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Optimization of waterless biodiesel production from palm stearin using response surface methodology

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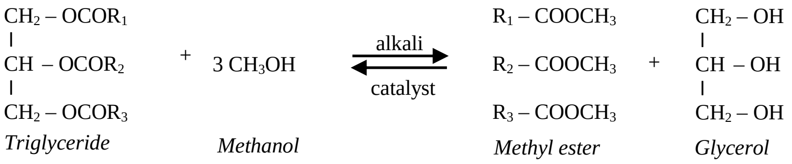
Abstract

In this research study, homogeneous transesterification of palm stearin using acetone as co-solvent and waterless purification of biodiesel were studied. The response surface methodology (RSM) statistical technique based on Box-Behnken design was applied to determine the optimum conditions for the transesterification process and the effects of the main parameters, such as the amounts of acetone, KOH catalyst concentration and reaction temperature on the biodiesel yield, including the flow rates of crude biodiesel passing through the ion exchange resin bed to remove soap and glycerin. The physical and chemical properties of biodiesel were determined according to biodiesel standard specifications. It was found that reaction temperature was the most important parameter. The optimum conditions were methanol to oil molar ratio of 8:1 with 24.7wt% acetone, 0.70wt% KOH catalyst, reaction temperature of 47°C and reaction time of 30 min. Furthermore, the study showed that the optimum condition for the waterless purification of initial soap content above 1,000 ppm was performed at the flow rate of 4.5 BV/h which reduced soap levels to below 50 ppm.

Keywords: *homogeneous transesterification, co-solvent, waterless purification, ion exchange resin bed, response surface methodology.*

1. Introduction

Biodiesel is an environmentally friendly alternative fuel that can replace petro-diesel with several advantages such as lower emissions of CO_2 and CO, and reduced unburned hydrocarbons and sulfur from the combustion. Conventionally, biodiesel is produced using the transesterification reaction of triglyceride (the vegetable oils and animal fats) with short chain alcohols such as methanol or ethanol, in the presence of suitable catalysts such as acid, base or enzymes, to form a mixture of fatty acid methyl esters. Transesterification is an equilibrium and reversible reaction during the conversion of oils/fats to biodiesel and glycerol. The reaction is shown in equation (1). The type of catalyst used depends on the amount of free fatty acid and water content in the raw materials. The alkali-catalyzed transesterification of vegetable oils using methanol is the most commonly employed reaction for the biodiesel production at the commercial scale. Several methods for biodiesel production, including mechanical stirring, supercritical alcohol, microwave processes, and co-solvent method have been developed (Patil et al., 2012; Thanh et al., 2013; Wang, Ou, Liu, Xue, & Tang, 2006). Because methanol and oil are immiscible, transesterification occurs in a heterogeneous system at the interface between the immiscible reactants. According to Thanh (2013), acetone is the best co-solvent for the biodiesel production at temperature of 25-35°C, further dependent on type of raw materials used while also able to increase the transesterification reaction rate effectively (Thanh et al., 2013). They applied this method to produce biodiesel from waste cooking oil, canola, and catfish oil. After the transesterification reaction, crude biodiesel is separated from the glycerin phase, however many contaminants are still be present in the biodiesel product depending on the technology of transesterification. The mixture of fatty acid methyl esters (crude biodiesel) should be purified to fulfill the biodiesel standard specifications. Downstream purification steps are needed to remove various impurities such as unconverted tri-glycerides (TG), mono-glycerides (MG), di-glycerides (DG), free fatty acids (FFA), glycerin, methanol, catalyst, soaps and others from crude biodiesel to prevent a significant damage of diesel engines. Removal of glycerides from biodiesel is an important step because when these compounds are heated, they tend to polymerize forming the deposits. They also increase the cloud point of biodiesel and complicate the operation of liquid-liquid phase separation due to their amphiphilic nature (Stojković, Stamenković, Povrenović, & Veljković, 2014). The glycerin content in biodiesel depends strongly on the residual content of methanol acting as co-solvent. When methanol is completely removed, the free glycerin content depends only on temperature. Even if methanol is not present hydrophilic glycerin can be solubilized in the oil phase by amphiphilic MG and DG. These glycerides can separate from the oil during storage and precipitate as a result of temperature changes or long residence times. Soluble glycerin is also a problem because glycerin polymerizes on hot surfaces with the formation of deposits. For all of these reasons glycerin should be completely removed. Furthermore, soaps are produced by the reaction of the remaining FFAs with alkaline homo-geneous catalysts in the transesterification reactor. Soaps are amphiphilic substances that bring phase separation and plugging problems in downstream steps. Additionally, these inorganic salts lead to corrosion in lines and vessels and they must also be completely removed in the final biodiesel product (Vera et al., 2011). The traditional water wash method causes several problems and also creates large amount of waste water during biodiesel purification. Water washing introduces water to the fuel, which can cause fuel degradation by hydrolysis. Therefore, the fuel must be dried to remove trace amounts of water, which causes an increased energy cost. Waterless purification and dry wash processes are additional methods of purification that have been developed to remove soap and glycerin from biodiesel. These methods utilize magnesium silicate as an adsorbent component, in the case of waterless purification, or ion exchange resins used in dry wash processing. Soap and glycerin can be removed from biodiesel by some combination of four mechanisms: filtration, ion exchange, adsorption and soap-glycerin interaction (Wall, Gerpen, & Thompson, 2011).



