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ปีที่ 6 ฉบับที่ 1 เดือนมกราคม – มิถุนายน พ.ศ.2554

Ultrasonic Irradiation Assisted Synthesis of Biodiesel from Crude Palm Oil Using Response Surface Methodology

Ittipon Worapun Prachasanti Thaiyasiut and Kulachate Pianthong
Department of Mechanical Engineering, Faculty of Engineering, Ubon Ratchathani University,
Ubonratchathani, 34190
E-mail: i.worapun@gmail.com

ABSTRACT

Crude palm oil (CPO) has been considered as a potential feedstock for biodiesel production in several tropical countries. Production of biodiesel from crude palm oil with 6 wt% of free fatty acid (FFA) using a low-frequency ultrasonic irradiation (40 kHz) technique was investigated in the present work. The objective of this study was to determine the relationship between various important parameters of the alkaline catalyzed transesterification process to obtain a high conversion to biodiesel. Response surface methodology (RSM) was used to statistically analyze and to optimize the operating parameters of that process. A central composite design (CCD) was adopted to study the effects of the methanol to oil molar ratio, the catalyst concentration, reaction temperature, and irradiation time on the conversion to biodiesel. The result from the RSM analysis indicated that the methanol to oil molar ratio, catalyst concentration and irradiation time had the most significant effects on the conversion to biodiesel. Moreover, a coefficient of determination (R^2) value of 0.93 shows the fitness of a second-order model for the present study. Based on this second order model, the optimum conditions for alkaline catalyzed transesterification of CPO were found to be a methanol to oil molar ratio of 6.44:1, catalyst concentration of 1.25 wt%, reaction temperature of 38.44 °C and irradiation time of 25.96 minutes. At the calculated optimum condition, the conversion to biodiesel reached to 97.85%. Under these same conditions, the experimental value was 98.02±0.6%. The developed mathematical model has been proven to adequately describe the range of the experimental parameters studied and to provide a statistically accurate prediction of the optimum conversion to biodiesel.

Keyword: crude palm oil; biodiesel production; ultrasonic irradiation; optimization; response surface methodology (RSM)

1. Introduction

Rising prices of crude petroleum oil in the past few years, depletion of fossil oil reserves and also increasing environmental concerns have prompted much research into the production of alternative energy substitutes for petroleum based fuels. Such alternative energy must be technically feasible,economically competitive, environmentally acceptable and readily available [1]. Among the different possible resources for production of alternative fuels, biodiesel derived from a variety of vegetable oils and animal fats appears to be

the most promising alternative to petroleum based diesel fuel because it is renewable in nature and can be produced locally as well as being environmentally friendly. In comparison with petroleum diesel fuels, biodiesel fuels have many advantages, in that they lead to a reduction in carbon dioxide (CO_2), carbon monoxide (CO), sulfur dioxide (SO_2), unburned hydrocarbon (HC), smoke opacity, and particulate matter emission released by diesel engines [2-3]. Most importantly, they are easily biodegradable and non-toxic [4].

A variety of feedstocks can be used around the world to produce biodiesel these being such substance as rape seed, soybean, canola, mustard, palm, sunflower, hemp, tallow, lard, yellow grease, jatropha, neem, castor, rubber seed, and tall [5]. Among feedstocks with a potential to produce biodiesel, palm oil stands out as being the second most abundant oil in the world next to soybean oil. As well, it is cheaper than canola, rape seed or soybean oil which would reduce the overhead costs of biodiesel production [6].

Palm oil is considered an excellent feedstock and plays a very important role for biodiesel production in South-East Asia, particularly in Thailand and Malaysia. In Thailand, palm oil has been considered as a prospective feedstock for biodiesel production, particularly due to the fact that it has the highest yield amongst Thailand's oil yielding plants [7]. Crude palm oil (CPO) is the basic raw oil product which is obtained through the extraction process from palm mesocarp. In addition, it consists of more than 90 wt% of triglycerides and 3-7 wt% of free fatty acid (FFA) [8]. In this work, the CPO was chosen as the raw material for synthesis biodiesel on the basic of availability, economic and energy value to reduce the cost of biodiesel production. Several methods are available for biodiesel production, the most popular being known as the transesterification reaction. During this process, the vegetable oils or animal fats are reacted with short-chain alcohols such as methanol or ethanol in the presence of an alkaline or acid catalyst to generate fatty acid methyl/ethyl esters and byproduct glycerin [9-10]. The alkaline catalyzed reaction gives a better conversion in a short time with lower amount of FFA. However, this process is not suitable for feedstock with high FFA content. On the other hand, acid catalyzed esterification followed by alkaline catalyzed transesterification is more suitable [11-12]. The transesterification reaction is mass-transfer-limited initially because the two reactants that is alcohol and vegetable oils are immiscible [10]. The reaction of triglyceride with alcohol can occurs only at the interfacial region between two liquids and thus the process is slow. As a result, vigorous mixing is required to increase the area of contact between the two immiscible phases and this produces an emulsion [13]. In addition, the mixing efficiency is one of the most important factors to be adjusted in order to improve the transesterification yield. Usually, a mechanical stirrer is used to create an emulsion between the two reactants that enhances the interfacial reaction. This consumes a great deal of energy and it not efficient [14].

