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Ultrasonic-assisted biodiesel production process from brassica carinata using response surface method

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Abstract

This research presents the product of biodiesel from Brassica carinata oil by transesterification process. The potassium hydroxide was a catalyst and ultrasonic irradiation (40 Hz, 400 w) was applied to reactor. The response surface mythology (RSM) in conjunction with the central composite design (CCD) was use to design the experimental. The process was carried out in a batch laboratory scale. The experimental investigates on influences of the ultrasonic energy used. The condition set up were methanol to oil molar ratio (5:1 – 7:1), catalyst concentration (1 – 2 wt%), reaction temperature (35 - 45 C˚) and reaction time (6 – 12 minute). The result found highly conversion around 99.71 % at methanol to oil molar ratio (5:1), catalyst concentration (2 wt%), reaction temperature (45C˚) reaction time (6 minute) condition. Thus , this research was successfully to product biodiesel from Brassica carinata oil.

1. Introduction

Biodiesel is an alternative fuel to petroleum production derived from renewable resources. It has lower emissions than petroleum-based diesel, biodegradable and helps reduce both greenhouse gas and sulfur emissions to the atmosphere. [1] The biodiesel is synthesized by transesterification of vegetable oils or animal fats with alcohol. Methanol is commonly used in the commercial biodiesel production by the transesterification reaction of triglyceride with methanol, and the most common form of biodiesel is methyl ester [2]

Application of ultrasonic energy in biodiesel production is an attractive and effective technique to solve the problems related with the immiscible nature of the reactants [2], subjecting ultrasonic wave to the reaction mixture force the fluids to generate huge number of cavitation bubbles which grow rapidly and subsequently undergo violent collapse. The vigorous collapses of these bubble will lead to the formation of micro jets generating fine emulsion between the reactants. Besides that, these collapses also generate local temperature increment with the reaction mixture. The use of ultrasonic energy in homogenous or heteroheneous biodiesel production has been investigated and encouraging results have been demonstrated. However, the use of heterogeneous acid catalyst for ultrasonic-assisted biodiesel production process still hardly reported [6]

The main objective of this study is to elucidate the rote of ultrasonic energy and its effects on the reaction. Transesterification of crude Bassica carinata oil with methanol has been conducted in the presence of methanol to oil molar ratio, catalyst concentration reaction, temperature reaction time for biodiesel production. The obtained experiment data have been used to generate a historical design and to identify the optimum conditions by means of a response surface methodology (RSM) [3]

2. Experimental

2.1 Materials and reagent

The raw oil in this study crude Brassica carinata (CBC). The crude CBC seeds were collected from field crops in Vientiane province in the central part of Laos. The CBC was obtained by grinding the seeds and extracted by hydraulic press machine. The CBC oil were filtrated to remove solid impurities and were then heat to evaporate the possible water present in it at 105˚c for 30 min

The chemicals used in the experiment which include potassium hydroxide (KOH), methanol

2.2 Experiment setup

An ultrasonic generator (KCME-KORN, Model AK-Nano/Bio-System 400 UL, Thailand) was use as the source of the ultrasonic irradiation for assisting the production of biodiesel. The processor operated at 40 kHz with the power 400 W. The ultrasonic irradiation times for the reaction adjustable from 3 to 15 min. All of experimental reaction were carried out in ultrasonic batch reactor (1000 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 10 mm and length of 120 mm The connection diagram and the actual experimental step of ultrasonic irradiation reactor are show in Fig.2.1

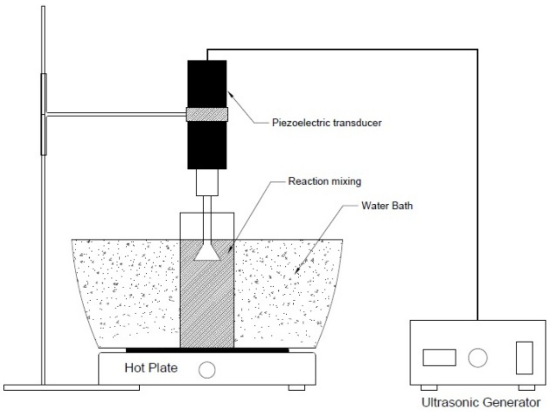

Fig. 2.1 The connection diagram experimental setup

2.3. Product analysis

The percentage conversion to biodiesel of the product in the alkaline catalyzed transesterification process was analyzed by Nuclear Magnetic Resonance (NMR) method. NMR analyses were preformed 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

2.4. Experimental design

A central composite design (CCD) was applied with four design factors methanol to oil molar ratio (X_1), catalyst concentration (X_2), reaction temperature (X_3) and reaction time (X_4). Four zero levels (central values) selected for the experimental design were the methanol to oil molar ratio (5:1 to 7:1), catalyst concentration (1 to 2 wt%),reaction temperature (35 to 45 ˚C) and reaction time (6 to 12 min), Table 1 [4].

