period can achieve higher yield than 2 hours of reaction period. However, when the reaction temperature was increase to the higher range values, the yield obtain is higher for 2 hours of reaction period than 4 hours of reaction period. The former observation can be easily explained as higher reaction period will ensure the transesterification reaction goes to completion, excess methanol will drive the reaction forward and higher wt% of catalyst used will increase the availability of active sites for the reaction to occur. However, at higher range of reaction temperature, the observations showed that using a combination of both, higher reaction temperature and higher reaction period or higher ratio of methanol to oil or higher wt% of catalyst used is not beneficial in increasing the yield of FAME. This is probably because at these conditions, the higher reaction temperature is already sufficient to push the reaction forward. If any of the other process variables were also to be set at a higher values, it will just push the reversible transesterification reaction backward, causing the yield of FAME to become rather

stagnant. This is reflected in the curve obtained for experiments carried out with a combination of higher range of reaction temperature and higher reaction period/ratio of methanol to oil/percent amount of catalyst (Figure. 5, 6 and 7). The yield obtain at these conditions is rather stagnant. This phenomena is further supported by the fact that reaction temperature is the most significant process variable that effect the yield of the FAME as indicated by the highest F value in the ANOVA (Table 4).

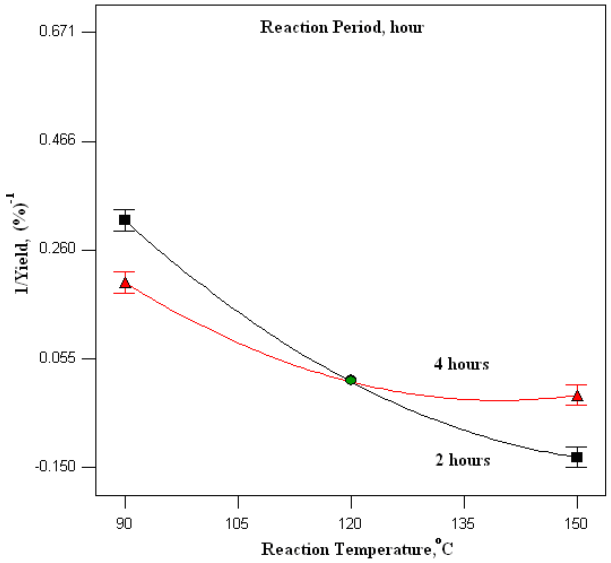

Figure 5 - Inverse Yield Verses Reaction Temperature at 2 hours and 4 hours of Reaction Period, Methanol to Oil Ratio of 8 and 6 wt% Catalyst.

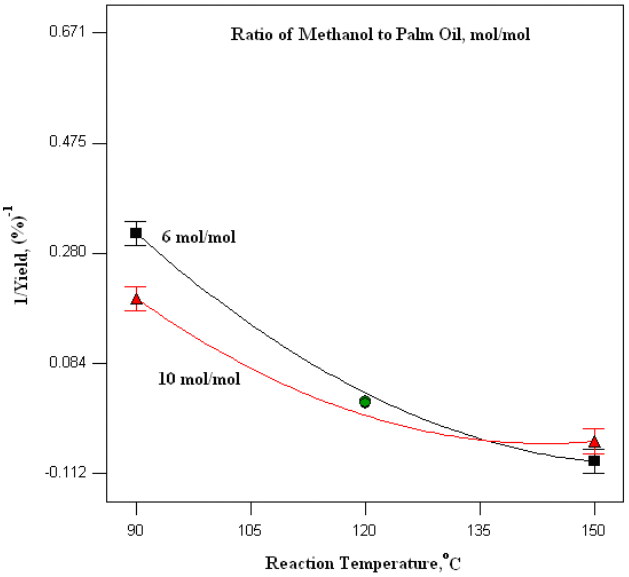

Figure 6 - Inverse Yield Versus Reaction Temperature at Methanol to Oil Ratio of 6 and 10, 3 Hours of Reaction Period and 6 wt% Catalyst.

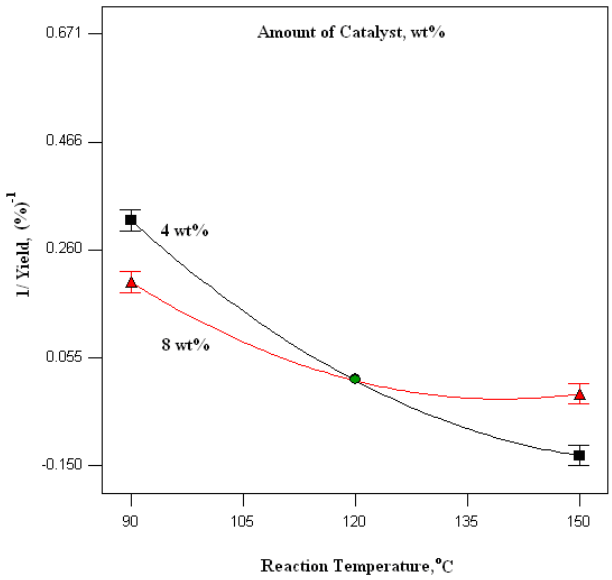

Figure 7 - Inverse Yield Versus Reaction Temperature at 4 wt% and 8 wt% Catalyst, 3 Hours of Reaction Period and Methanol to Oil Ratio of 8.

