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Optimization of High Free Fatty Acid Reduction in Mixed Crude Palm Oil Using Ultrasound: A Response Surface Methodology Approach

Krit Somnuk*, Thanansak Theppaya, Pruittikorn Smithmaitrie and Gumpon Prateepchaikul

ABSTRACT

Reduction of the acid value in mixed crude palm oil (MCPO) with methanol and acid-catalyst H_2SO_4 was carried out in an ultrasonic homogenizer at a low-frequency of 18 kHz with 1,000 W. This work was undertaken with fixed values of 1.62 $W.mm^{-2}$ for the high surface power density at the horn tip and 20 $W.mL^{-2}$ for the volumetric acoustic energy. The objective was to determine the relationship between various important parameters and the response variable of acid-catalyzed esterification to obtain the lowest acid value. Response surface methodology was used to optimize the operating parameters of the ultrasonic esterification process. A 5-level, 3-factor, central composite design was applied to optimize the three key reaction variables (methanol concentration, sulfuric acid concentration and ultrasonic irradiation time) to reduce the acid value of the MCPO from 28 $mg.g^{-1}$ KOH to less than 2 $mg.g^{-1}$ KOH. The results indicated that the factors have significant effects on the reduction of the acid value. Furthermore, optimization of the reduction of the acid value could be achieved with 24.8% (by volume) methanol, 3.7% (by volume) sulfuric acid and an ultrasonic irradiation time of 96 s.

Keywords: ultrasound, acid value, mixed crude palm oil, esterification, reduction

INTRODUCTION

Biodiesel is one of the important renewable fuel sources used in many countries in the world (Musango *et al*., 2011; Hosseini *et al*., 2012). Biodiesel is a renewable alternative fuel which can be produced from vegetable oil or animal fats without any diesel engine modification (Stavarache *et al*., 2005; Chauhan *et al.*, 2012). In Thailand, crude palm oil (CPO) and mixed crude palm oil (MCPO) have been used as alternative feedstocks to produce biodiesel (Worapun *et al*. 2012; Intarat *et al.*, 2014). However, the major problem in the production of biodiesel from MCPO or CPO is the free fatty acid (FFA) content. To achieve good conversion from MCPO to esters, the FFA should not exceed 1% by weight (Tadakittisarn *et al.*, 2011). This corresponds to an acid value of 2 $mg.g^{-1}$ KOH when using the base-catalyzed transesterification reaction to produce the biodiesel. If the acid value level exceeds this amount, it will react with alkali to produce soap (Somnuk *et al.*, 2013). As a result, the conversion of ester is decreased by the saponification reaction (Gerpen, 2005; Prateepchaikul *et al.*, 2009). In acid-catalyzed esterification, the FFA

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is converted to esters by direct esterification with the acid-catalyst and the esterification reaction is accelerated by using ultrasonic irradiation (Somnuk *et al*., 2013). This reaction is shown in Equation 1:

$$\underset{\text{FFA}}{RCOOH} + \underset{\text{Alcohol}}{R'OH} \xleftrightarrow[\text{ultrasonic irradiation}]{H_2SO_4} \underset{\text{Ester}}{RCOOR'} + \underset{\text{Water}}{H_2O} \quad (1)$$

where R and R′ denote any hydrocarbon chain.

