

Research Article

Response Surface Methodology for Biodiesel Production Using Calcium Methoxide Catalyst Assisted with Tetrahydrofuran as Cosolvent

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The present study was performed to optimize a heterogeneous calcium methoxide ($\text{Ca}(\text{OCH}_3)_2$) catalyzed transesterification process assisted with tetrahydrofuran (THF) as a cosolvent for biodiesel production from waste cooking oil. Response surface methodology (RSM) with a 5-level-4-factor central composite design was applied to investigate the effect of experimental factors on the percentage of fatty acid methyl ester (FAME) conversion. A quadratic model with an analysis of variance obtained from the RSM is suggested for the prediction of FAME conversion and reveals that 99.43% of the observed variation is explained by the model. The optimum conditions obtained from the RSM were 2.83 wt% of catalyst concentration, 11.6 : 1 methanol-to-oil molar ratio, 100.14 min of reaction time, and 8.65% v/v of THF in methanol concentration. Under these conditions, the properties of the produced biodiesel satisfied the standard requirement. THF as cosolvent successfully decreased the catalyst concentration, methanol-to-oil molar ratio, and reaction time when compared with biodiesel production without cosolvent. The results are encouraging for the application of $\text{Ca}(\text{OCH}_3)_2$ assisted with THF as a cosolvent for environmentally friendly and sustainable biodiesel production.

1. Introduction

Currently, heterogeneous catalysts have been developed for use in a transesterification reaction for biodiesel production due to the problems of homogeneous catalysts in terms of water treatment and the nonreusability of the catalyst. Although heterogeneous catalysts have many advantages [1], their disadvantages are also many such as a high oil-to-alcohol molar ratio, high temperature, and a long reaction time [2]. The addition of a cosolvent such as tetrahydrofuran (THF) to the reaction medium is an alternative way to enhance the reaction rate, as well as increasing the solubility and mass transfer between the oil and methanol [3]. THF is favorable because it can dissolve organic compounds on the hydrophobic site and bind water or alcohol on the hydrophilic

site [4]. In addition, THF is a nonhazardous and unreactive chemical with a low boiling point (67°C), and it can be distilled with methanol and recycled at the end of the reaction process. In the previous work [5], THF was used as a cosolvent to accelerate the biodiesel production using a calcium oxide (CaO) catalyst but no experiments have been reported on using THF as a cosolvent with $\text{Ca}(\text{OCH}_3)_2$ catalyst. Thus, our experiment represents the first report of such a study. Response surface methodology (RSM) has been applied to analyze research involving a complex variable process. RSM employs multiple regression and correlation analyses to assess the effects of two or more independent factor on the dependent variables. Its principal advantage is in reducing the number of experimental runs required to generate sufficient information for a statistically acceptable result. RSM has been

successfully applied in the study and optimization of biodiesel production from various feed stocks [6, 7].

In this study, we select $\text{Ca}(\text{OCH}_3)_2$ as heterogeneous catalyst in WCO biodiesel production because $\text{Ca}(\text{OCH}_3)_2$ showed higher activity and very low solubility compared to CaO catalyst in the transesterification of rapeseed oil [8]. Calcium methoxide ($\text{Ca}(\text{OCH}_3)_2$) was prepared from quick lime and its properties were analyzed using X-ray diffraction (XRD) and attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. The synthesized $\text{Ca}(\text{OCH}_3)_2$ was also tested as a heterogeneous catalyst assisted with THF in the transesterification of waste cooking oil (WCO). RSM was utilized for process optimization. The reusability of $\text{Ca}(\text{OCH}_3)_2$ in biodiesel production was also studied.

2. Materials and Methods

2.1. Materials. The WCO in this research was obtained from the Vehicle and Building Station, Kasetsart University, Bangkok, Thailand. The fatty acid composition in the WCO was 1.11 wt% myristic acid, 35.92 wt% palmitic acid, 4.65 wt% stearic acid, 46.02 wt% oleic acid, and 12.30 wt% linoleic acid. The calculated average molecular weight of the WCO based on the fatty acid composition was 855 g/mol and its free fatty acid content was 0.7 wt%. Quick lime powder was supplied by Suthagun Co., Ltd. (Thailand). Analytical grade methanol and n-heptane were purchased from Merck (Germany). Standard chromatographic grade fatty acid methyl esters (FAME) were purchased from Sigma-Aldrich (Switzerland).