Figure. 8 and 9 show the interaction between methanol to oil ratio with reaction period and wt% of catalyst used, respectively on the yield of FAME. When the experiments were carried out using shorter reaction period (2 hr) and lower wt% of catalyst (4%), an increase in methanol to oil ratio was found to increase the FAME yield. However, in contrast, when the experiments were carried out using longer reaction period (4 hr) and higher wt% of catalyst (8%), an increase in methanol to oil ratio was found to decrease the FAME yield. This result further strengthen the reasoning given in the earlier section that a combination of higher values of process variables used in the transesterification reaction always lead to lower FAME yield due to backward reaction. Apart from that, the drop in FAME yield at higher methanol to oil ratio could also due to catalyst leaching and deactivation. Suwannakarn et al. [12] reported that SO_4^{2-} species in the sulphated zirconia alumina catalyst could leached out with the presence of methanol, most likely as sulphuric acid, which will further reacted with alcohols to form monoalkly and dialkyl sulfate species. This is reported as the main route for catalyst deactivation. Lopez et al. [13] also reported that the highly electronegative sulfate ions can be lost from the catalyst in the presence of an alcohol as shown in Eq. (4):

$$(SO_4^{2-}/ZrO_2^{2+}) + 2CH_3O^-H^+ \leftrightarrow H_2SO_4 + (2CH_3O^-/ZrO_2^{2+}) \qquad (4)$$

The degree of catalyst deactivation is dependent upon the exposure to the quantity and duration of alcohol. Therefore, at higher methanol to oil ratio, more catalyst might get deactivated and caused a drop in FAME yield.

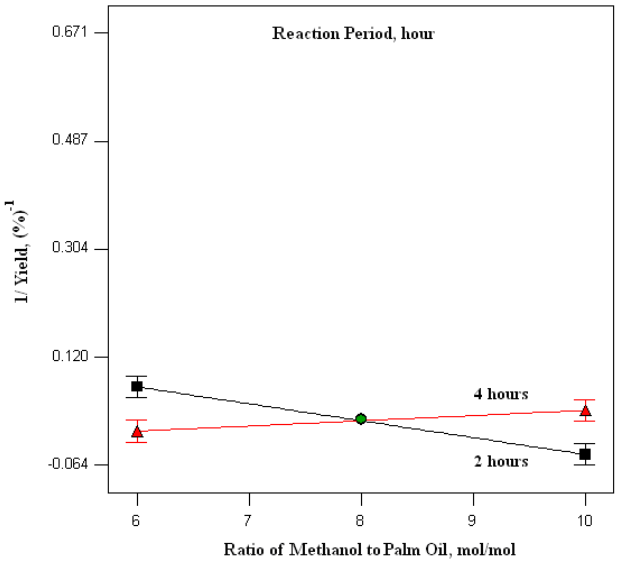

Figure 8 - Inverse Yield Versus Ratio of Methanol to Oil at 2 Hours and 4 Hours of Reaction Period and 6 wt% Catalyst.

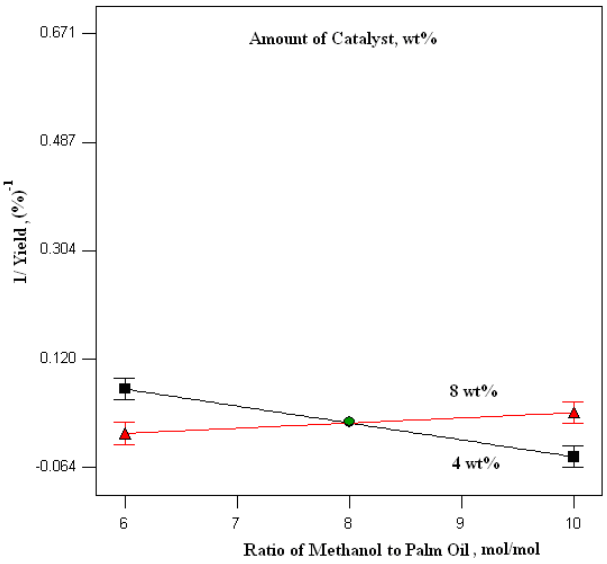

Figure 9 - Inverse Yield Versus Methanol to Oil Ratio at 4 wt% and 8 wt% Catalyst, 120 °C of Reaction Temperature and 3 Hours of Reaction Period.

Optimization of Process Variables. The results above have shown that the four transesterification process variables effect the yield of FAME, especially the interaction among the variables. Therefore, the next step is to optimize the process variables in order to obtain the highest yield using the model regression developed. Using the point prediction function in Design Expert, it was predicted that at the following conditions; 3 hours of reaction period, 127 °C of reaction temperature, methanol to palm oil ratio of 8 and 6 wt% of catalyst, an optimum FAME yield of 83.3% can be obtained. In order to verify this prediction, experiments were conducted and the results were comparable with the prediction. In most of the heterogeneous

catalyst transesterification study reported in the literature, a relatively either high reaction period or high reaction temperature is required in order to achieve a high yield in FAME. However, based on the optimization study, the conditions to obtain a relatively high yield in FAME can be easily achieved at 127 °C and 3 hrs of reaction time. Therefore, this study shows that sulphated zirconia alumina is a potential catalyst for the production of biodiesel from palm oil via heterogeneous transesterification.

CONCLUSIONS

Based on the experimental results obtained, it was found that all the process variables exhibited significant interaction effect on the yield of FAME. This shows the capability of design of experiment analysis in successfully capturing these effects. At the following conditions; 3 hours of reaction period, 127 °C of reaction temperature, methanol to palm oil ratio of 8 and 6 wt% of catalyst, an optimum FAME yield of 83.3% can be obtained. Therefore, it can be concluded that sulphated zirconia alumina is an effective catalyst for the production of biodiesel from palm oil via heterogeneous transesterification.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support from Science Fund and Universiti Sains Malaysia.

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