Low frequency ultrasonic irradiation is known to be a useful tool for the emulsification of immiscible liquids. Ultrasonic irradiation causes cavitation bubbles to from near the phase boundary between the alcohol and oil phases. The collapse of the cavitation bubbles disrupts the phase boundary and causes emulsification by ultrasonic jets that impinge one liquid upon

another. The cavitation may also lead to a localized increase in temperature at the phase boundary enhancing the transesterification reaction [14-15]. As reported in the literature, many researchers have successfully applied ultrasonic irradiation in the transesterification process. Difference kinds of raw material have been used to produce biodiesel by ultrasonic irradiation such as palm oil, canola oil, beef tallow, soybean oil and *jatropha curcus* oil. In addition, the research has been reported on the advantages of the ultrasonic irradiation assisted transesterification process presents such as excellent biodiesel yield, a much shorter reaction time, a low amount of catalyst and less energy consumption than with the conventional mechanical stirring method [16-21].

The main parameters affecting the transesterification reaction are the molar ratio of vegetable oils or fat oils to alcohol, catalyst concentration, reaction temperature, irradiation time, the free fatty acid content and the water content of the feedstocks [22]. However, optimization of the reaction parameters is very important in the transesterification reaction. In conventional multifactor experiments, optimization is usually carried out by varying a single factor while keeping all other factors fixed at a specific set of conditions. This method is time consuming and requires a large number of experiments. The limitations of the classical method can be avoided by optimizing all the relevant parameters by statistical experimental design [23-24].

Response surface methodology (RSM) is a well-known and effective statistical technique for designing experiments, building models and investigating complex processes [25-26]. The application of RSM to fine the optimum condition aimed to reduce the cost of expensive analysis methods and to minimize the number of experimental runs required to generate sufficient information for a statistically acceptable result [24].

This paper is a study of the optimization of the the process parameters in biodiesel production by alkaline catalyzed transesterification of triglycerides from CPO under ultrasonic irradiation assistance. The CPO with a high FFA (12 mg KOH/g) was processed in a two-step transesterification. The first step of the process was carried out using the following reaction conditions: methanol to oil molar ratio of 6:1, catalyst concentration (H_4SO_2) of 3 wt%, irradiation time of 30 minutes and reaction temperature of 30 ºC for reducing the FFA content of CPO to below 3 wt%. Special attention was paid to the second step to optimize the alkaline catalyzed transesterification condition. The purpose of this work focused on the development of a mathematical model that could describe the effects and relationships of the process variables towards the maximum conversion to biodiesel. RSM comprising a five-level-four-factor central composite design (CCD) was used to evaluate the interactive effect and to obtain the optimum conditions for alkaline catalyzed transesterification of CPO with respect to the methanol to oil molar ratio, catalyst concentration, reaction temperature and irradiation time.

2. Experimental and Methods

2.1 Materials

Crude palm oil (CPO) used in this study was obtained from a local palm oil mill in Suratthani province in the southern part of Thailand. The fatty acid composition of the crude palm oil was shown in Table 1. On the basis of

the chemical composition of the oil, the CPO molecular weight can be calculated as 890 g/mol. The acid value of the raw oil was measured to be 12 mg KOH/g oil, which corresponded to 6 wt% of free fatty acids (FFA). The chemicals used in the experiment which include sulfuric acid (H_2SO_4), potassium hydroxide (KOH), and methanol were purchased from the Merck Chemical Company (Germany), their purities being greater than 98%, 95%, and 99.8%, respectively. Chloroform-d (99.8%, containing 0.03% TMS) was purchased from Italmar (Thailand) Co. Ltd for nuclear magnetic resonance (NMR) analysis.

Table 1 Fatty acid composition of crude palm oil (CPO) used as raw material for biodiesel production.

Fatty acid	Structure*	wt%
Lauric	12:0	0.16
Myristic	14:0	0.99
Palmitic	16:0	43.03
Palmitoleic	16:1	0.19
Stearic	18:0	4.31
Oleic	18:1	39.47
Linoleic	18:2	10.82
Linolenic	18:3	0.29

* xx:y indicates xx carbons in the free fatty acid chain with y double bonds.