The reaction time can be shortened by using ultrasound instead of a mechanical stirrer (Worapun *et al*., 2012). In sonochemistry, ultrasound can generate acoustic cavitations through high intensity acoustic fields in the medium phase until they reach a cavitation phenomenon that creates a bubble collapse (Mason and Lorimer, 2002). Rapid physical and chemical reactions of the reaction mixture can occur when the bubbles collapse as the inside of the bubble may have a pressure as high as 506.6 MPa that causes an instant temperature rise to at least 7,200 °C (Mason and Lorimer, 2002). In addition, the ultrasonic field can increase the interface area between the immiscible fluids, resulting in rapid mixing in the liquids (Mason and Lorimer, 2002; Hsiao *et al.*, 2010). Most of the researchers whose work is reviewed below, believe that the physical effect of ultrasound on the formation of the fine emulsion between immiscible fluids is responsible for accelerating the homogeneous transesterification reaction (Avramović *et al*., 2010). Therefore, many researchers have studied biodiesel production using low free fatty acid with the oil and alcohols with alkali or an acid-catalyst under ultrasonic radiation. For example, in base-catalyzed homogeneous transesterification, Stavarache *et al*. (2005) studied the effects of alcohols on the transesterification of neat vegetable oil under ultrasound and mechanical stirring with a molar ratio of 6:1 (alcohol to oil) and an alkali-catalyst of 0.5, 1.0 and 1.5% by weight (NaOH and KOH), at room temperature. Frequencies of 28 kHz and 40 kHz and 60% of maximum ultrasonic power of 1,200 W were employed in this experiment. The results showed that normal-chain alcohols (methanol, ethanol, *n*-propanol and *n*-butanol) exhibited quite rapid reaction, producing yields of 88–98% ester within a 10–20 min reaction time under an ultrasonic frequency of 40 kHz and 0.5% by weight NaOH. Moreover, the yields of biodiesel in the ultrasonic process were higher than from traditional stirring and the ultrasonic system effected a reduction of soap. The low frequency ultrasound of 28 kHz produced a yield of 98% ester, but the reaction time was longer than that from the high frequency ultrasound treatment. Hanh *et al*. (2008) tested the methanolysis reaction with triolein, using 0.5, 1, 1.5 and 3% by weight KOH, molar ratios of 3:1, 4:1, 5:1, 6:1 and 9:1 (methanol to triolein) and a reaction time of 10–140 min with an ultrasonic cleaner (40 kHz with a maximum power of 1,200 W). They found that a higher yield of methyl esters depended on a higher amount of KOH and the molar ratio of methanol to triolein. The optimum conditions for the production of methyl ester under sonication conditions was a 6:1 molar ratio of methanol to triolein with 1% by weight KOH and a reaction time of 30 min.

In acid-catalyzed homogeneous transesterification, Santos *et al*. (2009) studied the production of methyl esters from *Oreochromis niloticus* oil with a molar ratio of 3:1 to 9:1 (methanol to FFA) and acid-catalyst H_2SO_4 of 0.50–2.0% by weight with samples taken at 1, 5, 10, 20, 30, 40, 60 and 90 min. The reaction operated at a low-frequency of 40 kHz using high-intensity ultrasound. Response surface methodology (RSM) was used to evaluate the influence of the molar ratio of methanol to FFA, the sulfuric acid concentration and the reaction temperature on the yield of methyl esters. The results indicated that the most important parameter affecting the reaction was the molar ratio of methanol to FFA. The maximum fatty acid methyl ester yield of 98.2% was achieved with a methanol to oil molar ratio of 9:1, 2% by weight KOH catalyst and a 90 min reaction time. Hanh *et al*. (2009) also

studied the production of fatty acid ethyl ester from oleic acid with various alcohols (methanol, ethanol, propanol, butanol, hexanol, octanol and decanol) under ultrasonic irradiation. The various imposed conditions were: molar ratio of 1:1–10:1 (alcohol to oleic acid), reaction temperature of 10–60 °C, acid-catalyst 0.5–10% weight (H_2SO_4) and an ultrasonic irradiation time of 1–10 hr. The results showed that the optimum conditions for producing maximum ester conversion in the batch esterification process was with a molar ratio of alcohol to oleic acid of 3:1, 5% by weight H_2SO_4 with an ultrasonic irradiation time of 2 hr and a reaction temperature of 60 °C. From the above findings, it could be concluded that in ultrasonic homogeneous transesterification, the main reason for using the base-catalyst rather than the acid-catalyst in the transesterification was because the base-catalyzed reaction time was shorter than that using the acid-catalyst. Nevertheless, an advantage of acid-catalyzed transesterification is that it can produce biodiesel from high FFA oil, whereas, as described earlier, using base-catalyst on oils containing FFA greater than 1% by weight is not practicable due to saponification.