2.2. Catalyst Preparation. $\text{Ca}(\text{OCH}_3)_2$ was prepared following the work of Suwanthai et al. [6]. Briefly, the quick lime powder was heated in a furnace at 700°C for 2 h. Then, 5 g of calcined quick lime powder was placed in a three-necked flask with 150 ml of methanol. The reaction of calcined quick lime and methanol was performed at 65°C for 2 h with vigorous stirring. After that, the residual $\text{Ca}(\text{OCH}_3)_2$ was collected by filtration and washed several times with methanol. Finally, the residual $\text{Ca}(\text{OCH}_3)_2$ was dried in an oven at 105°C for 1 h and kept in a desiccator until used.

2.3. Catalyst Characterization. The XRD analysis was carried out using a D8 Advance Bruker diffractometer (USA) with $\text{Cu } k_\alpha$ radiation to scan a 2θ range from 5° to 40° . The surface functional groups of the $\text{Ca}(\text{OCH}_3)_2$ catalyst were determined using ATR-FTIR on a Bruker Equinox 55 FTIR spectrometer (USA).

2.4. Transesterification Process. The transesterification reactions were carried out in a three-necked flask equipped with a reflux condenser and a thermometer on a magnetic stirrer heater at 65°C and 750 rpm. The $\text{Ca}(\text{OCH}_3)_2$ was added immediately to the flask when the reactants (oil and methanol) reached the required temperature. After the reaction was complete, the products were separated using centrifugation. The top layer consisted of biodiesel and the bottom layer contained a mixture of glycerol and $\text{Ca}(\text{OCH}_3)_2$.

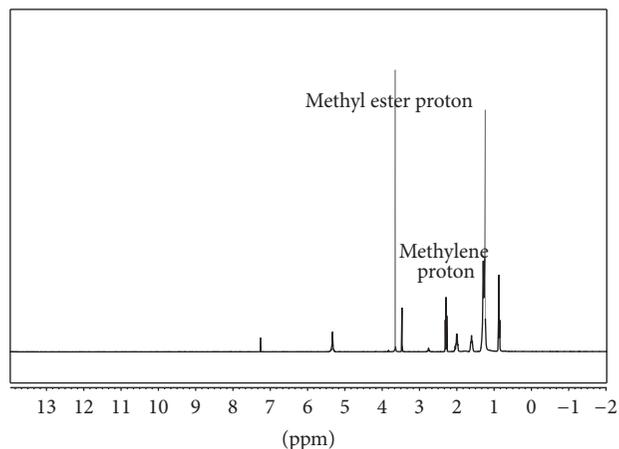


FIGURE 1: $^1\text{H-NMR}$ spectrum of WCO biodiesel.

The excess methanol contained in the biodiesel was further removed at 105°C in an oven. In the obtained biodiesel the % FAME conversion was investigated using proton nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$) [9].

2.5. Experimental Design and Statistical Analysis. RSM based on a central composite design (CCD) of experiments was used to optimize the biodiesel production process from the WCO and to investigate the influence of different transesterification process variables on the % FAME conversion. At five levels of independent variables ranging from -2 to $+2$, 30 experimental runs were carried out with the four independent variables: methanol-to-oil-molar ratio (A); catalyst concentration (B); reaction time (C); and cosolvent in methanol concentration (D). In addition, the 30 runs included 16 factorial points, 8 axial points, and 6 replicates at the center point to determine the experimental error for this study. The obtained experimental data was analyzed using a second-order polynomial (see (1)) to find the relationship between the independent variables and the % FAME conversion [6, 7].

$$Y = b_0 + \sum_{i=1}^k b_i x_i + \sum_{i=1}^k b_{ii} x_i^2 + \sum_{i=1}^k \sum_{j=1}^k b_{ij} x_i x_j, \quad (1)$$

where Y is the response (% FAME conversion), b_0 is the intercept, b_i , b_{ii} , and b_{ij} are the linear, quadratic, and interactive coefficients, respectively, k is the number of factors, and x_i and x_j are the independent variables under study.