2.2 Equipment

An ultrasonic processor (KCME-KORN, Model AK-Nano/Bio-system 400 UL,Thailand) was used as the source of the ultrasonic irradiation for assisted the production of biodiesel. The processor operated at 40 kHz with a power of 400 W. The ultrasonic irradiation times for the reactions were adjustable from 1 to 90 minutes. All the experimental reactions were carried out in an ultrasonic batch reactor (1000 ml) made of stainless steel and equipped with a thermocouple probe and a sampling port, as shown in Figure 1. An ultrasonic batch reactor was immersed in a water bath placed on the hot plate. The tip of a horn (titanium horn) with a diameter of 10 mm and a length of 120 mm was used to transmit the ultrasound into the solution and was submerged up to 55 mm dept into the mixture contained in the ultrasonic batch reactor (in the methanol phase). The temperature of the reaction mixture was controlled by a water bath.

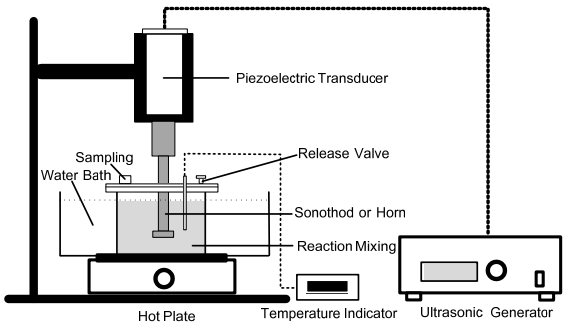

Figure 1 Schematic representation of experiment setup used for ultrasound assisted synthesis of biodiesel from crude palm oil (CPO)

2.3 Pre-treatment

The crude palm oil (CPO) in this study contains 6 wt% of free fatty acid (FFA), which is much higher than the safe limit for a direct transesterification reaction using an alkaline catalyst. The vegetable oils or animal fats used in an alkaline catalyzed transesterification reaction should contain less than 3 wt% of free fatty acid [27]. Hence, biodiesel production from high free fatty acid oil needs a two-step transesterification process; namely, pre-treatment (acid catalyzed esterification) followed by alkaline catalyzed

transesterification to get a high yield of biodiesel [28]. A pre-treatment process was performed to lower the FFA of the feedstock, the objective being to reduce the FFA of the CPO below 3 wt%. Selection of the experimental condition in the pre-treatment process was carried out on the basis of result obtained from our previous work [29], considering as the optimum conditions for the acid catalyzed esterification from crude *Jatropha curcus* L. oil by reducing the FFA content of crude *Jatropha curcus* L. oil from 12.5 to 3 wt%. The CPO was taken as the starting material. A methanol to oil molar ratio of 6:1 was used for the pre-treatment process using 3wt% of sulfuric acid (H_2SO_4) as a catalyst. The reaction was carried out with an ultrasonic irradiation time of 30 minutes with the reaction temperature under room temperature (30°C). After the acid catalyzed esterification reaction, the product was allowed to settle for 8 hrs or overnight before gum, unreacted methanol and water fraction at the bottom layer were removed. The acid value of the product from the acid catalyzed esterification was determined by a standard titration method (ASTM D664). In this process, the FFA of the raw oil was reduced from 6 wt% to below 2 wt%. The product was then used for the alkaline catalyzed transesterification process.

2.4 Experimental design

Response surface methodology (RSM) was employed in this work to evaluate the effect of various parameters on the alkaline catalyzed transesterification process. The experimental design for this reaction was carried out by utilizing a central composite design (CCD). A CCD with four independent variables at five levels was employed and the total number of experiments was 30 ($=2^k+2k+6$) where k is the number of independent variable [30] which included 16 factorial points, 8 axial points and 6 center points. The chosen independent parameters for the optimization in this study were methanol to oil molar ratio (X_1), the catalyst concentration (X_2), the reaction temperature (X_3) and irradiation time (X_4). The levels of methanol to oil molar ratio were selected in the ranges 3:1-12:1, the catalyst concentration was 0.5-1.5 wt%, the reaction temperature was 30-50°C and the irradiation time was 10-50 minutes. The response measured was the conversion to biodiesel (%) obtained from alkaline catalyzed transesterification of crude palm oil. The range and levels of the variables investigated in this study are presented in Table 2. The value of α (alpha) was fixed at 2. All variables at zero level constitute the center points while combination of variables consists of one at its lowest (-2) level or highest (+2) level with other variables at zero level constituting the axial points.