Biodiesel from high FFA content oil can be produced using a two-stage process, with the first-process of acid-catalyzed esterification followed by the second-process of base-catalyzed transesterification. In the first-step, the majority of FFA in the oil is converted to esters by acid-catalyst esterification. Consequently, the tri-, di- and mono-glyceride in the esterified oil is converted to esters by base-catalyst transesterification in the second-step. Currently, few researchers have studied the two-step process to produce biodiesel from high FFA content oils using ultrasound to accelerate the reactions, particularly in FFA reduction in oils. For example, Worapun *et al*. (2012) studied the optimization of biodiesel production from CPO using ultrasonic irradiation. The FFA level in the CPO was higher than the limitation for direct conversion of triglycerides to methyl ester by transesterification. Thus, the CPO should be treated to reduce the FFA content in the CPO from 6% to less than 3% by weight before being followed by base-catalyzed transesterification. The conditions used in the esterification reaction were: methanol to oil molar ratio of 6:1, sulfuric acid 3% by weight and an ultrasonic irradiation time of 30 min at 30 °C. RSM is an effective statistical technique for designing experiments, fitting the response surface models, and optimizing the response by building a regression model from the experimental data for analyzing the response which can then be used to evaluate the optimization of the relationship between the response and the independent variables via statistical techniques (Salamatinia *et al*., 2010; Lee *et al.*, 2011). The above discussion based on the available literature indicates that many researchers have studied the production and optimization of biodiesel from vegetable oils and alcohols with alkali or acid catalyzed transesterification under ultrasound. However, few researchers have studied the reduction of the high free fatty acid content in oils by acid-catalyzed esterification under ultrasonic radiation. Despite extensive searching, so far no researcher has been identified who studied the optimization of high free fatty acid reduction in oils using ultrasonic acid-catalyzed esterification. Moreover, it has been noted that most of either the transesterification or esterification reactions used low-intensity ultrasound to accelerate the reaction. As a result, the reaction time was typically long, whereas a shorter reaction time should be attainable through high-intensity ultrasound by increasing the acoustic energy density in a small ultrasonic reactor. Consequently, the objective of this present work was to study the optimization of three key parameters—namely, the concentration of methanol, the concentration of sulfuric acid and the ultrasonic irradiation time—in the reduction process to reduce the acid value of MCPO to be less than 2 $mg.g^{-1}$ KOH using acid-catalyzed esterification under ultrasonic irradiation. RSM—5-level 3-factor central composite design (CCD)—was employed to optimize these three parameters.

The most important objective was to determine the RSM of the relationship between the acid value in the esterified oil and these parameters.

MATERIALS AND METHODS

Materials

Mixed crude palm oil (MCPO) with an acid value of 28 $mg.g^{-1}$ KOH with a mean molecular weight of 772.1 $g.mol^{-1}$, 0.916 $kg.L^{-1}$ density, 18.17 cP viscosity at 60 °C and 14% by weight FFA content, was used as the raw material in acid-catalyzed esterification. All chemicals used in the experiments, including the 99% sulfuric acid (H_2SO_4) and 98% methanol (MeOH), were commercial grade. Potassium hydroxide, isopropyl alcohol and phenolphthalein of analytical grade were used to determine the acid value of the esterified oil.

Methods

Apparatus

Figure 1 shows a schematic diagram of the experimental setup. The 18 kHz, 1,000 W ultrasonic homogenizer was used as an ultrasound source to reduce the acid value of the MCPO. The SUS 316L cylindrical vessel was used as ultrasonic reactor. The dimensions of the ultrasonic reactor were 34 mm internal diameter, 150 mm height and 8 mm thickness. The 316L stainless steel ultrasonic horn was tuned to a half-wave acoustic wavelength (λ/2). The horn, working at a fixed frequency of 18 kHz was 135 mm long and had a horn tip diameter of 28 mm. The 220V, 50/60 Hz ultrasonic generator converted electrical power from single-phase mains to the frequency and voltage for the ultrasonic transducer and created mechanical vibrations, which were then transmitted to the aluminum ultrasonic booster to increase the amplitude between the ultrasonic transducer and the ultrasonic horn. The ultrasound was transmitted from the horn tip to the oil and chemical reactant. The ultrasonic irradiation time was controlled using a digital timer which was installed in the ultrasonic generator and a direct current cooling fan was installed on the top of the ultrasonic homogenizer to chill the piezoelectric transducers.