Statistical analysis of the model was performed to evaluate the analysis of variance (ANOVA) and Design-Expert software (State Ease Inc., Minneapolis, MN, USA) was used to design the experiments and carry out the regression and graphical analysis of the data [6, 7].

2.6. Proton Nuclear Magnetic Resonance Spectroscopy ($^1\text{H-NMR}$). Figure 1 shows the $^1\text{H-NMR}$ spectra of the WCO biodiesel that $^1\text{H-NMR}$ was performed for monitoring the transesterification reaction in the form of % FAME conversion.

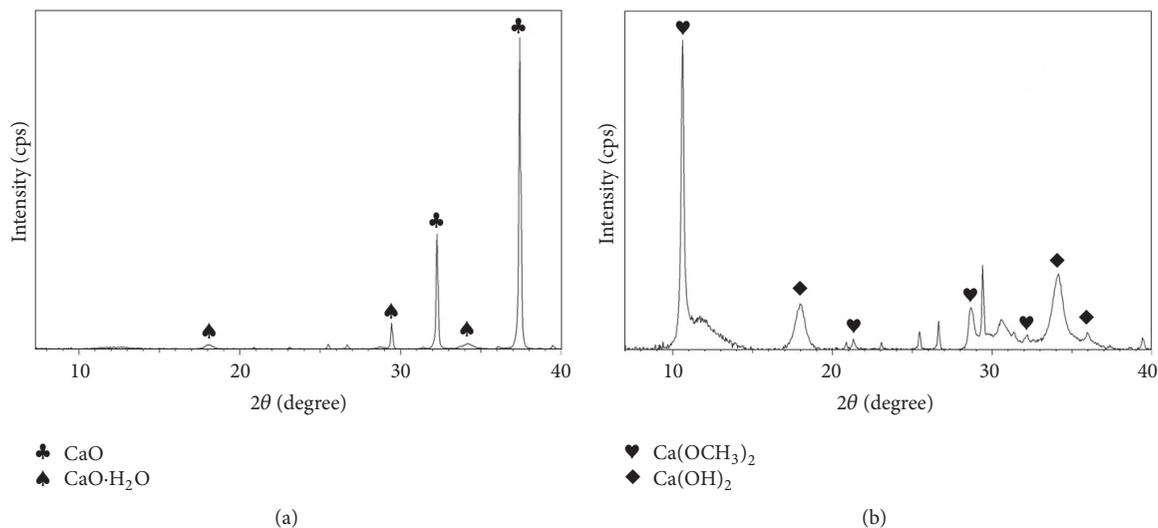


FIGURE 2: XRD patterns. (a) Calcined quick lime powder. (b) Ca(OCH₃)₂.

The % FAME conversion was analyzed following Knothe [10]. Briefly explained, the chemical shift at 3.6 ppm represented the methyl ester protons and at 2.3 ppm represented the methylene protons (α -CH₂). An equation to calculate the % FAME conversion is shown in [9, 10]

$$C = 100 \times \left\{ \frac{2A_{ME}}{3A_{\alpha-CH_2}} \right\}, \quad (2)$$

where C is the percentage of FAME conversion, A_{ME} is the integration value of the protons of the methyl esters and $A_{\alpha-CH_2}$ is the integration value of the methylene protons.

2.7. Physicochemical Characterization of Produced Biodiesel. The purified biodiesel obtained from transesterification was tested to evaluate its fuel properties using the recommended standard method: kinetic viscosity at 40°C (ASTM D445), density at 15°C (EN ISO 3675), acid value (ASTM D 664), water and sediment (ASTM D2709), and fatty acid methyl ester purity (EN 141003). All properties were analyzed in duplicate and reported as the average value.