2.5 Experimental procedure

Initially, 300 g of CPO was added to the reactor which was preheated to the desired temperature on a heating plate before the reaction was started. The catalyst (KOH) was dissolved in methanol to the desired amount before the solution was charged into the reactor. The mixing intensity of the ultrasonic irradiation was fixed at 40 kHz frequency and supported by a power of 400 watts. Molar ratio of methanol to oil, catalyst concentration, reaction temperature and irradiation time were set according to the values proposed in the design of the experiment as shown in Table 2. After the reaction was completed, the reaction product was allowed to separate overnight by gravity before removing the glycerol layer from the bottom in a separation funnel. This upper phase consisted of methyl

ester or biodiesel, the lower phase was glycerol. The biodiesel was washed several times with small amount of fresh hot water until the washing water was found to be neutral. Finally, the alcohol and water content was evaporated by means of heating. Then, the percentage conversion to biodiesel was determined and calculated from an NMR spectrometer.

2.6 Statistical analysis

The experimental data (Table 3) obtained by CCD procedures were analyzed by the response surface methodology using the following second-order polynomial equation, developed to describe the relationship between the predicted response variable (conversion to biodiesel) and the independent variable of the transesterification process. This is given as Eq. (1):

$$y = \beta_o + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i>j}^{k} \sum_{j}^{k} \beta_{ij} x_i x_j + e \qquad (1)$$

where y is the response (conversion to biodiesel); β_o, β_i, β_{ii}, and β_{ij} are intercept, linear, quadratic and interaction constant coefficients respectively; K is the number of factors studied and optimized in the experiment; e is the random error and x_i and x_j are the encoded independent variables. The Design Expert version 8.0.4 (STAT-EASE Inc.) software was used for regression and graphical analysis of the experimental data. A statistical analysis of the model was performed to evaluate the analysis of variance (ANOVA). The quality of the model fit was evaluated using the coefficients of determination (R^2) and a response surface plot was developed using a fitted quadratic polynomial equation obtained from regression analysis.

2.7 Product analysis

The biodiesel products were analyzed by Nuclear Magnetic Resonance (NMR) method. NMR analyses were performed on a Bruker DMX 300 MHz spectrometer using chloroform-d ($CDCl_3$) as the solvent. For each analysis, 0.2 ml of each biodiesel sample was dissolved in 0.4 ml of deuterated chloroform and transferred to an NMR probe (5mm internal diameter). Spectra were recorded at room temperature with tetramethylsilane (TMS) as internal standard. The relaxation times were measured for all samples using an inversion recovery pulse sequence. The conversion to biodiesel was determined by the ratio of the signals at 3.68 ppm (hydrogen of the methoxy groups in the methyl esters) and 2.30 ppm (hydrogen of the methylene groups of all fatty acid derivatives). The conversion to biodiesel can be calculated by the following Eq (2):

$$\text{Conversion to biodiesel (\%)} = [(A/3)/(B/2)] \times 100 \qquad (2)$$

where A is the peak area of hydrogen of the methoxy groups in the methyl esters and B is the peak area of hydrogen of the CH_2 groups of all fatty acid derivatives.

Table 2 Independent variables and their levels used for response surface design

Independent variables	Levels*				
	- α (-2)	-1	0	+1	+ α (+2)
X_1: Methanol to oil molar ratio	3	4.5	6	7.5	9
X_2: Catalyst concentration (wt%)	0.5	0.75	1	1.25	1.5
X_3: Reaction temperature (°C)	30	35	40	45	50
X_4: Irradiation time (min)	10	20	30	40	50

*Transformation of variable levels from coded (X) to uncoded could obtained as: X_1 = 6+1.5X, X_2 = 1+0.25X, X_3 = 40+5X and X_4 = 30+10X

Table 3 Experimental design matrix and results

Std	Methanol to oil molar ratio (-) X_1	Amount of catalyst (wt %) X_2	Reaction temperature (°C) X_3	Reaction time (min) X_4	Conversion to biodiesel (%)	
					Experimental	Predicted
1	4.50	0.75	35.00	20.00	90.09	89.47
2	7.50	0.75	35.00	20.00	93.02	92.85
3	4.50	1.25	35.00	20.00	96.15	95.31
4	7.50	1.25	35.00	20.00	98.04	97.96
5	4.50	0.75	45.00	20.00	90.00	89.47
6	7.50	0.75	45.00	20.00	92.17	92.18
7	4.50	1.25	45.00	20.00	97.09	95.95
8	7.50	1.35	45.00	20.00	97.56	97.93
9	4.50	0.75	35.00	40.00	94.79	93.92
10	7.50	0.75	35.00	40.00	98.29	97.98
11	4.50	1.25	35.00	40.00	95.24	93.78
12	7.50	1.25	35.00	40.00	97.09	97.12
13	4.50	0.75	45.00	40.00	94.00	92.63
14	7.50	0.75	45.00	40.00	95.69	96.03
15	4.50	1.25	45.00	40.00	93.46	93.13
16	7.50	1.25	45.00	40.00	96.62	95.80
17	3.00	1.00	40.00	30.00	85.03	87.62
18	9.00	1.00	40.00	30.00	94.34	93.68
19	6.00	0.50	40.00	30.00	90.01	90.79
20	6.00	1.50	40.00	30.00	95.24	96.4
21	6.00	1.00	30.00	30.00	94.79	95.98
22	6.00	1.00	50.00	30.00	93.90	94.66