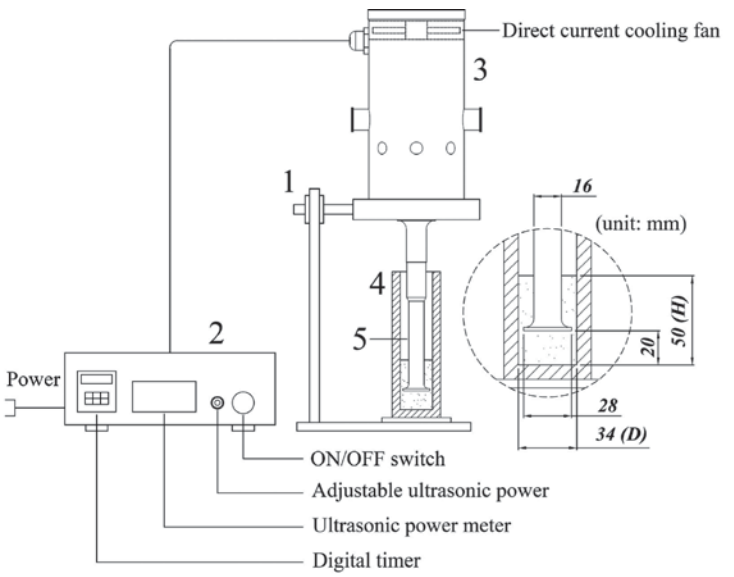

Figure 1 Schematic diagram of the experimental setup used for ultrasonic irradiation assisted for reduction of high free fatty acids content in the mixed crude palm oil: 1) Support stand with ring clamp; 2) Ultrasonic generator; 3) Ultrasonic homogenizer; 4) Ultrasonic reactor; 5) Ultrasonic horn.

Procedures

Initially, a predetermined amount of MCPO (approximately 36–48 mL) was poured into a 100 mL beaker. It was preheated on a hot plate to lower its viscosity, and the temperature of the heated oil was maintained at 60 °C. When the MCPO was heated to the desired reaction temperature, methanol, followed by sulfuric acid, at calculated amounts from the required ratios were added into the beaker. The liquids were mixed at a controlled speed for about 5 s using a magnetic bar stirrer inside the beaker to ensure good mixing of the pre-mix, particularly as the sulfuric acid has a heavy phase and normally mixes poorly with MCPO in the ultrasonic process. The well-mixed reactant mixture was then poured into the ultrasonic reactor and the ultrasonic homogenizer was turned on to accelerate the chemical reaction. The ultrasound power level can be expressed as ultrasonic power (W), ultrasound intensity ($W.mm^{-2}$) and acoustic energy density ($W.mL^{-1}$). The intensity of ultrasonic power, I_{us}, transmitted to a mixture from a horn tip surface is given by Equation 2 (Klíma *et al.*, 2007):

$$I_{US} = \frac{P_{US}}{A} \quad (2)$$

where P_{US} is the ultrasonic power transmitted to a mixture in watts and A is the surface area of the horn tip in square millimeters.

The acoustic energy density (AED) or volumetric energy density can be defined using Equation 3 (O'Donnell *et al.*, 2010):

$$AED = \frac{P_{US}}{V_{\text{total}}} \quad (3)$$

where P_{US} is the ultrasonic power in watts and V_{total} is the total volume of the mixture in milliliters.

The probe location and the change in the total volume of the mixture may affect the ultrasound intensity and the acoustic energy density which transmit waves to accelerate a reaction; therefore, the following parameters were fixed for all the experiments: high surface power density of 1.62 $W.mm^{-2}$ at the horn tip, volumetric acoustic energy of 20 $W.ml^{-1}$ and 1.47 aspect ratio (H/D) of the ultrasonic reactor, where H is the highest level of mixture and D is the diameter of the reactor. Each sample was quickly cooled with 0 °C water to stop the reaction. In the purification process before the acid value analysis, all samples of esterified oil were washed with water in the separatory funnel to eliminate the residual acid-catalyst, methanol and other impurities. The acid value in the purified sample was analyzed using the Official Method Cd 3a-63 for Acid Value (American Oil Chemists Society, 1998). The acid value level was calculated using Equation 4 (Marchetti and Errazu, 2008):

$$Acid\ value = \frac{(titrant\ volume) \times (N\ of\ titrant) \times 56.1}{weight\ of\ sample} \quad (4)$$

where N is the normality of KOH, the titrant volume is measured in milliliters and the sample weight is measured in grams.

Experimental design

RSM with 5 levels and 3 factors in a CCD was used to optimize the FFA in the MCPO reduction using the high-intensity ultrasound. Multiple regression analysis was used to obtain a quadratic (second-order) polynomial model to predict the acid value in esterified oil. A general second-order polynomial equation can be expressed as shown in Equation 5 (Salamatinia *et al.*, 2010:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1} \sum_{j=i+1} \beta_{ij} x_i x_j + \varepsilon \quad (5)$$

where Y is the response (acid value), x_i and x_j are the uncoded independent variables (methanol, sulfuric acid and ultrasonic irradiation time), β_0, β_i, β_{ii}, and β_{ij} are the intercept, linear, quadratic and interaction constant coefficients, respectively; k is the number of variables and ε is the error.