3. Results and Discussion

3.1. Catalyst Characterization. In this study, the XRD results were compared with the standard diffraction pattern in the data base of the International Center of Diffraction Data (ICDD). Figure 2(a) shows the XRD patterns of the calcium oxide (CaO) obtained from the calcined quick lime powder. The diffraction peaks at 2θ of 32.28° and 37.58° were attributed to the CaO (ICDD file number 00-001-1160) and three diffraction peaks at 2θ of 18.12°, 28.73°, and 34.23° were attributed to calcium oxide hydrate (CaO·H₂O) (ICDD file number 00-002-0969). Figure 2(b) shows the XRD of Ca(OCH₃)₂ catalysts from calcined quick lime powder after reacting with methanol under reflux conditions. The four diffraction peaks that appeared at 2θ of 10.62°, 21.31°, 28.69°, and 32.24° were assigned to the characteristic peak of Ca(OCH₃)₂ (ICDD file number 00-031-1574) and ICDD file number 01-070-5492 for Ca(OH)₂ [9].

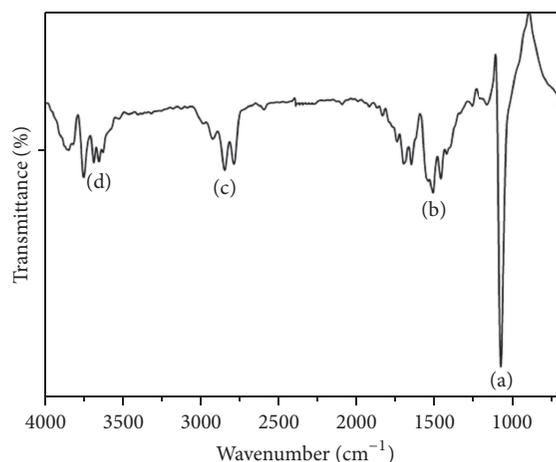


FIGURE 3: ATR-FTIR spectrum of Ca(OCH₃)₂.

The distinct peak at 1072.40 cm⁻¹ (a) is assigned to the -C-O bond stretching vibration. A series of peaks at 1462.02 cm⁻¹ (b), 2841.10 cm⁻¹ (c), and 3645.40 cm⁻¹ (d) are the -C-H bending vibration, -CH₃ stretching vibration, and -OH stretching vibration, respectively.

3.2. Optimization of Reaction Conditions by RSM. RSM was employed to evaluate the relations between the response (% FAME conversion) and the four reaction variables. The coded and uncoded independent variables for reaction experiment parameter were designed as shown in Table 1. Thirty experiments were performed in a randomized order. The results

TABLE 1: Reaction condition variables and levels for CCD.

Reaction condition variables	Symbol code	Range and levels				
		-2	-1	0	+1	+2
Methanol-to-oil molar ratio	<i>A</i>	6	8	10	12	14
Catalyst concentration (wt%)	<i>B</i>	1.5	2	2.5	3	3.5
Reaction time (min)	<i>C</i>	30	60	90	120	150
THF in methanol (% v/v)	<i>D</i>	4.5	6	7.5	9	10.5

TABLE 2: Experimental design with observed and predicted values from transesterification of WCO.