$$\begin{array}{llcll} CH_2-OCOR_1 & & & R_1-COOCH_3 & CH_2-OH \\ | & & & & | \\ CH-OCOR_2 \;+ & 3\,CH_3OH & \underset{catalyst}{\overset{alkali}{\rightleftharpoons}} & R_2-COOCH_3 \;+ & CH-OH \\ | & & & & | \\ CH_2-OCOR_3 & & & R_3-COOCH_3 & CH_2-OH \\ \textit{Triglyceride} & \textit{Methanol} & & \textit{Methyl ester} & \textit{Glycerol} \end{array} \qquad (1)$$

2. Objectives

In this work, alkali-catalyzed trans-esterification using acetone as a co-solvent was used for the biodiesel production from palm stearin at temperature below 60°C and the mixture of fatty acid methyl esters were refined by dry washing using ion exchange resins. The main goal of this study was to determine the optimum conditions and investigate the effects of the operating parameters (amount of acetone, KOH catalyst, reaction temperature and amount of ion exchange resins in purification step) on the biodiesel yield. Response surface methodology (RSM) was used for statistical analysis of the experimental data and Box-Behnken design (BBD) was applied to determine the optimum conditions for maximizing the biodiesel yield with low soap-glycerin content.

3. Materials and methods

3.1 Materials

Palm stearin used in this work was obtained from Morakot Industries PCL. The properties and fatty acid composition of palm stearin are shown in Table 1. Methanol (99.8% purity), acetone (99.8% purity), potassium hydroxide (99.8% purity) were used as the main chemicals for biodiesel production. The ion exchange resins used in the purification step was cation exchange resin PTC-108(H+) from Pall Tech Company. It was a polystyrene sulfonate gel type with particle size of 0.3 to 0.9 mm.

3.2 Biodiesel preparation

Biodiesel production procedures

The system used for transesterification consisted of a one liter glass batch reactor immersed in a water bath equipped with a thermostat to maintain the desired reaction temperature. For each experiment, 100 g of melted palm stearin was premixed with a known amount of acetone until the mixture formed a single phase and then a solution of KOH catalyst and methanol was added to the reactor. In previous work, methanol to oil molar ratio of 8:1 was found to be the best molar ratio (Kamthita, Srisuwan, & Setthachuae, 2013). The speed of the stirrer was constant at 300 rpm and the reaction proceeded for 30 min. The optimization useful RSM statistical technique had been applied to the complex variation process. Thereafter, reaction products, the mixture of biodiesel and glycerin, were transferred to a separator funnel and phase separation was allowed for 1-2 h. After the completion of phase separation, the remaining acetone and methanol in the biodiesel phase was recovered by an evaporator at 60^{o}C under a vacuum pressure of 50 kPa for 1 h.

Biodiesel purification process

The crude biodiesel was produced by using the optimum conditions determined from previous step and the amounts of soap and free fatty acid were assessed. For each test, the crude biodiesel was treated with measured potassium hydroxide dissolved in methanol to produce the desired levels of soap. Thereafter, the crude biodiesel was purified by passing through the ion exchange resin bed under constant temperature. Figure1 shows the equipment used in the purification experiments. The resin bed had a volume of 15 mL and was packed with cation exchange resin PTC-108(H+) in the glass column. The crude biodiesel was pumped through the column at a desired flow rate by means of a peristaltic pump (Masterflex L/S Model 77200-50) in a down-flow mode. The optimization useful RSM statistical technique had been applied to the complex variation process. The purified biodiesel was analyzed to determine the amount of fatty acid methyl ester (FAME) and the effectiveness of purification. Finally, the soap content and free fatty acid values were measured before and after processing. Soap content in the effluent biodiesel was monitored until the soap levels exceeded the specification levels of about 50 ppm (EN 14214 specification for alkalinity less than 5.0 mg/kg). Each time when the crude biodiesel was started at new soap level, the resin bed must be replaced. Furthermore, the purification step was started by introducing the crude biodiesel containing new soap level of 1,000 ppm at the flow rate of 4.5 BV/h through the resin bed volume of 15 mL to determine how long the removal efficiency of the resin bed remained unchanged.