The independent variables—concentration of methanol (M), concentration of sulfuric acid (A) and ultrasonic irradiation time (T)—were studied in the optimization of the reduction of acid value

(*AV*) of the MCPO after the pretreatment. In the case of three variables, the axial parameter (α_x) is 1.682 (for rotatable CCD). The axial parameter for rotatability can be expressed as shown in Equation 6:

$$\alpha_x = \sqrt[4]{2^k} \quad (6)$$

where α_x is the axial parameter for rotatability and k is the number of variables.

This experiment was designed for five levels of varying independent variables. The coded independent variables used in this study are shown in Table 1.

RESULTS AND DISCUSSION

Experimental results

Eighteen experiments (designated as test 1 to test 18) were carried out to determine the optimal conditions for acid value reduction in the MCPO. Table 2 shows the experimental design

Table 1 Coding of independent variables.

	Independent variable	Coded level				
		-1.682	-1	0	+1	+1.682
M	Methanol concentration (% by volume)	3.2	10	20	30	36.8
A	Sulfuric acid concentration (% by volume)	0.3	1	2	3	3.7
T	Ultrasonic irradiation time (s)	10	30	60	90	110

Table 2 Experimental design matrix and results where total volume of any mixture of mixed crude palm oil (MCPO), methanol and sulfuric acid is 50 mL.

Test No.	MCPO	Methanol *M*		Sulfuric acid *A*		Ultrasonic irradiation time *T*	Acid value *AV*
	(mL)	(mL)	(%)	(mL)	(%)	(s)	mg.g^{-1} KOH
1	41.6	8.3	20	0.1	0.3	60	10.560
2	41.0	8.2	20	0.8	2	60	6.091
3	44.2	4.4	10	1.3	3	30	13.205
4	38.2	11.5	30	0.4	1	30	1.494
5	36.0	13.3	36.8	0.7	2	60	7.505
6	37.6	11.3	30	1.1	3	30	2.271
7	41.0	8.2	20	0.8	2	60	5.847
8	44.2	4.4	10	1.3	3	90	9.969
9	45.0	4.5	10	0.5	1	90	24.711
10	40.4	8.1	20	1.5	3.7	60	4.049
11	45.0	4.5	10	0.5	1	30	13.943
12	37.6	11.3	30	1.1	3	90	7.226
13	41.0	8.2	20	0.8	2	60	7.218
14	38.2	11.5	30	0.4	1	90	4.310
15	47.5	1.5	3.2	1.0	2	60	18.890
16	41.0	8.2	20	0.8	2	10	13.214
17	41.0	8.2	20	0.8	2	60	6.206
18	41.0	8.2	20	0.8	2	110	9.496

% = % by volume.

matrix and the test results. It was found that the acid value of the esterified oil ranged from 24.711 to 1.494 mg.g^{-1} KOH with tests 9 and 4 giving the maximum and minimum acid values, respectively. Only tests 4 and 6 could reduce the acid value to less than 3 mg.g^{-1} KOH—the other tests could not attain this required acid value threshold.

Response surface models of results and statistical analysis

The response surface model data in Table 2 were analyzed using a multiple regression model to fit a quadratic polynomial equation. The model showed that the relationship between the FFA and the three independent variables was obtained in terms of a second-order equation. Equation 7 shows the regression model.

$$AV = \beta_0 + \beta_1 M + \beta_2 T^2 + \beta_3 AT + \beta_4 AM + \beta_5 M^2 \quad (7)$$

where AV is the acid value, A is the sulfuric acid concentration, M is the methanol concentration and T is the ultrasonic irradiation time.

A good model was selected by using statistical techniques consisting of consideration of the coefficient of multiple determination (R^2), the standard error and the adjusted coefficient of determination ($R^2_{adjusted}$) of the response models, as listed in Table 3. The R^2 value of 0.829 indicates quite a good fit for the model and the model was not over fitted based on the values of R^2 and $R^2_{adjusted}$ (0.829 and 0.758, respectively) as they do not differ greatly.