23	6.00	1.00	40.00	10.00	96.62	97.14
24	6.00	1.00	40.00	50.00	98.04	99.46
25	6.00	1.00	40.00	30.00	96.15	96.57
26	6.00	1.00	40.00	30.00	95.94	96.57
27	6.00	1.00	40.00	30.00	96.15	96.57
28	6.00	1.00	40.00	30.00	97.57	96.57
29	6.00	1.00	40.00	30.00	97.00	96.57
30	6.00	1.00	40.00	30.00	96.62	96.57

3. Results and Discussion

3.1 Model fitting and ANOVA

In an effort to optimize the reaction parameters of alkaline catalyzed transesterification on the conversion of CPO for biodiesel production, we selected a CCD with a five-level four-factor design that addressed methanol to oil molar ratio (X_1), catalyst concentration (X_2), reaction temperature (X_3), and irradiation time (X_4). Table 3 shows these experimental parameters and the results of both experimental values and predicted values on the basis of the CCD experimental design. All of the 30 designed experiments were conducted and the results analyzed via multiple regression. As shown in the table, the conversion to biodiesel (experimental values) ranged from 90.00 to 98.04% with the design points no.5 and no.24 giving the minimum and maximum conversion to biodiesel, respectively. The minimum conversion was obtained at a 4.5:1 methanol to oil molar ratio, 0.75 wt% catalyst concentration, 45 °C reaction temperature, and 20 minutes irradiation time, whereas, the maximum conversion was obtained at 6:1 methanol to oil molar ratio, 1 wt% catalyst concentration, 40°C reaction temperature and 50 minutes irradiation time. A quadratic polynomial equation was obtained from the design experimental data (table 3) and the following equations were generated to predict the conversion to biodiesel yield, as shown below (in terms of the code factors):

$$Y = 96.9 + 0.91X_1 + 1.69X_2 - 0.11X_3 + 0.59X_4 - 0.36X_1 1X_2 - 0.099X_1X_3 + 0.085X_1X_4 - 0.13X_2X_3 - 0.68X_2X_4 + 0.24X_3X_4 - 0.92X_1^2 - 0.88X_2^2 - 0.60X_3^2 - 0.18X_4^2 \quad (3)$$

Here, Y is the response variable, that is the conversion to biodiesel, and X_1, X_2, X_3, and X_4 are the actual values of the predictors, namely methanol to oil molar ratio, catalyst concentration, reaction temperature and irradiation time, respectively.

Statistical analysis of the model was performed to evaluate the analysis of variance (ANOVA) and to check the adequacy of the empirical model. In this investigation, the desired level of confidence was considered to be 95%. The result of ANOVA for the selected quadratic model is summarized in Table 4. The coefficients of the response surface model as provided by Eq. (1) were also evaluated. The *p*-values (probability of error value) are used as a tool to check the significance of each of the coefficients, which also indicate the interaction strength of each parameter. According to Table 4, the *p*-value of the model was less than 0.0001 demonstrating high significance in predicting the response values and

the suitability of the deduced model (a model term *p*-value <0.05 indicates that the model is significant at the 95% confidence interval). The Model *F*-value of 14.24 implies that the model is significant, there being only a 0.01% chance that a model *F*-value this large could occur due to noise.

Any lack of fit is the weighted sum of the squared deviations between the mean response at each parameter level and the corresponding fitted value. The *p*-value of the lack of fit was 0.079 (p>0.01), which indicated that there was no significance relative to a pure error (ie no significant lack of fit is good). The *F*-value of 3.74 implies that there is a 7.90% chance that a lack of fit this large could occur due to noise when the model is fitted to the observed experimental data. At the same time, the low value of the coefficient of variation (CV=0.92) indicated that the results of the fitted model are reliable.

The quality of the model fit was evaluated by the coefficient of determination (R^2), this value being calculated to be 0.93 for the response. This implies that 93% of the experimental data confirm compatibility with the data predicted by the model. The R^2 value is always between 0 and 1, and its magnitude indicates the aptness of the model. For a good statistical model, the R^2 value should be close to 1.0. The adjusted coefficient of determination (Adj. R^2) value reconstructs the expression with all the significant terms included, its value of Adj. R^2 = 0.86 also confirming that the model was highly significant. The value of the regression coefficients R^2 = 0.93, and especially Adj. R^2 = 0.86, indicates a high correlation between the experimentally observed and predicted values and explains any variability in the response.