Table 1 Fatty acid composition and properties of refined palm stearin as feedstock

Property	Value
Fatty acid composition (wt%)	
Myristic acid (C14:0)	0.9
Palmitic acid (C16:0)	57.4
Stearic acid (C18:0)	4.8
Oleic acid (C18:1)	30.7
Linoleic acid (C18:2)	6.2
Free fatty acid (% as palmitic)	0.058
Moisture and volatile matter (%)	0.03
Iodine value (IV: cyclohexane method)	36.68

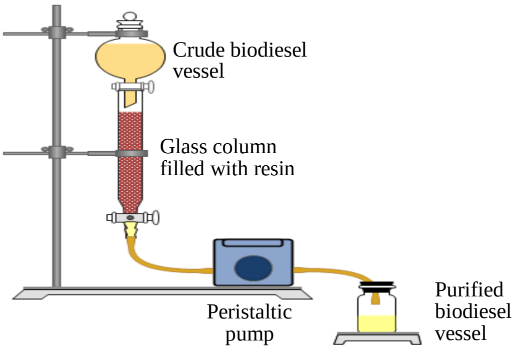


Figure 1 Purification setup

The Box-Behnken design (BBD) was applied to determine the optimum conditions for maximizing the biodiesel yield with low soap-glycerin content. The selected parameters and their levels were based on the previous studies of biodiesel production (Hamze, Akia, & Yazdani, 2015; Silva et al., 2011; Thanh et al., 2013; Wall et al., 2011). A 3-level-3-parameter BBD was applied in the transesterification step optimization requiring 16 experiments. The effects of the operating parameters, i.e., the amount of acetone, KOH catalyst concentration and reaction temperature were the independent variables to maximize the FAME content of biodiesel. Thereafter, a 3-level-2-parameter BBD was applied in the purification step optimization requiring 10 experiments. The effects of the operating parameters, i.e., the initial soap content and the flow rate of crude biodiesel passing through the resin bed were the independent variables to minimize soap level in the effluent biodiesel. The parameters in both coded and uncoded levels are shown in Tables 2 and 3, respectively. Response surface method-logy statistical technique was used for the experimental data analysis by Sigma Plot 12. Response surface plots were developed using the fitted quadratic polynomial equation obtained from regression analysis and experiments were carried out to validate the predictive equation.

Table 2 Operating parameters and levels used for transesterification step

Operating parameters	Symbols (uncoded)	Code levels		
		-1	0	+1
Amount of acetone, wt%	A	10	20	30
KOH concentration, wt%	C	0.5	1.0	1.5
Reaction temperature, ^{o}C	T	40	45	50

Table 3 Operating parameters and levels used for purification step

Operating parameters	Symbols (uncoded)	Code levels		
		-1	0	+1
Initial soap, ppm	S	400	800	1200
Flow rate, BV/h*	F	4.0	5.0	6.0

$$* \, bed\ volume\ per\ hour \; = \; \frac{volume\ per\ hours\ of\ treated\ liquid}{volume\ of\ resin}$$

3.3 Experimental design

The response factors in both steps were correlated to the selected parameters using linear/quadratic model. The general form of linear and quadratic model is expressed as follows:

$$Y \;=\; \beta_o + \sum_{i=1}^{2} \beta_i X_i \qquad (2)$$

$$Y \;=\; \beta_o + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum_{i=1}^{2} \sum_{j=i+1}^{2} \beta_{ij} X_i X_j \qquad (3)$$

where Y is the predicted biodiesel yield, $X_{i,}\ X_j$ are the uncoded independent variables and $\beta_o, \beta_i, \beta_{ii}$ and β_{ij} are the model coefficients.

3.4 Biodiesel characterization

The FAME content was measured using gas chromatography according to EN14103. The equipment used for this analysis included Agilent Technologies, model 7890A Series GC, HP-INNOWax column and a flame-ionization detector (FID).

The soap level was determined using the AOCS method Cc 17-79, (Wall et al., 2011). One hundred (100) mL of acetone containing 2% deionized water was used as a solvent for each sample. To provide a blank, each batch of acetone solvent was titrated with HCl to the point of a slight color change of bromophenol blue indicator to faint yellow prior to adding the biodiesel sample. Thereafter, adding a measured quantity of biodiesel, the solvent/sample mixture was titrated with 0.001 N HCl to the blue-to-yellow endpoint of the bromophenol blue. Soap levels were calculated using the following equation:

$$\underset{as\ potassium\ palmitate}{Soap\ (ppm)} \;=\; \frac{V \times H \times 294.1 \times 1{,}000}{m} \qquad (4)$$

where V is the volume of HCl solution spent in titration (mL), H is the HCl concentration (Normality), molar mass of potassium palmitate is 294.1 g/mol and m is the sample mass (g).

