ABSTRACT: Plant-based ethyl esters can be used directly as biodiesel or as a bio-resource for other industries such as lubricant and detergents. In this work, production of ethyl ester from chemical transesterification of palm oil with ethanol using sodium ethoxide as catalyst has been optimized by Box-Behnken design and response surface methodology. Catalyst concentration was found to be the most significant parameter affecting the conversion rate of the reaction. The interaction of temperature and molar ratio of ethanol to palm oil had minor effect on the conversion rate. A reduced cubic model was developed to navigate the design space. It was predicted by the model at optimum reaction conditions, that is 1.2 wt% of sodium ethoxide and 12:1 molar ratio of ethanol to oil at 25 °C, that as high as 98% ethyl ester can be achieved. It was then verified experimentally that close to 100% conversion rate is achievable under these optimum conditions. © 2011 Curtin University of Technology and John Wiley & Sons, Ltd.

KEYWORDS: transesterification; design; optimization; palm oil; ethanol; response surface methodology

INTRODUCTION

An increase in the concern on the protection of environment from biologically hazardous wastes and the limitation of petrochemical resources has led to the development in the field of green chemistry. Consequently, petrochemical resources are gradually being replaced with bio-resources such as vegetable oils as the raw materials for various industrial applications.[11]

Alkyl esters of vegetable oils such as methyl and ethyl esters can be applied directly as biofuel or in the formulation of various products such as lubricants and cleaning agents.[2,3] The production of biodiesel from methyl and ethyl esters of vegetable oils had been studied by several researchers.[4–10] A review paper by this research group provides extensive information on this process, as well.[11] Although methanol provides favorable physical and chemical properties, as well as availability at low cost,[12] ethanol is still preferable in some applications because of the fact that it can be obtained from renewable natural base stocks.[13,14]

Transesterification of palm oil with ethanol to produce ethyl esters (ethanolysis) is shown in Eqn 1.[15]

\[
\text{CH}_2\text{COOR} + 3 \text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{catalyst}} 3 \text{CH}_2\text{CH}_2\text{COOR} + \text{CH}_2\text{OH}
\]

Molar ratio of ethanol to palm oil is 3:1 based on the stoichiometric Eqn 1. However, an amount of alcohol higher than the stoichiometric amount is often required to accelerate the reaction and to ensure complete conversion of triglyceride.

Experimental design and response surface methodology (RSM) have been used by researchers to determine the optimum conditions in transesterification reactions involved in methanolysis and ethanolysis. As an example, Jeong et al.[16] conducted an optimization study on methanolysis of lard by using central composite design. Chin et al.[17] used central composite design to optimize the methanolysis of waste cooking palm oil. An optimization study by using factorial design and RSM has been performed by Silva et al.[18] on the transesterification of castor oil with ethanol. Furthermore, ethanolysis of various vegetable oils including high oleic sunflower oil and high and low erucic Brassica carinata oil was investigated by Bouaid et al.[19] by using factorial design and RSM.

In this research, the main aim is to optimize the transesterification of palm oil with ethanol as there is no published data on the optimization of ethanolysis.
of palm oil in the literature so far. The variables investigated in this study were temperature, molar ratio of ethanol to oil, and catalyst concentration. The optimization of reaction parameters was conducted through an experimental design by using DESIGN-EXPERERT (version 8.0.1) software (State-Ease Inc, Minneapolis, MN, USA). The results obtained were presented as three-dimensional (3D) and contour graphs, which were discussed by means of RSM. A point prediction has been performed by the software as well.

**MATERIALS AND METHOD**

**Materials**

Refined cooking palm oil (palm olein) was purchased from the local market. Ethanol (99.8% purity) and anhydrous sodium sulfate were obtained from R&M Chemicals (Essex, UK). Technical grade sodium ethoxide (≥95%) was purchased from Fluka Chemicals (Castle Hill, NSW, Australia). GC-grade n-Hexane was purchased from Merck Chemicals (Selangor Darul Ehsan, Malaysia). Ethyl ester standards for GC analysis were purchased from Sigma-Aldrich (St. Louis, MO, USA).

**Experimental procedure**

Transesterification of palm oil with ethanol, to produce ethyl ester, has been conducted by placing 50 g of palm olein in a 150 mL jacketed glass reactor equipped with a Graham coil condenser. The required amount of catalyst for each experiment was dissolved in ethanol and was then added to the reactor. All the reaction blends were agitated with magnetic stirrer at a speed of 600 r/min. A reaction time of 120 min was employed to ensure the completion of the reaction at all the designed conditions. The product of reaction existed in two phases, and the separated phases was simplified by adding diethyl ether. The lower layer contains glycerol, and the soap formed during the reaction was separated and disposed. The upper phase containing ethyl ester was separated and washed with distilled water until no change in color in the rinse water (by using phenolphthalein indicator) was observed. The ethyl ester phase was filtered through anhydrous sodium sulfate and diethyl ether, and non-reacted ethanol was separated by evaporation as well. The product was analyzed using gas chromatography (GC) analysis.