The adequacy of the regression model was tested using the probability of error value (P-value), as detailed in Table 3. The statistical significance of this model was proven using the results of the analysis of variance, particularly the F-test for the relationship between the three independent variables and the dependent variable, as shown in Table 4. The P-value was used for testing the statistical significance of each regression coefficient and the F-test was used to test the overall significance of the model. The three

Table 3 Coefficient values of response surface model.

Coefficient	Value	Confidence limits		P-value
		-95%	95%	
β_0	28.6999	21.165	36.235	0.0000026
β_1	-1.6547	-2.441	-0.868	0.0006294
β_2	0.0015	0.001	0.002	0.0035147
β_3	-0.0787	-0.128	-0.029	0.0047527
β_4	0.1640	0.012	0.316	0.0369516
β_5	0.0211	0.004	0.038	0.0200329

Coefficient of multiple determination = R^2= 0.829, R^2 adjusted = 0.758, SE = 2.898.

Table 4 ANOVA table for the response surface model.

Source	Sum of squares	Mean square	F_0	F_{signif}	Degrees of freedom
Regression	489.27	97.854	11.65	0.000287	5
Residual	100.78	8.399			12
Lack-of-fit error	99.69	11.077	30.3780	0.00858	9
Pure error	1.09	0.365			3
Total	590.05				17

independent variables in the quadratic model will contribute a negligible effect when their *P*-values are more than 0.05, at the 95% confidence level, whereas independent variables with smaller *P*-values than 0.05 indicate a higher, significant contribution. According to Table 3, $\beta_1 M$ is the most significant term in the response model because the *P*-value of the constant coefficient is the lowest. Therefore, methanol is the most important parameters to be considered in the acid value reduction of acid-catalyzed esterification. The priority of the other parameters are successively: $\beta_2 T^2$, $\beta_3 AT$, $\beta_5 M^2$ and $\beta_4 AM$ based on a comparison of their *P*-values. In the analysis of variance, the F_0 value obtained was compared to its corresponding critical value F_{crit} or $F_{(\alpha,i,\ \text{n-1-}i)}$, which was found from the table of the *F*-distribution for a given significance level with i and (n-1-i) degrees of freedom, where α is the confidence level, i is the number of regression coefficients except for the intercept term and n is the number of experimental data (Somnuk *et al.*, 2013). The F_0 value of 11.65 obtained in this model was higher than F_{crit}, which for $F_{(0.05,5,12)}$ was 3.11. Thus, this response model is significant, and the significance of this quadratic model can be confirmed by F_{signif} which should be less than the 0.05 of the confidence level. According to Table 4, F_{signif} = 0.000287, which is far less than 0.05, thus the model is significant.

Response surface plot

Figures 2, 3 and 4 show the relationship between the dependent and independent variables using the response surface and contour plots. The effect of sulfuric acid and methanol on the acid value of the esterified oil when the ultrasonic irradiation time is held at zero is shown in Figure 2. The lower-most acid value in esterified oil can be achieved with a methanol concentration of 30–36.8% by volume with the sulfuric acid concentration in the range 0.3–0.9% by volume. Interaction in these ranges between the concentrations of methanol and sulfuric acid catalyst which affects the reduction of the acid value means that the methanol concentration increases with a decrease in the sulfuric acid concentration. Under these conditions, the minimum acid value could be reduced to 2.3 mg.g^{-1} KOH. The effect of the ultrasonic irradiation time and methanol concentration on the acid value of the esterified oil