Acid value was measured according to ASTM D664 by titrating with KOH to the phenolphthalein end point. A mixture of 50% toluene and 50% propanol was used as a solvent for each sample. To provide a blank, each batch of solvent mixture was titrated with KOH to the clear-to-pink endpoint of the phenolphthalein indicator, prior to adding the biodiesel sample. Then the titration was performed with 0.1 N KOH to the clear-to-pink endpoint of the phenolphthalein. The acid value and free fatty acid (FFA) content were calculated using the following equations:

$$Acid\ value\ \left(\frac{mgKOH}{g}\right) = \frac{V \times K \times 56.1}{m}$$

$$\%FFA\ (as\ palmitic\ acid) = \frac{Acid\ value}{2.19} \qquad (5)$$

where V is the volume of KOH solution spent in titration (mL), K is the KOH concentration (Normality), molar mass of potassium hydroxide is 56.1 g/mol and m is the sample mass (g).

4. Results and discussion

4.1 Optimization of transesterification process

The relationships between the biodiesel yield as response and three operating parameters (amount of acetone (A), KOH concentration (C), and reaction temperature (T)) were studied using RSM based on Box-Behnken design. Sixteen experiments were applied and the code variables, experimental and predicted biodiesel yield are shown in Table 4. The linear, quadratic and the parameter interaction effects were considered to determine the optimum conditions for the biodiesel yield. The regression model was tested using analysis of variance (ANOVA). The significance of each parameter was analyzed by the probability value (p-value) as shown in Table 5. At 95% confidence level, the p-values less than 0.05 indicate that all of terms except C^2, A^2 and CA, were significant. The coefficient of determination (R^2) and adjusted coefficient of determination (Adj. R^2) for this process were 0.9805 and 0.9512, respectively. The determined value of the coefficient indicates the data fit a statistical model. The model is quite appropriate for experimental relationships between the parameters and the response. The predicted model for the biodiesel yield in term of coded parameter was shown in Equation (6).

$$\begin{aligned} Y = {} & -1066.509 + 45.9976T + 80.4617C \\ & + 4.4594A - 0.4626T^2 - 10.6946C^2 \\ & -0.0293A^2 - 1.3892TC - 0.0641TA \\ & +0.0019CA \end{aligned} \qquad (6)$$

From the results of ANOVA, the linear term of reaction temperature (T) has the lowest p-value (0.0002) among the other parameters. These results revealed the reaction temperature is the most important parameter in biodiesel production via the transesterification reaction of triglyceride using acetone as co-solvent. Furthermore, the interaction effects between reaction temperature and other parameters, the significance of the interaction parameters in the model was less than 0.05 which indicated the significant effects of those parameters. Because of immiscibility of a mixture of methanol and oils and high viscosity of oils, the transesterification process is usually performed near the boiling point of methanol, 60^{o}C to reduce the viscosity and increase mass transfer of methanol and oils. In this work, palm stearin feedstock became solid phase at temperature below 45^{o}C, the transesterification reaction in the presence of acetone was carried out under mild conditions, at temperatures below 60^{o}C. As the amount of acetone increased, the viscosity of the reaction mixture decreased and the difference between the densities of biodiesel and glycerin phases increased, resulting in a reduced time required for phase separation. It was found that acetone as co-solvent can effectively increase the transesterification reaction rate. The result was consistent with the study of Thanh et al. (2013) that the homogeneous transesterification system between triglyceride and methanol takes place at the molecular level, leading to a higher fatty acid methyl ester yield and shorter reaction time. However, the linear term of catalyst concentration (C) and amount of acetone (A) with p-value less than 0.05 were significant while their quadratic term of catalyst concentration (C^2) and amount of acetone (A^2) with p-value more than 0.05 were less significant. The interaction effects between catalyst concentration and amount of acetone (CA) with p-value much more than 0.05 were insignificant. Therefore, determination of the optimum conditions for biodiesel production using acetone as co-solvent requires considering the interaction effects of the reaction temperature with the two other parameters.

