The optimization of Biodiesel production from Brassica carinata using ultrasonic irradiation-assisted by response surface methodology

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ABSTRACT

This research presents the production of biodiesel from Brassica carinata oil by using ultrasonic irradiation as a reactor. The potassium hydroxide is a catalyst and 40 Hz 400 W ultrasonic irradiation is applied as a reactor. The Response Surface Methodology (RSM) in conjunction with the central composite design (CCD) was used to design the experimental. The process was carried out in a batch laboratory scale. The experiment setup were 5:1–7:1 of methanol to oil molar ratio, 1–2 wt% of catalyst concentration, 35-45°C of reaction temperature and 6–12 minute of reaction time. From the result, it is found that the maximum percentage of conversion to biodiesel is 99.71% at 5:1 of methanol to oil molar ratio, 2 wt% of the catalyst concentration, 45°C of the reaction temperature and 6 minute of the reaction time. The predicted optimum conversion to biodiesel percentage by quadratic polynomial is 99.02% at 5:1 of methanol to oil molar ratio, 1.69 wt% of catalyst concentration, 35 °C of reaction temperature and 6 minute of reaction time. This conversion to biodiesel percentage have been verified by the 0.9137 of determination coefficient (R^2), 0.8332 of the adjust determination coefficient (Adj. R^2) and 0.94% of standard error.

Keyword: Biodiesel, ultrasonic irradiation, brassica carinata, optimization

1. Introduction

The diesel engine has been widely used in industry, transportation, power generation, mineral machine, and agricultural machine. However, the diesel engine still using energy from fossil also increasing greenhouse gas and sulfur emissions to the atmosphere. Biodiesel is possible choices, because it is renewable and lower emissions released from diesel engine.

The production of biodiesel can be generated from soybean oil, rapeseed oil, sunflower oil, palm oil, jatropha oil, rubber seed oil or animal fat with alcohols. The transesterification is chemical process between triglycerides and alcohols. During the process can use alkaline or acid catalyst. The production of transesterification process was methyl or ethyl esters and glycerin [1].

Application of ultrasonic irradiation in biodiesel production is an attractive and effective technique to solve the problems related with the immiscible nature of the reactants [2] . A low frequency ultrasonic irradiation could be useful for the transesterification of triglyceride with alcohol. Ultrasonic provides the mechanical energy for mixing and the required activation energy for initiating the transesterification reactants [3] . Ultrasonic increases the chemical reaction speed and yield of the transesterification for vegetable oils and animal fats into biodiesel [4]. Mootabadi at al. [5] have investigated on 20 kHz ultrasonic cavitation assisted transesterification of palm oil in presence of three alkaline earth metal oxide catalysts, (CaO, SrO and BaO) . The catalytic activity was in the sequence of CaO < SrO < BaO. At optimum conditions, 60 min was required to achieve 95% yield compared to 2–4 h with conventional stirring. Also, the yields achieved in 60 min increased from 5.5% to 77.3% (CaO), 48.2% to 95.2% (SrO), and 67.3% to 95.2 (BaO).

Conventionally, the optimization study for biodiesel production process was performed with the variation of one component at a time and the response is a function of a single parameter (one-variable-at-a-time technique) that is much time consuming and exorbitant in cost. This technique does not include interactive effects among the variables and it does not depict the complete effect of the parameters on the process. However, application of response surface methodology (RSM) technique in multivariable system is able to provide a research strategy in studying the interaction of the parameters using statistical methods. The experiment model of biodiesel synthesis which developed by using RSM is able to simulate the reaction under various transesterification conditions with good estimations of errors. [6]

The main objective of this study is apply the Response Surface Methodology (RSM) for biodiesel production from Brassica carinata by using ultrasonic irradiation as a reactor. The optimum and effect of parameters compose of methanol to oil molar ratio, catalyst concentration, reaction temperature and reaction time were analyzed.

2. Materials and methods

2.1. Materials and reagents

The oil in this study is crude Brassica carinata (CBC) oil. The CBC seeds were collected from field crops in Vientiane province of Lao people's Democratic Republic (Lao PDR). The CBC seed was grinded and then the oil was extracted from seed by hydraulic press machine. The CBC oil was filtrated to remove solid impurities and then was heated to evaporate the moisture in the oil at 105°C for 30 minute.