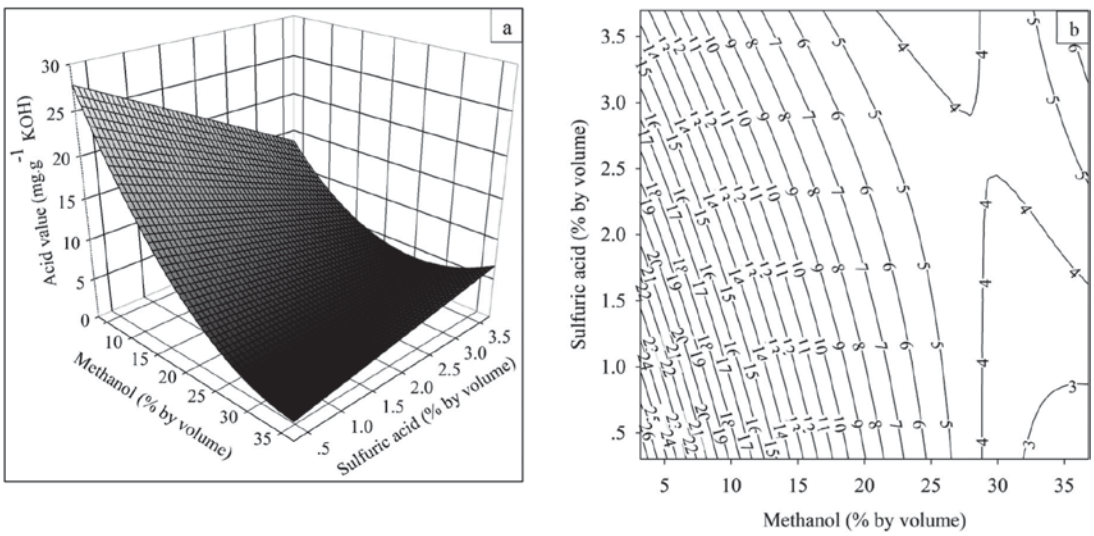

Figure 2 Sulfuric acid concentration and methanol concentration on the acid value of the esterified oil when ultrasonic irradiation time is held at zero level: (a) Response surface plot; and (b) Contour plot.

when the sulfuric acid concentration is held at zero is shown in Figure 3. The lower-most acid value of the esterified oil can be achieved at a methanol concentration of 28–34% by volume with an operated ultrasonic irradiation time of 40–65 s. However, under these conditions, the minimum acid value could only be reduced to 3.9 $mg.g^{-1}$ KOH. Lastly, the effect of the ultrasonic irradiation time and sulfuric acid on the acid value in esterified oil when the methanol concentration is held at zero is shown in Figure 4. The lower-most acid value of esterified oil could be achieved at a sulfuric

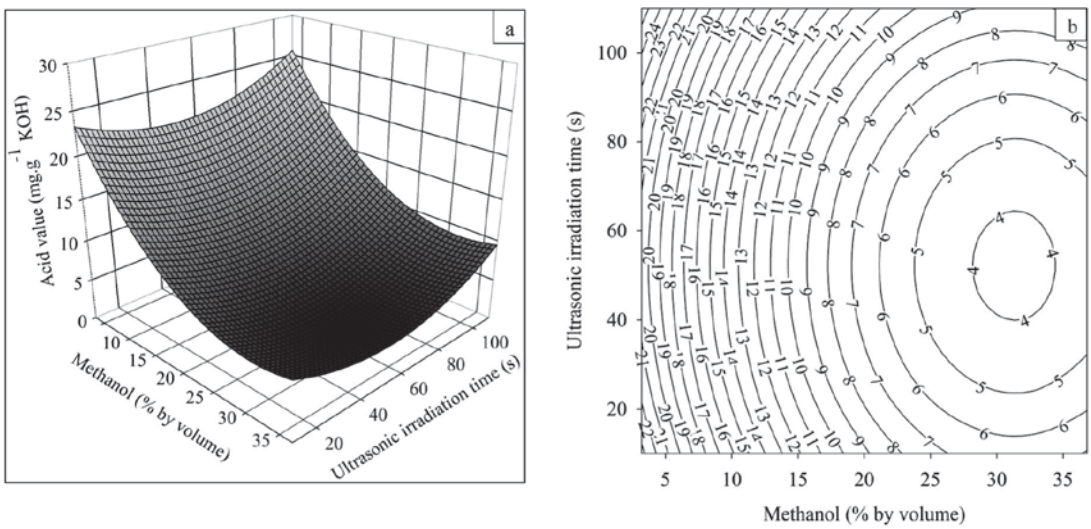

Figure 3 Ultrasonic irradiation time and methanol concentration on the acid value of the esterified oil when sulfuric acid concentration is held at zero level: (a) Response surface plot; and (b) Contour plot.