Table 4 Box-Behnken arrangement of uncoded and coded parameters and experimental, predicted results in the transesterification step

Run No.	**T, (°C)**	**C, (wt%)**	**A, (wt%)**	**Biodiesel yield (%)**	
				Experimental	**Predicted**
1	40 (-1)	0.5 (-1)	10 (-1)	57.26	58.96
2	40 (-1)	0.5 (-1)	30 (+1)	74.39	73.43
3	40 (-1)	1.5 (+1)	10 (-1)	63.14	62.49
4	40 (-1)	1.5 (+1)	30 (+1)	77.78	76.99
5	50 (+1)	0.5 (-1)	10 (-1)	88.34	89.20
6	50 (+1)	0.5 (-1)	30 (+1)	90.12	90.85
7	50 (+1)	1.5 (+1)	10 (-1)	77.80	78.84
8	50 (+1)	1.5 (+1)	30 (+1)	82.15	80.52
9	40 (-1)	1.0 (0)	20 (0)	72.88	73.57
10	50 (+1)	1.0 (0)	20 (0)	91.45	90.46
11	45 (0)	0.5 (-1)	20 (0)	94.94	92.61
12	45 (0)	1.5 (+1)	20 (0)	87.17	89.21
13	45 (0)	1.0 (0)	10 (-1)	89.56	86.61
14	45 (0)	1.0 (0)	30 (+1)	92.04	94.69
15	45 (0)	1.0 (0)	20 (0)	92.59	93.58
16	45 (0)	1.0 (0)	20 (0)	93.98	93.58

Table 5 Summary output from data analysis in transesterification step

ANOVA	**Significance F**	**p-value**
Regression	0.0002	
Intercept		0.0001
Linear ; T		0.0002
C		0.0079
A		0.0049
Square; T*T		0.0003
C*C		0.1344
A*A		0.1067
Interaction; T*C		0.0079
T*A		0.0112
C*A		0.9918

The response surface plots and the contour plots of the biodiesel yield obtained by Equation (6) were shown in Figure 2. In each contour graph, the interaction effect of the two parameters was plotted while the remaining parameter was fixed at the medium values (20wt% amount of acetone, 1.0wt% KOH catalyst concentration and reaction temperature of 45°C). Figure 2(a) shows the response surface plots and the contour plots of the biodiesel yield for interaction effects of the parameters of C and A at the medium value of temperature (T). The contour plots show that the biodiesel yield is more than 95% with using KOH catalyst concentration ranging from 0.5 to 0.9wt% and amount of acetone ranging from 18 to 30wt%. Figure 2(b) shows the response surface plots and the contour plots of the biodiesel yield for interaction effects of the parameters of T and A at the medium value of KOH catalyst concentration (C). The contour plots show that the biodiesel yield is more than 95% using reaction temperature ranging from 46 to 48°C and amount of acetone ranging from 22 to 27.5wt%. Figure 2(c) shows the response surface plots and the contour plots of the biodiesel yield for interaction effects of the parameters of C and T at the medium value of amount of acetone (A). The contour plots show that the biodiesel yield is more than 95% with using KOH catalyst concentration ranging from 0.5 to 0.9wt% and reaction temperature ranging from 46 to 48.5^{o}C. To achieve the maximum biodiesel yield, the optimum conditions were performed at the reaction time of 30 min, methanol to oil molar ratio of 8:1, 24.7wt% acetone, 0.70wt% KOH catalyst and reaction temperature of 47^{o}C. The predicted yield at the optimum conditions was evaluated as 96.6%. The yield of the biodiesel sample prepared under the optimum conditions obtained 96.3% which validate the accuracy of the predictive model.

4.2 Optimization of purification process

The relationships between the soap content as response and two operating parameters (the initial soap content (S) and the flow rate of crude biodiesel (F)) were studied using RSM based on Box-Behnken design. Ten experiments were applied and the code variables, experimental and predicted soap content are shown in Table 6. The quadratic regression and the parameter interaction effects were considered to determine the optimum conditions for minimizing soap level. The regression model was tested using analysis of variance (ANOVA). The significance of each parameter was analyzed by the probability value (p-value) as shown in Table 7. P-values less than 0.05 were considered significant for each parameter. The coefficient of determination (R^2) for this process was 0.9912, indicating the data fit a statistical model. The model is quite appropriate for experimental relationships between the parameters and the response. The predicted model for the soap content in term of coded parameter was shown in Equation (7).

$$Y = 150.8976 - 0.0593S - 61.1357F$$
$$-1.6696\text{x}10^{-5}S^2 + 6.9286F^2 + 0.0243SF \quad (7)$$

The response surface plot and the contour plot of the soap content obtained by Equation (7) are shown in Figure 3. Considering the interaction effects between the initial soap levels and the flow rate of crude biodiesel, the significance of the interaction parameters in the model was less than 0.05 indicating significant effects of those parameters. To achieve lower soap level from the initial soap levels higher than 1000 ppm, the flow rate used was below 4.5 BV/h to keep the limiting soap levels at 50 ppm ensuring that the acid values did not exceed the biodiesel specification levels. It can be seen that the increase of initial soap levels in crude biodiesel caused a decrease in the flow rate of biodiesel passing through the resin bed. The limiting soap levels in effluent biodiesel depended on the initial soap content and flow rate of crude biodiesel passing through the resin bed including number of bed volume.