The fatty acid compositions of CBC were analyzed by the Thailand institute of Scientific and Technological Research (TISTR) with gas chromatographic method as shown in Table 1. The main composition are 45.4% of Erucic acid (C22:1), 16.59% of Linolelaidic acid (C18:2 n-6), 10.29% of Octade-catrienoic acid (C18:3 n-3), 10.24% of Elaidic acid (C18:1 n-9), and 6.21% of

Eicosenoic acid (C20:1 n-9). Knowing the fatty acid composition, the molecular mass of the CBC can be then estimated. In this study, the molecular mass of CBC was determined as 974.23 g/mole.

Table 1
Fatty acid composition of crude Brassica carinata seed oil

Fatty acid composition	Results (%wt)
C12:0	0.06
C14:0	0.1
C16:0	3.24
C16:1t9	0.04
C16:1 n-7	0.18
C18:0	1.09
C18:1n9	10.24
18:2n6	16.59
C18:3 n-3	10.29
C20:0	0.86
C20:1 n-9	6.21
C20:2 n-6	0.84
C20:3 n-3	0.15
C22:0	1.02
C22:1	45.4
C22:2	1.28
C23:0	0.04
C24:0	0.6
C24:1	1.73

The catalyst used in the experimental is KOH which 98. 8% purity. And reactant is methanol which 98% purity.

2.2. Experimental setup

Ultrasonic processor (KCME-KORN, Model AK-Nano/ Bio-System 400 UL) was used as the source of the ultrasonic irradiation for assisting the produce of biodiesel. The processor operated at 40 kHz with the 400 watt. The ultrasonic irradiation times for the reaction was adjust from 1 to 12 minute. All of experimental reaction were carried out in ultrasonic batch reactor (500 mL) made from stainless steel. An ultrasonic batch reactor was immersed in a water batch on the hot plate. The tip of a horn diameter is 10 mm and 120 mm length and transmit the ultrasound into the solution was submerged up to 55 mm deep into solution contained in the ultrasonic batch reactor. The temperature of the reaction mixture was controlled by water bath. A temperature indicator was used for measuring the reaction temperature as shown in Fig 1.

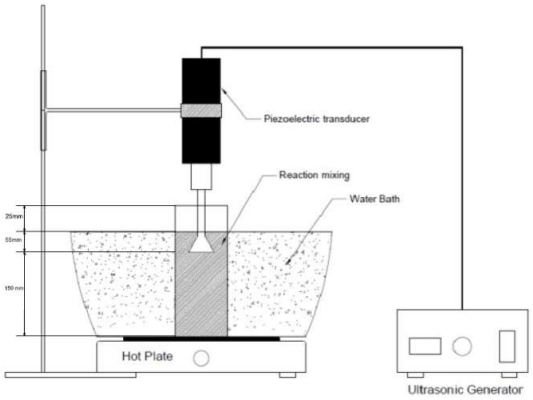

Fig. 1 The connection diagram experimental

2.3. Experimental design

A central composite design (CCD) was applied with four independent variables: methanol to oil molar ratio (X_1) , catalyst concentration (X_2), reaction temperature (X_3) and reaction time (X_4). The experimental designs were 5:1 to 7:1 of methanol to the oil molar ratio, 1 to 2 wt% of catalyst concentration, 35 ˚C to 45 ˚C of reaction temperature and 6 minutes to 12 minutes of reaction time as shown in Table 2.

Table 2
Independent variables for experimental design

Independent variables	Levels				
	-2(-α)	-1	0	1	2(α)
Methanol to oil molar ratio (X_1)	4	5	6	7	8
Catalyst concentration(X_2)	0.5	1	1.5	2	2.5
Reaction temperature(X_3)	30	35	40	45	50
Reaction time (X_4)	3	6	9	12	15

The experimental design was obtained by 2^4 factorial which CCD for five levels of four independent variables. The CCD experimental were design giving 30 experiments according to 2^k+2k+2, where k is the number of independent variables, which included 16 factorial points, 8 axial points and 6 center points [7]. The regressions were analyzed by Design Expert 9 (STAT-EASE Inc) software [8]. The model was verified by observation of the coefficients of determination (R^2). A quadratic polynomial equation is shown in Equation (1).