The yield of ethyl ester is defined as the conversion rate. It is used to express the percentage of the conversion of triglyceride (palm oil) to ethyl ester, which is calculated using Eqn 2.

$$Y = \frac{\Sigma C_{EE}}{w_O} \times 100$$ (2)

Where $C_{EE}$ refers to the concentration of the ethyl ester transesterified product which includes ethyl laurate, ethyl myristate, ethyl palmitate, ethyl stearate, ethyl oleate, ethyl linoleate, and ethyl linolenate (mg/ml), and $w_O$ refers to the weight of the oil analyzed by GC (mg). The product was analyzed using gas chromatography.

Statistical design of experiments and data analysis was carried out using the DESIGN-EXPERT (version 8.0.1) software for the study of three variables at three levels of each factor by Box-Behnken method. The variables used in this study were temperature range of 25 to 75 °C, ethanol to oil molar ratio from 6:1 to 12:1 and catalyst concentration of C$_2$H$_5$ONa from 0.5 to 1.5 wt% based on the operating conditions investigated by other research teams. Catalyst concentration represents the initial amount of catalyst used in the reaction in terms of the weight percent of the initial amount of oil.

**RESULTS AND DISCUSSION**

The experimental design of the study on the effect of the parameters in terms of coded and actual values as well as ethyl ester yields obtained in each run are presented in Table 1. The linear and quadratic models suggested by the software indicated that the quadratic model was significant. The significant parameters shown were the catalyst concentration and its square value. However, in this work, the lack of fitness for the model was undesired and could not be improved by removing the insignificant terms. Therefore, the quadratic model was modified by the addition of the interactive term of temperature and square molar ratio ($AB^2$), which has resulted in a reduced cubic model for fatty acid ethyl ester. Consequently, all of the model terms except the square molar ratio ($B^2$) are desirable. The insignificant term of $B^2$ could not be eliminated from the model because the hierarchy of the model would be disarrayed.

Equation 3 shows the model for fatty acid ethyl ester ($Y$) in terms of coded values, in which $A$, $B$, and $C$ are referred to temperature, molar ratio of ethanol to oil and catalyst concentration, respectively.

$$Y = +91.99 + 3.20 A + 1.37 B + 8.29 C$$ \( -1.46 AB - 3.00 AC - 3.64 BC - 1.34 A^2 \) \( -0.51 B^2 - 6.14 C^2 - 5.97 AB^2 \) (3)

The model for fatty acid ethyl ester in terms of actual factors is presented in Eqn 4, in which the parameters of temperature, molar ratio of alcohol to oil, and catalyst concentration were expressed as coded values, and the yield of ethyl ester was expressed as actual values.

$$Y = +91.99 + 3.20 A + 1.37 B + 8.29 C$$ \( -1.46 AB - 3.00 AC - 3.64 BC - 1.34 A^2 \) \( -0.51 B^2 - 6.14 C^2 - 5.97 AB^2 \) (4)
catalyst concentration are denoted by $T$, $M$, and $C$, respectively.

\[
Y = +95.36625 - 1.3938 \, T - 19.02292 \, M + 99.4875 \, C + 0.45857 \, TM - 0.2398 \, TC - 2.42333 \, MC - 2.144 \times 10^{-3} \, T^2 + 1.27083 \, M^2 - 24.55 \, C^2 - 0.026556 \, TM^2
\]  

A statistical analysis of variance (ANOVA) was conducted by DESIGN-EXPERT (version 8.0.1) software for investigating the fitness of the model and significance of variables. Table 2 shows the $p$-value less than 0.0001 for the model, which implies that the model is significant. Besides, the predicted $R$-squared and the adjusted $R$-squared for the model are 0.9490 and 0.9946, respectively. This indicates a good agreement because the difference is less than 0.2. The noise ratio for this model is 58.256 ($>>4$) indicating an adequate signal. Hence, the model can be used to navigate the design space. The precision and accuracy of the model in predicting the percentage of fatty acid ethyl ester in different reaction conditions, which represents a good conformity between predicted conversion rates and the actual amounts of conversion rate, can be observed in Fig. 1.

Three-dimensional plots and contour plots in the studied range of variables for the model presented for fatty acid ethyl ester are shown in Figs (2a to 4b).

Table 2. Analysis of variance for the fatty acid ethyl ester model.