$$\underset{\textit{Soap}}{\mathrm{Na^{+}\ {}^{-}O - CO - R}} + \underset{\textit{Active site on resin}}{\mathrm{H^{+} - resin}} \rightarrow \underset{\textit{Inactive site on resin}}{\mathrm{\overset{+}{Na} - resin}} + \underset{\textit{Fatty acid}}{\mathrm{HO - CO - R}} \quad (8)$$

Table 6 Box-Behnken arrangement of uncoded and coded parameters and experimental, predicted results in purification step

Run No.	S, (ppm)	F, (BV/h)	Soap content (ppm)	
			Experimental	Predicted
1	400 (-1)	4.0 (-1)	29.4	29.7
2	400 (-1)	6.0 (+1)	62.7	65.5
3	1200 (+1)	4.0 (-1)	39.4	38.8
4	1200 (+1)	6.0 (+1)	111.6	113.4
5	400 (-1)	5.0 (0)	43.8	40.7
6	1200 (+1)	5.0 (0)	70.3	69.1
7	800 (0)	4.0 (-1)	36.6	36.9
8	800 (0)	6.0 (+1)	96.7	92.1
9	800 (0)	5.0 (0)	56.6	57.6
10	800 (0)	5.0 (0)	54.3	57.6

Table 7 Summary output from data analysis in purification step

ANOVA	Significance F	p-value
Regression	0.0003	
Intercept		0.0720
Linear ; S		0.1555
F		0.0686
Square; S*S		0.3347
F*F		0.0468
Interaction; S*F		0.0064

The mechanisms of soap removal via ion exchange dependent upon the sulfonic acid functional groups which exchange the hydrogen ions with the potassium ions from the soap. During the reaction, free fatty acids created from the soap were released into the effluent biodiesel and completed the conversion of soap to free fatty acids, which were not achieved at a soap content greater than 1000 ppm. After methanol was removed from the biodiesel solution, the soap and glycerin were precipitated and then filtered prior to the purification step.

At optimum conditions for biodiesel preparation, the crude biodiesel was produced and then purified by passing through the ion exchange resin bed under constant temperature. A column with 15 mL of swelled resin was used to purify the crude biodiesel containing 1000 ppm of soap, using a flow rate of 4.5 BV/h. The relationship after purification between the soap content, free fatty acid value and bed volumes is shown in Figure 3. It was found that the soap content rapidly decreased from the initial content of 1000 ppm to below 50 ppm while the free fatty acid value increased from the initial content of 0.0486% to 0.103%. Ion exchange resins remove soap from biodiesel involves the reaction in the Equation (8) which occurs on the surface or within the pores of the resin. The resins exchange the hydrogen ion with the potassium ion in the soap. The free fatty acid portion is released into the effluent biodiesel which has a higher percentage of free fatty acids. Figure 4 shows that the purification process was performed continuously from 0 to 25 BV, while the soap content still decreased below 50 ppm and after 25 BV, the soap content in the effluent biodiesel began to increase above 50 ppm. The effluent biodiesel was quite clear. As the ion exchange resin ages, the effluent free fatty acids value decreases and the effluent soap level increases. When the resin bed was used until 40 BV, the effluent biodiesel became slightly cloudy. The average soap content and free fatty acid values in the effluent biodiesel from 0 to 40 BV were 48.4 ppm and 0.0924% respectively which satisfied the biodiesel specification.

4.3 Properties of the optimized palm stearin biodiesel

Conversion of triglycerides into fatty acid methyl esters is performed using the transesterification reaction. Properties of triglycerides and biodiesel are related to their fatty acid compositions. Fatty acids chain length and the number of double bonds affect the physical and chemical characteristics of fatty acids. Transesterification does not change fatty acid composition of the primary oils (Salvi, & Panwar, 2012). In this work, the refined palm stearin was used as feedstock. It becomes solid phase at temperatures below 45^{o}C. Transesteri-fication in the presence of acetone can be performed at temperatures below 60^{o}C and effectively increase the transesterification reaction rate. Comparing the physical and chemical properties of optimized palm stearin biodiesel before and after purification via ion exchange resin as listed in Table 8 show the higher level of methyl ester contents, lower soap levels, higher acid values and decreased cloud point. The biodiesel soap level was decreased because soap was removed by a combination of filtration, ion exchange and adsorption. After methylation, filtration is most effective when methanol content in biodiesel is low because methanol increases the solubility of soap and glycerin in the biodiesel. Adsorption is the primary mechanism for glycerin capture with ion exchange resins (Wall et al., 2011). Adsorption occurs when polar contaminants such as glycerin, attach themselves to the resin bead surface due to the attraction of intermolecular forces. The resins exchange the hydrogen ion with the potassium ion in the soap. These mechanisms of biodiesel purification are indicative of the removal of impurities from biodiesel.