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i>j}^{k} \sum_{j}^{k} \beta_{ij} x_i x_j + e \qquad (1)$$

Where, Y is the predicted response (conversion to biodiesel), β_0, β_i, β_{ii}, and β_{ij} are regression coefficients, k is the number of studied factors and optimized in the experiment; e is the random error, x_i and x_j are the encoded independent variable [9].

2.4. Experimental procedure

The experimental was performed according to following procedure: 500 mL of CBC oil was added to the reactor then was preheated to the desire temperature by heating plate before the reaction started. The mixing intensity of the ultrasonic irradiation was fixed at 40 kHz frequency and 400 watt power supplied. The methanol to oil molar ratio, catalyst concentration, reaction temperature and reaction time were set according to the values proposed in the design.

2.5. Product analysis

The conversion to biodiesel was analyzed by NMR method that performed on a Bruker DMX 300 MHz spectrometer using chloroform-d ($CDC1_3$) 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. Spectra was recorded at room temperature with tetramethyl-silane as internal standard [10]. The percentage conversion to biodiesel can be calculated by Equation (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 peak area of hydrogen of the CH_2 groups of all fatty acid derivatives.

3. Results and discussions

3.1. Conversion to biodiesel percentage by ^1H NMR analysis

The conversion to biodiesel percentage of CBC oil was analyzed by the Department of Chemistry, Ubon Ratchathani University with NMR method as show in Table 3. The maximum presented of conversion to biodiesel is 99.71%. at 5:1 of methanol to oil molar ratio, 2 wt% of catalyst concentration, 45 C° of reaction temperature and 6 minute of reaction time conditions.

The percentage of conversion to biodiesel were used to select from Independent variables of alkaline catalyzed transesterification process with methanol to oil molar ratio (X_1), catalyst concentration (X_2), reaction temperature (X_3) and reaction time (X_4). These experimental parameters and the percentage of conversion to biodiesel were shown in Table 3.

The CCD was experimental design. All of the 30 designed experiments were conducted and analyzed. The minimum and maximum of conversion to biodiesel are 70.36 % and 99.71 % at design point No. 19 and No. 7 respectively. The maximum percentage of conversion to biodiesel was obtained at 5:1 of methanol to oil molar ratio, 2 wt% of catalyst concentration, 45 °C of reaction temperature and 6 minute of reaction time.

Table 3
Experimental design matrix and results of conversion to biodiesel

Run	Real variables				Conversion to biodiesel
	X_1	X_2	X_3	X_4	
1	5	1	35	6	91.63
2	7	1	35	6	88.73
3	5	2	35	6	98.62
4	7	2	35	6	94.49
5	5	1	45	6	91.04
6	7	1	45	6	89.30
7	5	2	45	6	99.71
8	7	2	45	6	97.49
9	5	1	35	12	89.15
10	7	1	35	12	88.44
11	5	2	35	12	99.07
12	7	2	35	12	96.30
13	5	1	45	12	93.51
14	7	1	45	12	90.26
15	5	2	45	12	98.98
16	7	2	45	12	97.01
17	4	1.5	40	9	99.12
18	8	1.5	40	9	93.31
19	6	0.5	40	9	70.36
20	6	2.5	40	9	99.46
21	6	1.5	30	9	96.26
22	6	1.5	50	9	97.22
23	6	1.5	40	3	95.55
24	6	1.5	40	15	97.17
25	6	1.5	40	9	95.70
26	6	1.5	40	9	96.70
27	6	1.5	40	9	95.50
28	6	1.5	40	9	95.50
29	6	1.5	40	9	96.00
30	6	1.5	40	9	95.40

The properties of the maximum of conversion to biodiesel were tested by the Department of Chemical Technology, Chulalongkorn University with gas chromatographic method. The results are shown in Table 4.

Table 4
Fuel properties of methyl ester from Brassica carinata oil

Fuel properties	Test method	Results	Biodiesel Standard D6751
Specific gravity	ASTM D1298	0.89	0.86-0.9
Viscosity (cSt)	ASTM D4455	5.6	1.6-6
LHV (MJ/kg)	ASTM D5865	41.94	N/A
Flash point (°c)	ASTM D97	80	100
Fire point (°c)	ASTM D97	82	182