<table>
<thead>
<tr>
<th>Source</th>
<th>Fatty acid ethyl ester</th>
<th>$p$ value, probability &gt; F</th>
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</thead>
<tbody>
<tr>
<td>Model</td>
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<tr>
<td>$A$</td>
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<tr>
<td>$B$</td>
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<tr>
<td>$C$</td>
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<tr>
<td>$AC$</td>
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</tr>
<tr>
<td>$BC$</td>
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<td>$A^2$</td>
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<tr>
<td>$B^2$</td>
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<tr>
<td>$C^2$</td>
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<td>Significant</td>
</tr>
<tr>
<td>$AB^2$</td>
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<td>Significant</td>
</tr>
<tr>
<td>Lack of fit</td>
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<td>Adequate precision</td>
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<td>58.256</td>
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</table>

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**Figure 1.** Predicted conversion rates by the model vs actual values. This figure is available in colour online at www.apjChemEng.com.
can be seen in Fig. 2(a and b) that an increase in the molar ratio of ethanol to oil increases the conversion rate of ethanolysis of palm oil with 1 wt% catalyst in the temperature range of 25 to 50°C. By increasing the molar ratio of ethanol to oil from 6:1 up to 9:1 in the temperature range of 50 to 75°C with 1 wt% catalyst, the conversion rate is improved; whereas, higher molar ratios at the same temperature range (50 to 75°C) will lead to a reduction in the ethyl ester yield. Figure 3(a and b) indicates that with a molar ratio of 9:1 in the whole studied range of temperature (25 to 75°C), catalyst concentration has a positive effect on the conversion rate of reaction. In this way, as high as 95% ethyl ester can be achieved with 1.2% of catalyst. Furthermore, Fig. 4(a and b) shows that with molar ratios below 9:1 at 50°C, an increase in catalyst concentration improves the ethyl ester product. For molar ratios higher than 9:1 at 50°C, catalyst concentration up to 1.2 wt% has a positive effect on conversion rate. However, catalyst concentration greater than 1.2 wt% will not cause any significant increase in ethyl ester yield. Conversely, catalyst concentration greater than 1.2 wt% will cause a decrease in the conversion rate at molar ratio close to 12:1. The decrease of conversion rate at this range can be explained by the submersion and coverage of the active sites of catalyst by the excess amount of alcohol, which deactivates the catalyst and inhibits the conversion of triglyceride as suggested by Shu et al.\(^{[26]}\) in the methanolysis of waste vegetable oils.
The experimental results presented in Table 1 show that in the ethanolysis of palm oil at 25°C, 12:1 molar ratio and 1 wt% of C\textsubscript{2}H\textsubscript{5}ONa can achieve 96% fatty acid ethyl ester. This conversion rate has also been obtained at higher temperature of 50°C with lower ethanol to oil molar ratio of 6:1 and higher catalyst concentration of 1.5 wt%. In this work, the optimization of palm oil ethanolysis has been conducted both graphically and numerically. Figure 5 shows the overlay plot for minimum 90% conversion rate with 1.0 wt% catalyst. The plot indicates that a minimum conversion rate of 90% ethyl ester is achievable over a wide range of reaction parameters. On the other hand, Fig. 6(a and b) represents the overlay plots for minimum conversion rate of 95% with 1.0 wt% and 1.2 wt% of catalyst, respectively. It is obvious from Fig. 6a that 95% ethyl ester can be achieved with 12:1 molar ratio of ethanol to oil at 25°C using 1.0 wt% catalyst. The overlay plot in Fig. 6b shows that when the catalyst concentration increases to 1.2 wt%, as high as 95% ethyl ester is achievable either at 25°C with 12:1 molar ratio, or at higher than 60°C with 9:1 molar ratio of alcohol to oil. By using the point prediction function of the software, the model predicted the optimum reaction conditions of 12:1 molar ratio of alcohol to oil, 1.2 wt% of catalyst and 25°C would result in 97.82% conversion rate. This result was verified experimentally with 99.68% ethyl ester.

With these findings, it can be deduced that the catalyst concentration is the most significant parameter affecting the conversion rate in the ethanolysis of palm oil. This result is in conformity with other investigations on the ethanolysis of sunflower oil, Brassica carinata oil and castor oil.\textsuperscript{[18,19]} However, the interaction of alcohol to oil molar ratio and temperature cannot be excluded because obtaining desirable conversion rates at lower molar ratios of ethanol to oil necessitates higher temperatures as compared with the optimum conditions at room temperature of 25°C.

**CONCLUSION**

In this paper, the effect of reaction parameters optimized by Box-Behnken design and RSM on base-catalyzed ethanolysis of palm oil was investigated to enable the development of a reduced cubic model with good conformity between the actual experimental conversion rates and the values predicted by the model. The molar ratio of 12:1 for alcohol to oil and 1.2 wt% of catalyst at 25°C were determined as the optimum reaction conditions to achieve a possible close to 100% ethyl ester. Catalyst concentration is...
found to be the most influencing parameter on the production of ethyl esters, however, at reaction temperatures higher than room temperature the interaction of other parameters cannot be neglected.

Acknowledgement

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