Run number	A: methanol-to-oil molar ratio	B: catalyst concentration (wt%)	C: reaction time (min)	D: THF concentration (v/v%)	Observed FAME (%)	Predicted FAME (%)
1	8 (-1)	2 (-1)	60 (-1)	6 (-1)	71.17	68.98
2	12 (+1)	2 (-1)	60 (-1)	6 (-1)	71.43	71.99
3	8 (-1)	3 (+1)	60 (-1)	6 (-1)	84.85	86.73
4	12 (+1)	3 (+1)	60 (-1)	6 (-1)	91.94	92.26
5	8 (-1)	2 (-1)	120 (+1)	6 (-1)	73.83	73.79
6	12 (+1)	2 (-1)	120 (+1)	6 (-1)	78.71	77.14
7	8 (-1)	3 (+1)	120 (+1)	6 (-1)	93.25	94.02
8	12 (+1)	3 (+1)	120 (+1)	6 (-1)	95.87	99.88
9	8 (-1)	2 (-1)	60 (-1)	9 (+1)	83.44	80.06
10	12 (+1)	2 (-1)	60 (-1)	9 (+1)	84.3	81.59
11	8 (-1)	3 (+1)	60 (-1)	9 (+1)	89.76	89.38
12	12 (+1)	3 (+1)	60 (-1)	9 (+1)	92.74	93.41
13	8 (-1)	2 (-1)	120 (+1)	9 (+1)	84.56	82.30
14	12 (+1)	2 (-1)	120 (+1)	9 (+1)	85.4	84.16
15	8 (-1)	3 (+1)	120 (+1)	9 (+1)	94.02	94.09
16	12 (+1)	3 (+1)	120 (+1)	9 (+1)	98.22	98.46
17	6 (-2)	2.5 (0)	90 (0)	7.5 (0)	81.03	83.15
18	14 (+2)	2.5 (0)	90 (0)	7.5 (0)	91.34	90.54
19	10 (0)	1.5 (-2)	90 (0)	7.5 (0)	50.57	56.33
20	10 (0)	3.5 (+2)	90 (0)	7.5 (0)	92.83	88.38
21	10 (0)	2.5 (0)	30 (-2)	7.5 (0)	81.72	83.68
22	10 (0)	2.5 (0)	150 (+2)	7.5 (0)	94.19	93.54
23	10 (0)	2.5 (0)	90 (0)	4.5 (-2)	91.94	89.41
24	10 (0)	2.5 (0)	90 (0)	10.5 (+2)	95.24	99.08
25	10 (0)	2.5 (0)	90 (0)	7.5 (0)	97.75	95.02
26	10 (0)	2.5 (0)	90 (0)	7.5 (0)	95.61	95.02
27	10	2.5	90	7.5	93.33	95.02
28	10	2.5	90	7.5	96.1	95.02
29	10	2.5	90	7.5	93.16	95.02
30	10	2.5	90	7.5	94.19	95.02

for each point base on the CCD experimental plans are shown in Table 2. The response obtained from the regression analysis was correlated with the four independent variables using second-order polynomial equation (see (3)). The % FAME conversion obtained at the design points of different reaction conditions is shown in Table 2. The observed values varied between 50.57% at 1.50% catalyst concentration, 10 : 1 methanol-to-oil molar ratio, 90 min reaction time, and 7.5% THF in methanol concentration and 98.22% at 3% catalyst concentration, 12 : 1 methanol-to-oil molar ratio, 120 min reaction time, and 9% THF in methanol concentration.

The Design-Expert software was used to determine and evaluate the coefficients of the full regression model equation

and their statistical significance. The quadratic regression model used to predict the % FAME conversion is shown in

$$\begin{aligned}
 Y = & -231.274 + 10.387A + 140.443B + 0.393C \\
 & + 12.464D + 0.628AB + 0.001AC - 0.124AD \\
 & + 0.041BC - 2.811BD - 0.014CD - 0.511A^2 \\
 & - 22.666B^2 - 0.002C^2 - 0.086D^2,
 \end{aligned} \tag{3}$$

where Y is the response variable of % FAME conversion and A , B , C , and D are the actual values of the predicted methanol-to-oil molar ratio, catalyst concentration, reaction time, and THF in methanol concentration, respectively.

TABLE 3: ANOVA for the response surface quadratic model.

Source of variation	Sum of squares	df ^a	Mean square	F-value	P value ^b	Significant at 5% level
Model	2957.24	14	211.23	20.65	<0.0001	Yes
A	81.96	1	81.96	8.01	0.0127	Yes
B	1541.28	1	1541.28	150.69	<0.0001	Yes
C	145.88	1	145.88	14.26	0.0018	Yes
D	140.12	1	140.12	13.70	0.0021	Yes
AB	6.31	1	6.31	0.62	0.4443	No
AC	0.11	1	0.11	0.011	0.9174	No
AD	2.23	1	2.23	0.22	0.6474	No
BC	6.14	1	6.14	0.60	0.4506	No
BD	71.11	1	71.11	6.95	0.0187	Yes
CD	6.64	1	6.64	0.65	0.4329	No
A ²	114.74	1	114.74	11.22	0.0044	Yes
B ²	880.73	1	880.73	86.11	<0.0001	Yes
C ²	70.46	1	70.46	6.89	0.0191	Yes
D ²	1.03	1	1.03	0.10	0.7550	No
Residual	153.42	15	10.23			
Lack of fit	137.45	10	13.74	4.30	0.0604	No
Pure error	15.97	5	3.19			
Cor total	3110.66	29				