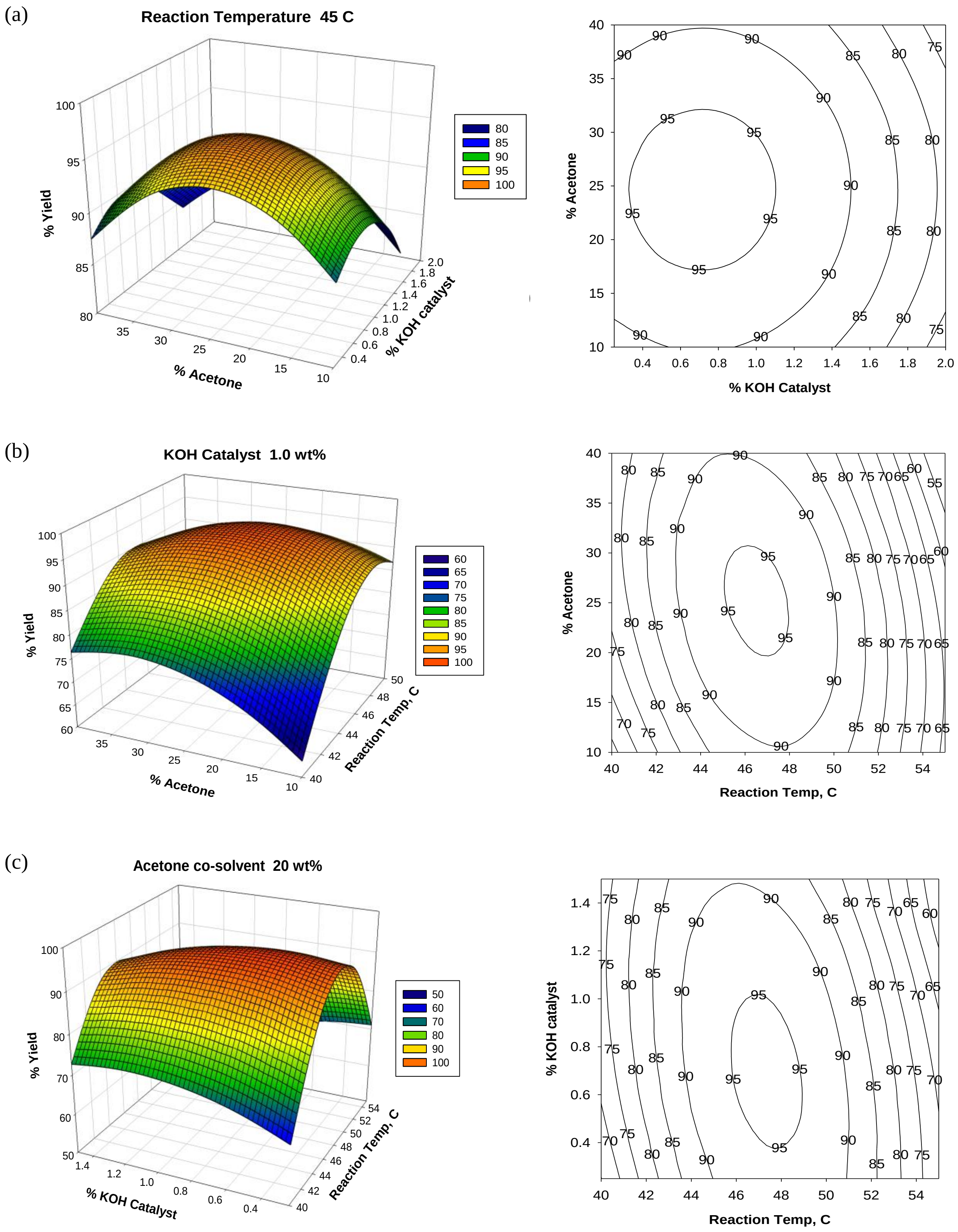


Figure 2 Response surface plots for interaction effect of parameters on biodiesel yield;
(a) C and A at the medium value of T; (b) T and A at the medium value of C; (c) C and T at the medium value of A