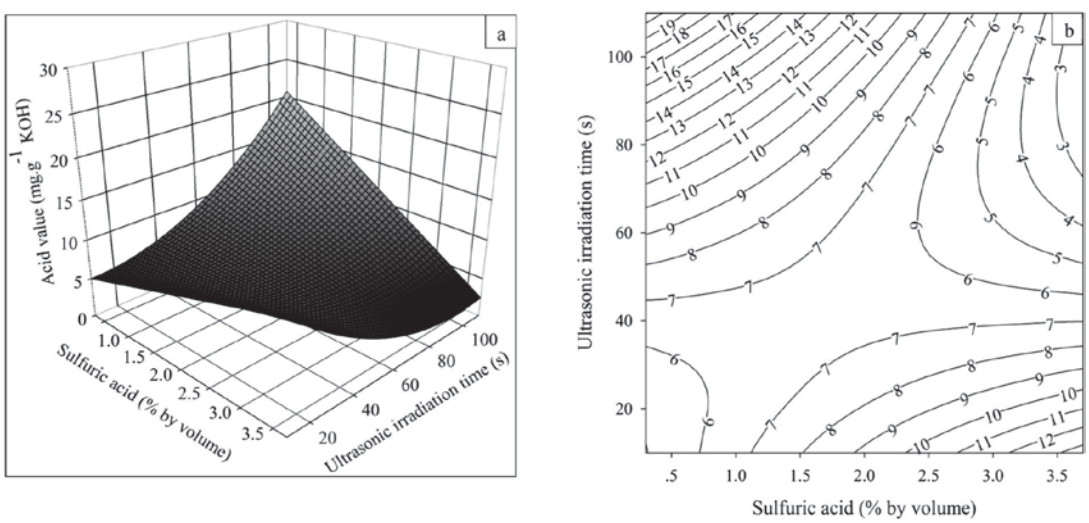

Figure 4 Ultrasonic irradiation time and sulfuric acid concentration on the acid value of the esterified oil when sulfuric acid concentration is held at zero level: (a) Response surface plot; and (b) Contour plot

acid concentration of 3.5–3.7% by volume with an operated ultrasonic irradiation time of 70–110 s. Under these conditions, the minimum acid value could now be reduced to 2.1 $mg.g^{-1}$ KOH. The P-value on the interaction between the sulfuric acid concentration and the ultrasonic irradiation time ($\beta_3 AT$) was very highly significant, indicating that both parameters exert high interaction.

Optimum conditions for reducing the acid value

The optimum conditions to reduce the acid value in the MCPO to be less than 2 $mg.g^{-1}$ KOH are shown in Figures 2, 3 and 4. These are: 24.8% by volume of methanol (molar ratio of 5:1), 3.7% by volume of sulfuric acid and an irradiation time of 96 s. The Solver function in the Microsoft© Excel spreadsheet software (Microsoft Corp.; Redmond, WA, USA) , was used to solve Equation 7. The model predicts that the minimum acid value of the esterified oil using acid catalyzed esterification obtained under these optimum conditions is 1.667 $mg.g^{-1}$ KOH. Therefore, the optimal condition was verified to confirm the predicted model. The results showed that the acid value in the MCPO was sharply reduced from 28 to 1.685 $mg.g^{-1}$ KOH, which was close to the acid value of 1.667 $mg.g^{-1}$ KOH from predicted model.

CONCLUSION

The acid value reduction of the MCPO with methanol in the presence of H_2SO_4 was performed in an ultrasonic homogenizer at a low-frequency of 18 kHz with an input capacity of 1,000 W. The response surface methodology and the multiple contour plots showed that optimization to reduce the acid value could be achieved with 24.8% by volume methanol (molar ratio of 5:1), 3.7% by volume sulfuric acid and an irradiation time of 96 s. A derived second-order polynomial equation was verified as statistically significant at both the model and individual parameter levels. The concentration of methanol (methanol-to-oil molar ratio), the concentration of sulfuric acid and the irradiation time were established as significant for reducing the acid value. Most importantly, the key parameter in the regression equation is the concentration of methanol. A shorter reaction time can be better achieved through using an ultrasonic homogenizer, compared with the mechanical batch process, while also obtaining a comparable production volume. The study proved that the ultrasonic process is very efficient, time saving and cost effective for acid-catalyzed esterification with short-chain alcohols to reduce the acid value. Moreover, the results and methodologies of this study were used in the specifications of the MCPO flow rate, methanol flow rate, sulfuric acid flow rate and residence time in the ultrasonic reactor, for use in a continuous system of acid-catalyzed esterification for free fatty acids reduction in MCPO using a static mixer coupled with high-intensity ultrasonic irradiation (Somnuk *et al*., 2013).

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