A 2^4 full-factorial CCD for three levels of the four independent variable was used in this work giving a total of 30 experiments according to 2^k+2k+2 , where k is the number of independent variables [5]. The twenty four experiments were improved with six replications at the center points to evaluate the pure error. For regression and graphical analyses of the date, Design Expert 9 software was employed by taking the maximum production conversion values as the design experiment responses. A general second degree form of the polynomial equation is as shown in Equation (2.1)

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i \succ j}^{k} \sum_{j}^{k} \beta_{ij} x_i x_j + e \qquad (2.1)$$

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 factors studied and optimized in the experiment; e is the random error and x_i and x_j are the encoded independent variable.

Table 1

Coded and actual reaction variables used in the experimental

Independent variables	Levels		
	-1	0	1
Methanol to oil molar ratio X_1	5	6	7
catalyst concentration X_2	1	1.5	2
reaction temperature X_3	35	40	45
reaction time X_4	6	9	12

3. Results and discussion

3.1 Regression model and analysis of variance (ANOVA)

In an effort to optimized the reaction parameters of alkaline catalyzed transesterification on the conversion of CBC for biodiesel production, we selected a CCD with four factor design that addressed methanol to oil molar ratio (X_1), catalyst concentration (X_2), reaction temperature (X_3) and reaction time (X_4). Table 2 shows these experimental parameters and the results of experimental values on the basis of the CCD experimental design. All of the 30 designed experiments were conducted and the results analyzed, the conversion to biodiesel ranged from 70.36 % to 99.71 %. with design point no. and no. giving the minimum and maximum conversion of biodiesel. The minimum conversion was obtained at 6:1. methanol to oil molar ratio, 0.5 wt%. catalyst concentration, 40˚C. reaction temperature and 15-min.reaction time, whereas, the maximum conversion of biodiesel. The minimum conversion was obtained at 5:1 methanol to oil molar ratio, 2 wt%. catalyst concentration, 45˚C reaction temperature and 6-min reaction time. A quadratic polynomial equation was obtained from the design and the following equation were generated to predict the conversion to biodiesel, as shown below

$$Y = 95.8 - 1.3X_1 + 4.91X_2 + 0.53X_3 + 0.21X_4 - 0.16X_1X_2 + 0.083X_1X_3 + 0.14X_1X_4 - 0.091X_2X_3 + 0.024X_2X_4 + 0.17X_3X_4 + 0.17X_1^2 - 2.65X_2^2 + 0.31X_3^2 + 0.21X_4^2 \quad (3.1)$$

Here, Y is response (conversion of biodiesel),and X_1,X_2,X_3 and X_4 are the values in the code form of the studied variable.

Table 2

Central composite design matrix for four variables

Run	Real variables				Conversion to biodiesel (%)
	M/O	Catalyst concentration	Reaction temp (˚C)	Reaction time (min)	
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	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

Statistical analysis of the model was performed to evaluate the analysis of variance (ANOVA), the result of ANOVA for the selected quadratic model is summarized shown in the Table- 3. Results from the fitting of the experimental data to a second-order response surface model. High significance of the regression model can be seen in the Fisher *F*-test for model (F=11.35) with very small probability value (Prop.>F<0.0001). According to the value of the determination coefficient (R^2=0.9137), it could be inferred that 91.37% of the effect on the conversion to biodiesel could be attributed to the variation in the independent variables and remaining response could be explained as residues.

The results from table 3 indicated that the empirical model on conversion to biodiesel for Brassica carinuta give good predictions at high confidence level 91.37%, the model *F*-model of 11.35 implied the model was significant. The *p*-value of the model was less than 0.0001 indicating the signify-cance of the model. The value of the determination coefficient (R^2=0.9137) indicated that only 9% of the total variation. The adjust determination coefficient (Adj. R^2=0.8332) is also high.

Table.3

Analysis of variance (ANOVA) for the quadratic model

Sources of variations	Sum of squares	Degrees of freedom	Mean squares	*F*-value	Prob.>*F*
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.=2.31, Std.Dev.=2.31

Effect of different reaction variables on the response can be studies based on data in Table 4. The table provides the standard error and Prop >P values that indicate the significance of each coefficient. In general, the smaller Prop.>P value indicate higher significance of the corresponding coefficient [6]. It can be seen in the table 4 that the most influencing variables on the model response were the Methanol to oil molar ratio and catalyst concentration. Beside their single effects, the in-fluences of their squared values and the two –level interaction between these two parameters were also found to significantly affect the process conversion