The regression coefficients and the corresponding *p*-values of the coefficients are listed in Table 5. The significance of each parameter in the model can be accessed from its *p*-value, *p*-values less than 0.05 indicating that each of the model terms is significant. It can seen from the *p* values calculated for each model term that three linear coefficients of X_1, X_2 and X_4, three quadratic coefficients of X_1^2, X_2^2 and X_3^2, and one cross-product coefficients of X_2X_4 were significant at the 1% level (*p* values <0.001), whereas the other coefficients of the model do not indicate significant effects for the conversion to biodiesel (*p* values <0.05).

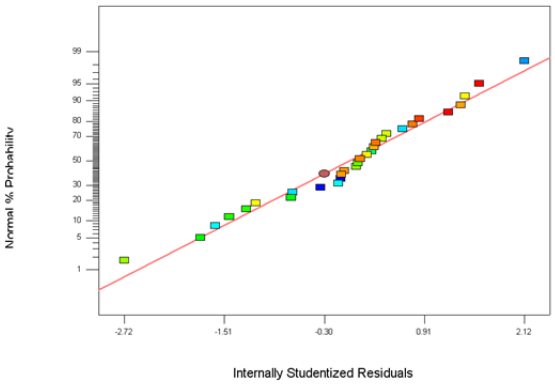

Figure 2 Normal probability plot of residuals

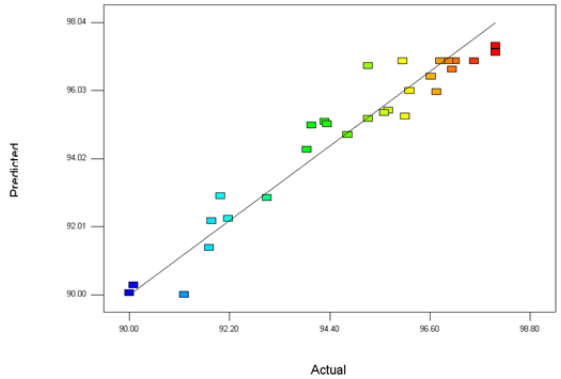

Figure 3 Plot of actual and predicted value of the conversion to biodiesel in the ultrasonic irradiation assisted biodiesel production process.

The normal probability plot of residuals and studentized residuals are presented in Figure 2. This figure indicates that there is a characteristic dispersion of constant variables in the data. Figure 3 shows the actual values obtained from the experiments versus the predicted values using the model equation developed. From this figure, the pointed cluster around the diagonal line indicates a good agreement between the predicted and the experimental conversion values which prove the reliability of the model developed. Thus, the model adequately explains the experimental range studied. This is further supported by the value of the correlation coefficient, R^2 which was found to be very close to unity (0.93).

3.2 Influence of the parameters on the conversion to biodiesel

Contour plots are graphical representation of the regression equation for the optimization of the reaction conditions. Figures 4a-f show contour plots between the independent and dependent variables for different fixed parameters. The effect of varying the methanol to oil molar ratio and catalyst concentration on the synthesis biodiesel production from crude palm oil at an irradiation time of 30 minutes and a reaction temperature of 40 ºC is shown in figure 4a. At a lower methanol to oil molar ratio, the conversion to biodiesel increased with increase in catalyst concentration. A similar pattern was followed when increasing the methanol to oil molar ratio. Therefore, a combined increase in methanol to oil molar ratio and catalyst concentration improve the conversion to biodiesel, the methanol to oil molar ratio and catalyst concentration being individually significant parameters (Table 4). Figure 4b represents the effect of the methanol to oil molar ratio, reaction temperature and their combined interaction on the biodiesel production process at an irradiation time of 30 minutes and catalyst concentration of 1 wt%. From the figure, it can be seen that the conversion to biodiesel increased with the increasing reaction temperature reaching its peak value at a methanol to oil molar ratio of 6.75:1 before then dropping in the range from 6.75:1 to 7.50:1. Figure 4c show the effect of methanol to oil molar ratio, irradiation time and their reciprocal interaction on the process at a catalyst concentration of 1 wt% and reaction temperature of 40 ºC. In this figure, the conversion to biodiesel increased with increasing irradiation time and reached a maximum value when the methanol to oil molar ratio was at a threshold level of 6.75:1. Beyond this level, conversion to biodiesel slightly decreased. Figure 4d depicts the effect of catalyst concentration, reaction temperature and their mutual interaction at an irradiation time of 30 minutes and methanol to oil molar ratio of 6:1. Continuous increase in the conversion to biodiesel was achieved with the increase in catalyst concentration in the range considered but the rate of improvement decreased towards the upper value. It is evident that the conversion to biodiesel is improved by increasing the reaction temperature from 35 to 42.5 ºC, but the effect then peaks and no additional improvement occurs with further rises of reaction temperature. The effect of differing catalyst concentration and irradiation time at a methanol to oil molar ratio of 6:1 and reaction temperature of 40 ºC is presented in figure 4e. As in the case of alkaline catalyzed transesterification, the catalyst concentration and irradiation time that were used both had a positive impact on the conversion. This increased linearly with irradiation time and non-linearly at a decreasing rate with a higher catalyst concentration. Thus the catalyst concentration and