3.2. Regression model and analysis of variance (ANOVA)

Among the models that fitted to the response (linear, two factor interaction (2FI), quadratic and cubic polynomial), the quadratic model was selected due to higher order polynomial with signification. The quadratic polynomial model was suggested. The additional model cubic polynomial was not aliased by the RSM [11]. A quadratic polynomial

equation obtained from the design and the following equation was generated to predict the conversion to biodiesel as shown in Equation (3).

$$Y = 95.8 - 1.3X_1 + 4.91X_2 + 0.53X_3 + 0.21X_4 - 0.16X_1X_2 + 0.083X_1X_3 + 0.14X_1X_4 - 0.091X_2X_3 + 0.024X_2X_4 + 0.17X_3X_4 + 0.17X_1^2 - 2.65X_2^2 + 0.31X_3^2 + 0.21X_4^2 \quad (3)$$

Here, Y is response conversion to biodiesel and X_1, X_2, X_3 and X_4 are the values in the experimental form the studied variables.

Table.5
Analysis of variance (ANOVA) for the quadratic model

Sources of variations	Sum of squares	Degrees of freedom	Mean squares	*F*-value	*P*-value
Model	846.49	14	60.46	11.35	0.0001
Residual	79.94	15	5.33	-	-
Lack of fit	78.74	10	7.87	32.81	0.0006
Pure error	1.2	5	0.24	-	-
Total	926.42	29	-	-	-

R^2=0.9137, Adj. R^2=0.8332, C.V.=2.45, Std.Dev.=2.31

Statistical analysis of the model was performed to evaluate the analysis of variance (ANOVA), the desired level of confidence was considered at 92% of quadratic model as shown in Table 5. The *p*-value (probability of the error) of the model was less than 0. 0001 demonstrating high significant in predicting the response values and the suitability of deduced model (a model term *p*-value<0.0001 indicates that the model is significant at the 95% confidence interval). The *F*- value of the model was 11.35 that implies the model is significant, there being only a 0.01% chance that model *F*-value is large could occur due to noise. The lack of fit is the weighted sum of squared deviations between the mean responses at each parameter level and the corresponding fitted value. The *p*-value of lack of fit was 0.0006 that indicated there was significant relative to a pure error. The *F*- value of lack of fit was 32.81 implies that there is a 0.06% chance that a lack of fit this large could occur due to noise. The high value of R^2 (0.9137) is an indication that the fitted model can be used for prediction with reasonable precision. The goodness of fit the model was evaluated by the adjusted coefficient of determination (Adj.R^2). The value of the Adj.R^2 (0.8332) that indicates a high proportion of variability (83.32%) in the response variables to the four predictor variable and a very small portion of variability. The coefficient of variation (CV= 2.45) indicated the results of the fitted model reliable.

Effect of different independent variables on the response surface can be studied on data in Table 6. The standard error and *P*-values indicate the significant of each coefficient. In general, the smaller *P*-values indicate higher significant of the corresponding variables [12]. As the linear effect (X_1) and (X_2) were considered, 5% level being significant was found. The X_2 term had the most significant linear effect. In term of interaction effect not found to be significant at 5% level. However, for quadratic effect, the X_2^2 was found to be significant effect on conversion to biodiesel.

Table.6
Regression coefficients for second-order polynomial model

Model term	Estimate coefficient	Standard error	*P*-value
Intercept	95.8	0.94	
X_1	-1.3	0.47	0.0143
X_2	4.91	0.47	<0.0001
X_3	0.53	0.47	0.2758
X_4	0.21	0.47	0.6678
X_1X_2	-0.16	0.44	0.7911
X_1X_3	0.083	0.44	0.8874
X_1X_4	0.14	0.44	0.8075
X_2X_3	-0.091	0.44	0.8773
X_2X_4	0.024	0.58	0.9669
X_3X_4	0.17	0.58	0.7716
X_1^2	0.17	0.58	0.6971
X_2^2	-2.65	0.58	<0.0001
X_3^2	0.31	0.58	0.4980
X_4^2	0.21	0.58	0.6388

3.3. The interaction between the parameters

The interactive effect between methanol to oil molar ratio and the catalyst concentration while the other variables kept at their center values was shown in Fig.2. The high percentage of conversion to biodiesel was obtained at high catalyst concentration and low methanol to oil molar ratio.