3.2 The interaction between the parameters

Fig.3.1-3.3 shows the three-dimension (3D) re-sponse surfaces to estimate conversion to biodiesel over independent variables. The interaction between methanol to oil molar ratio and catalyst concentration at reaction temperature of 45˚C and reaction time 12 min on conversion of biodiesel from Brassica carinuta. The conversion to biodiesel increased when the methanol to oil ratio was 5:1 at catalyst con-centration within the range of 1.5 to 2 wt%

The interactive effect between methanol to oil molar ratio and the catalyst concentration while the other parameters kept at their center values is shown in Fig. 3.1, the increment of methanol to oil molar affected of conversion to biodiesel slightly. The maximum conversion to biodiesel was obtained at higher catalyst concentration and lower methanol to oil molar ratio profile. This might be due to the fact that the most important factor is the catalyst con-centration. The results clearly indicated that the optimum concentration of KOH required for effective transesterification was about 2 wt% [7].

The interactive effect between catalyst concen-tration and the reaction temperature while keeping the other parameters at their center value can be seen in Fig.3.2. the maximum conversion to biodiesel was obtained at higher catalyst concentration and higher reaction temperature.

The interactive effect between catalyst concen-tration and the reaction time while keeping the other parameters at their center value can be seen in Fig.3.3. the maximum conversion to biodiesel was obtained at higher catalyst concentration and lower reaction time.

Table.4

Results of regression analysis for full 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

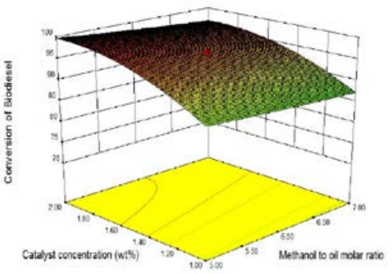

Fig.3.1 interaction methanol to oil molar ratio and catalyst concentration

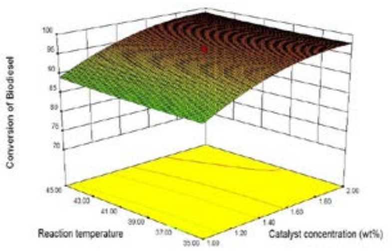

Fig.3.2 interaction catalyst concentration and reaction temperature

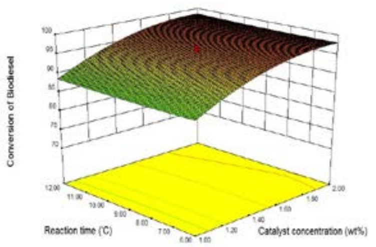

Fig.3.3 interaction catalyst concentration and reaction time

3.3 Optimization of process parameters

Within then experimental range studied, optimum condition for synthesis biodiesel from Brassica carinuta were predicted using optimization function of the Design Expert software version 9.0. In numerical optimization, the independent variable parameters with include methanol to oil molar ratio, catalyst concentration, reaction temperature, and reaction time were set within the range between (-1) and (+1) while the conversion to biodiesel was set to maximum value. The constraints used for the optimum study is summarized in Table 5

The optimal values of the selected variables were obtained by solving the regression equation 3.1. The optimum condition are shown in Table 6. The experimental data obtained for conversion to biodiesel were found to be reasonably close (within 9% of accuracy). The response surface analysis indicated that the predicted optimum conversion to biodiesel of Brassica carinuta transesterification was 95.80% at methanol to oil molar ratio of 7:1, catalyst concentration of 2 wt%, reaction temperature of 35˚C, and reaction time 11.98 min. additional experiment was carried out to validate the optimization result obtained by the response surface analysis optimum conversion to biodiesel of 93.79% is well agreed with the predicted values 95.8%, with a relatively insignificant error 0.94%.

Table.5

Experimental results at the optimum conditions model

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 (min)	Range	6	12
Conversion to biodiesel (%)	Maximize	70.36	99.71

Table.6

Experimental and predicted response at the optimum conditions model

Optimal condition				Condition to biodiesel		
X_1	X_1	X_1	X_1	Experimental	Predicted	Error(%)
7	2	35	11.98	93.79	95.80	0.94

4. Conclusion

The RSM was a useful tool to investigate the optimum condition for conversion to biodiesel and was successfully applied to assess the effects of multiple variable, including the methanol to oil molar ratio, catalyst concentration, reaction temperature, and reaction time for conversion to biodiesel. The coefficients of determination (R^2) were found to be 0.9137. The maximum conversion to biodiesel, as predicted by quadratic polynomial was established to be 95.80% under condition 7:1 methanol to oil molar ratio, 2 catalyst concentration(wt%), 35 reaction temperature, and 11.98 reaction time. Validation experiment verified the accuracy/fit models employed suggesting its suitability.

5. Acknowledgments

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