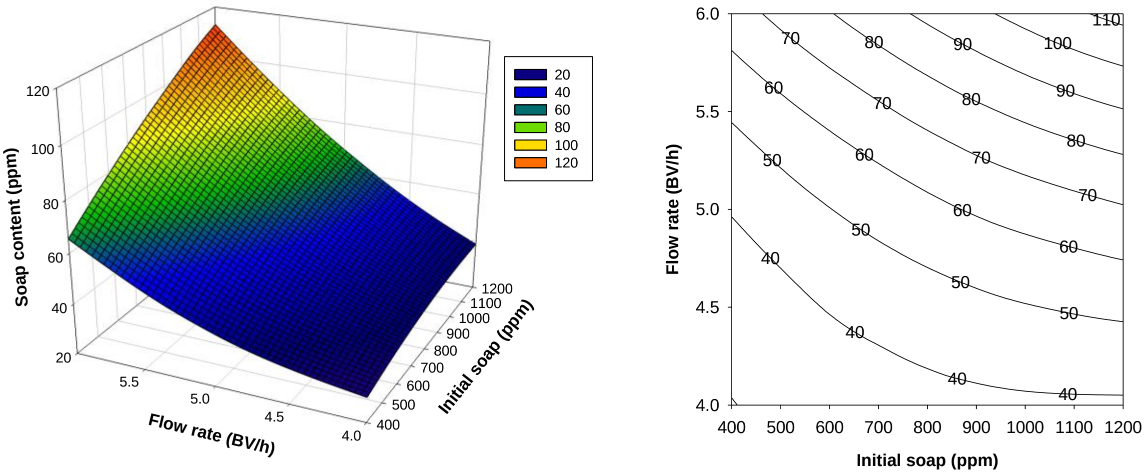


Figure 3 Response surface plots for interaction effect of parameters on soap content.

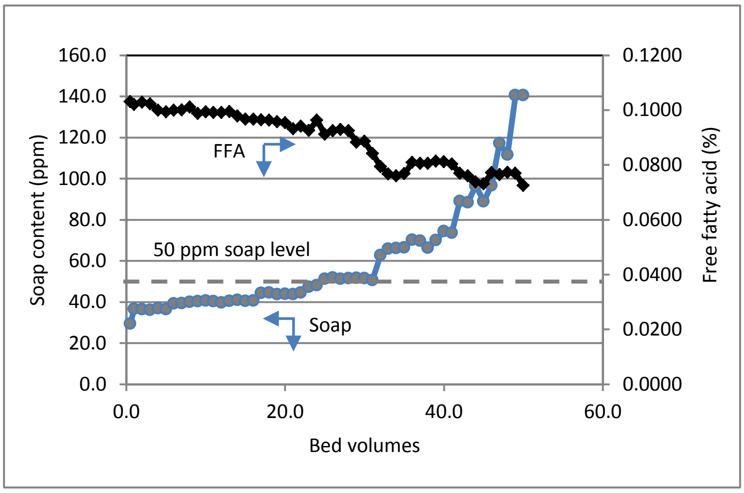


Figure 4 Effect of resin lifetime on soap content and free fatty acid value.

Table 8 Properties of optimized palm stearin biodiesel

Property	Purification		EN 14214	ASTM D6751
	Before	After		
Methyl ester content (%)	96.7	98.4	Min. 96.5	
Density at 15°C (kg/m^3)	875	870		860 - 900
Viscosity at 40°C (cSt)	4.5	4.4		3.5 - 5.0
Acid value (mgKOH/g)	0.11	0.21		Max. 0.50
Alkalinity (mg/kg)	81	3.9	Max. 5.0	
Free fatty acid (%)	0.049	0.092	-	-
Soap content (ppm)	1036	48.4	-	-
Cloud point (°C)	23	15	-	-
Pour point (°C)	15	13.5	-	-

5. Conclusion

The response surface methodology based on Box-Behnken design was successfully applied to investigate the effects of the operating parameters for waterless biodiesel production obtained from refined palm stearin to maximize the biodiesel yield with low soap content. According to the ANOVA results, the interaction effects between reaction temperature, amount of acetone and KOH catalyst indicated the reaction temperature was the most important parameters. The palm stearin feedstock became solid phase at temperature below 45°C. Transesterification in the presence of acetone can be performed at temperature below 60°C and effectively increase the transesterification reaction rate. To achieve the maximum biodiesel yield, the optimum conditions were performed at the reaction time of 30 min, methanol to oil molar ratio of 8:1, 24.7wt% acetone, 0.70wt% KOH catalyst and reaction temperature of 47°C. The optimized biodiesel sample yield obtained was close to the predicted value. Accordingly, the small degree of error less than 0.5% indicated the high accuracy of the model. During the purification step, at an initial soap level higher than 1000 ppm, the flow rate must be controlled below 4.5 BV/h to achieve desirable low soap and acid levels. The physical and chemical properties of the produced waterless biodiesel satisfied the standard biodiesel specification.

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7. References

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