irradiation time were significant and positively correlated to the conversion to biodiesel. Figure 4f shows the effect of reaction temperature, irradiation time and their mutual interactions at a methanol to oil molar ratio of 6:1 and catalyst concentration 1 wt%. Increases in reaction temperature did not significantly affect the conversion to biodiesel at any of the tested methanol to oil molar ratios indicating that the reaction temperature is not greatly influential on the synthesis of CPO to biodiesel because the cavitation from ultrasonic irradiation may also lead to a localized reaction temperature increase with an overly high value tending to induce methanol evaporation.

Table 4 Analysis of variance (ANOVA) for response surface quadratic model

Source	Sum of squares	Degrees of freedom	Mean squares	*F*-value	*P*-value
Model	151.22	14	10.8	14.24	<0.0001
Residual	11.38	15	1		
Lack of fit	10.04	10	1	3.74	0.0790
Pure error	1.34	5	0.27		
Cor total	162.6	29			
CV= 0.92%, R^2=0.93, Adj. R^2=0.89, Predicted R^2=0.85					

Table 5 Result of regression coefficients analysis and significant of response surface quadratic model

Factor	Coefficient Estimate	Degree of feedom	Standard Error	95% CI Low	95% CI High	*p*-value
Intercept	96.90	1	0.36	96.14	97.66	
X_1	0.91	1	0.18	0.53	1.29	< 0.0001
X_2	1.69	1	0.18	1.31	2.07	< 0.0001
X_3	-0.11	1	0.18	-0.49	0.27	0.5484
X_4	0.59	1	0.18	0.21	0.97	0.0047
X_1X_2	-0.36	1	0.22	-0.83	0.10	0.1155
X_1X_3	-0.099	1	0.22	-0.56	0.37	0.6566
X_1X_4	0.085	1	0.22	-0.38	0.55	0.7017
X_2X_3	-0.13	1	0.22	-0.60	0.33	0.5445
X_2X_4	-0.68	1	0.22	-1.15	-0.22	0.0067
X_3X_4	0.24	1	0.22	-0.23	0.70	0.2901
X_1^2	-0.92	1	0.17	-1.28	-0.57	< 0.0001
X_2^2	-0.88	1	0.17	-1.23	-0.52	< 0.0001
X_3^2	-0.60	1	0.17	-0.95	-0.24	0.0027
X_4^2	-0.18	1	0.17	-0.53	0.18	0.3038

3.3 Process optimization

The optimal values of the selected variables were obtained by solving the regression equation (Eq. (3)) using the software Design Expert 8.0.4. This model was employed to find the value of the process variables for the maximum conversion to biodiesel. The optimal value of the predictors for CPO biodiesel synthesis alkaline catalyzed transesterification obtained from the model equation are methanol to oil molar ratio of 6.44:1, catalyst concentration of 1.25 wt%, reaction temperature of 38.44 °C and irradiation time of 25.96 minutes. The model predicts that the maximum conversion to biodiesel that can be obtained under these optimum conditions is 97.85%.