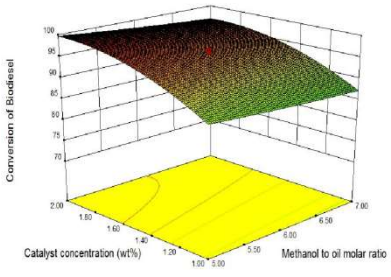

Fig.2 interaction methanol to oil molar ratio and catalyst concentration

The Fig. 3 shows the interactive effect between catalyst concentration and reaction temperature while the other variables kept at their center values. The high percentage of conversion to biodiesel was obtained at high catalyst concentration and low reaction temperature, also the catalyst concentration had more effect than reaction temperature.

The interactive effect between catalyst concentration and reaction time while the other variables kept at their center values was shown in Fig. 4. The high percentage of conversion to biodiesel was obtained at high catalyst concentration and low reaction time, moreover the catalyst concentration had more effect than reaction time. The most important independent variables were catalyst concentration and methanol to oil molar ratio.

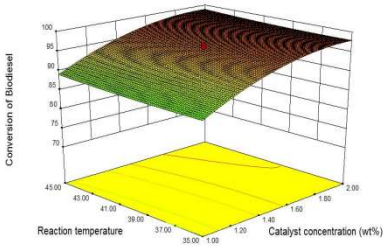

Fig.3 interaction catalyst concentration and reaction temperature

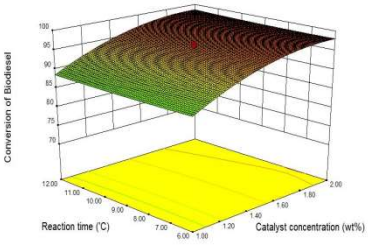

Fig.4 interaction catalyst concentration and reaction time

3.4. Optimization of process parameters

The experimental range were studied, optimum conditions for synthesis biodiesel from CBC were predicted using optimization function of the Design Expert software version 9.0. In numerical optimization, the independent variables with methanol to oil molar ratio, catalyst concentration (wt%) , reaction temperature (° C) and reaction time (minute) were set within the range between (-2) and (+2) while the conversion to biodiesel to setup minimum and maximum value [12] . The constraints used for the optimum study as shown in Table 7.

Table.7

Rang of input parameters and response for optimization

Criteria	Goal	Lower limit	Upper limit
Methanol to oil molar ratio X_1	Range	5	7
Catalyst concentration X_2 (wt%)	Range	1	2
Reaction temperature X_3 (°C)	Range	35	45
Reaction time X_4 (minute)	Range	6	12
Conversion to biodiesel (%)	Maximize	70.36	99.71

The optimum values of the selected independent variables were obtained by solving the regression Equation 3. The experimental data obtained for the conversion to biodiesel were found maximum percentage 99.71% [10]. The response surface indicated the predicted optimum percentage of conversion to biodiesel was 99.02 % by transesterification process. Additional experiment was carried out to validate. The optimization result obtained by the response surface analyzed optimum conversion to biodiesel 98.84% at 5:1 of methanol to oil molar ratio, 1.69 wt% of catalyst concentration, 35°C of reaction temperature and 6 minutes of reaction time conditions. It is well agreed with the predicted values 99.02%, with a relatively standard error 0.94%.

The prediction and experiment were response values at these optimum conditions. The average conversion to biodiesel from the experimental was 99.84% and very close to the prediction, as detailed in Table 8.

Table.8

Experimental and predicted response at the optimum conditions model

Optimal condition				Conditions to biodiesel		
X_1	X_2	X_3	X_4	Experimental	Predicted	Error (%)
5	1.69	35	6	98.84	99.02	0.94

4. Conclusion

The RSM was a useful tool to investigate the optimum condition for biodiesel production from Brassica carinata oil. The interactive effect from multiple independent variables, including the methanol to oil molar ratio, catalyst concentration, reaction temperature and reaction time to the conversion to biodiesel were investigated. The main conditions that affect to percentage of conversion to biodiesel were catalyst concentration and methanol to oil molar ratio. The optimum conversion to biodiesel predicted by quadratic polynomial was 99.02% at 5:1 of methanol to oil molar ratio, 1.69 wt% of catalyst concentration, 35 C° of reaction temperature and 6 minute of reaction time conditions. This optimum has been verified by 0.9137 of R^2, 0.8332 of Adj.R^2 and 0.94% of

standard error. Thus, this statistical model is adequate for predicting the conversion to biodiesel of Brassica carinata.

5. Acknowledgements

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