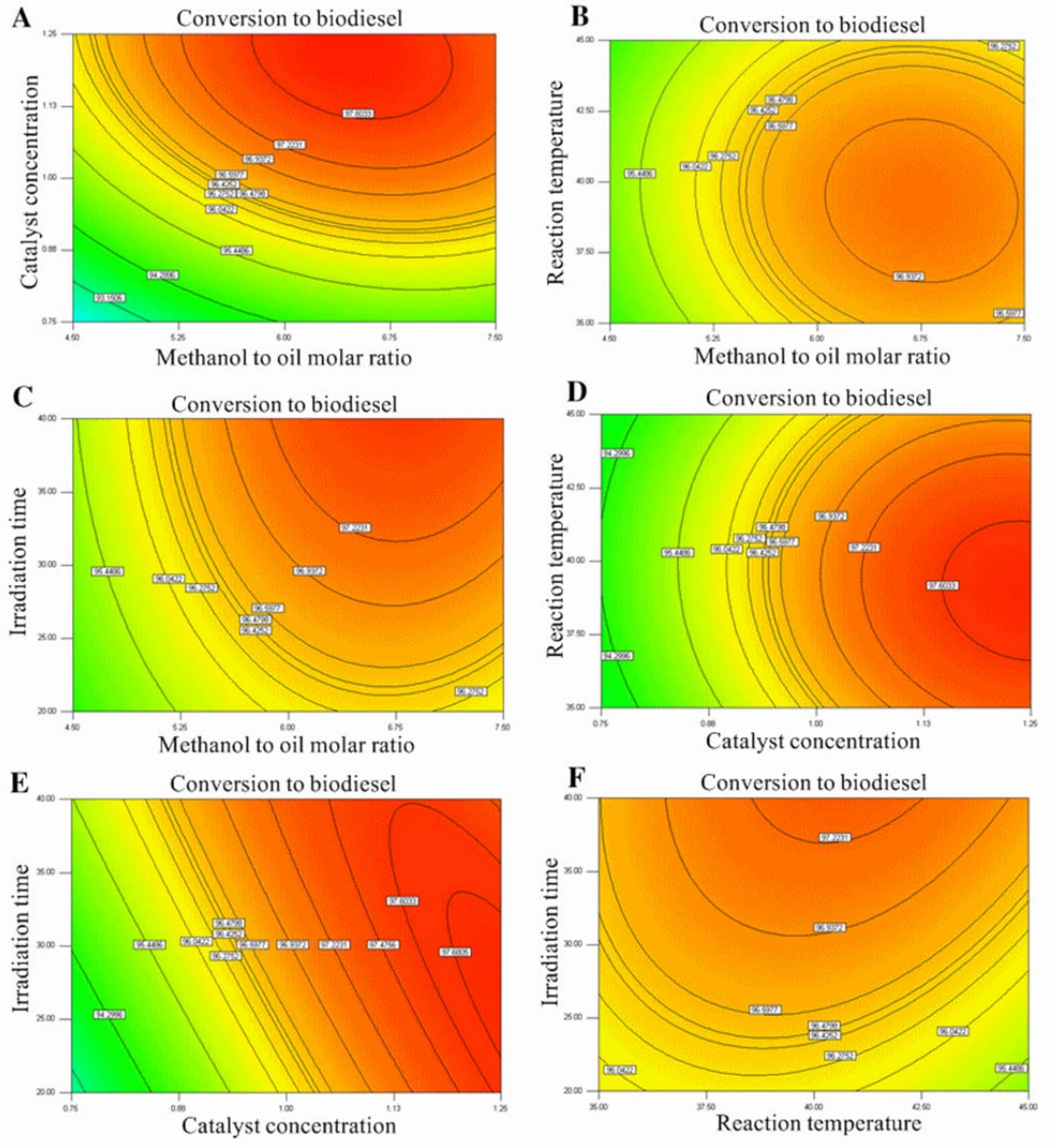

Figure 4 Contour plot of conversion to biodiesel (wt%)

Table 6 Verification experimental at optimum conditions.

Optimum condition				Conversion to biodiesel (%)	
Methanol to oil molar ratio	Catalyst concentration (wt%)	Reaction temperature (°C)	Irradiation time (min)	Experimental	Model predicted
6.44:1	1.25	38.44	25.96	98.02	97.85
Mean ± standard deviation (n=3)					

3.4 Verification of predictive model

In order to verify the prediction of the model, the optimum response values were tested under these predicted conditions: methanol to oil molar ratio 6.44:1, catalyst concentration 1.25 wt%, reaction time 38.44 °C and irradiation time of 25.96 minute. This set of conditions had been determined to be optimum by the RSM optimization approach and was also used to validate the experimental and predict the values of the response using the model equation. Table 6 shows the predicted and experimental response values at the optimum conditions. The average conversion to biodiesel yield from the experiments was 98.02±0.6. The result demonstrated the validation of the RSM model indicating that the model was adequate for alkaline catalyzed transesterification process.

4. Conclusions

The response surface methodology (RSM) method was successfully applied to the model to optimize conditions for the transesterification reaction parameters for biodiesel production from CPO using ultrasonic irradiation assistance. The effect of methanol to oil molar ratio, catalyst concentration and irradiation time were found to be the most significant for conversion whereas reaction temperature had very little importance. However, the model represents a significant step forward in precisely predicting the conversion to biodiesel at any point in the range of the variables. The optimum values of the parameters were methanol to oil molar ratio 6.44:1, catalyst concentration 1.25 wt%, reaction temperature 38.44 °C and irradiation time of 25.29 minutes. Under these optimum conditions, the predicted and experimental value gave the conversion to biodiesel to above 97.85% and 98.02±0.6, respectively.

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