^adf = degree of freedom; ^bP > 0.05 is not significantly different at the 5% level.

The obtained data were evaluated using analysis of variance (ANOVA) for fitting a quadratic response surface model by the least squares method and to assess the quality of the fit. The significance of each coefficient parameter was determined by probability value (*P* value) as shown in Table 3. At the 95% confidence level, $F_{\text{model}} = 20.65$, the *P* value less than 0.05 clearly indicated that the high significance of the fitted model and is showing the reliability of the regression model for predicting the % FAME conversion [6, 11]. Furthermore, the variables of *A*, *B*, *C*, *D*, *BD*, A^2 , B^2 , and C^2 were found to be significant at the 95% confidence level according to the computed high *F*-value and the *P* values at the 5% level.

Thus, these statistical tests indicated that the selected model is satisfactory for predicting the % FAME conversion within the range of the experiment variables studies. The *P* value of the lack of fit was 0.0604, which reveals that it was not significant. Therefore, the number of experiments was sufficient to study the effect of the variable factors on % FAME conversion [6, 12]. The suitability of the model was tested using the determination coefficient (R^2). The high value of R^2 (0.9507) indicates that the fitted model can be used to predict reasonably precise outcome [6].

Figure 4 represents the actual results obtained from the experiments versus the predicted data by empirical model. The values of the adjusted determination coefficient (R^2_{adj}) and the determination coefficient (R^2) were 0.9046 and 0.9507, respectively. The high value of both coefficients justifies an excellent correlation between the independent variables and supports a high significance of the model. Meanwhile, the coefficient of variation was 3.66%. The relatively low value of the coefficient of variation reveals better reliability for this fitted model [6, 13].

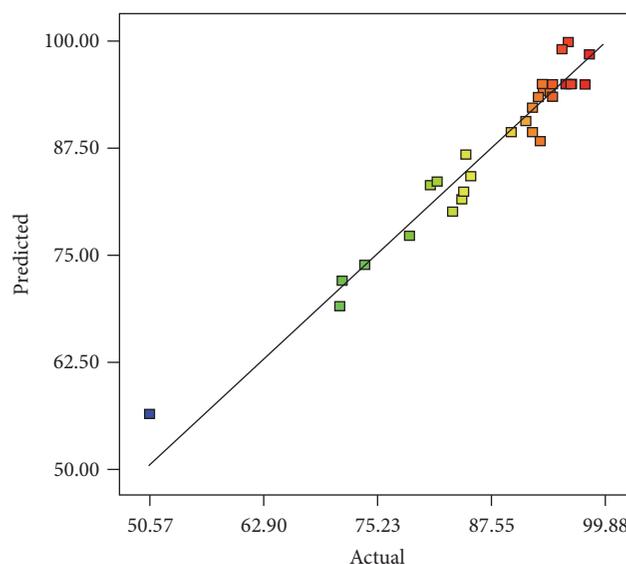


FIGURE 4: Plot of predicted % FAME conversion versus actual % FAME conversion.

The effects of the process variables on the FAME conversion were studied by plotting three-dimensional surface curves against any two independent variables while keeping the other variables at their central (0) level [14]. The 3D curves of the response from the effect of independent variables are shown in Figures 5(a)–5(f).

Figure 5(a) illustrates the effect of catalyst concentration and THF in methanol concentration on the % FAME conversion at 90 min reaction time and a 10:1 methanol-to-oil molar ratio. The result reveals that the % FAME

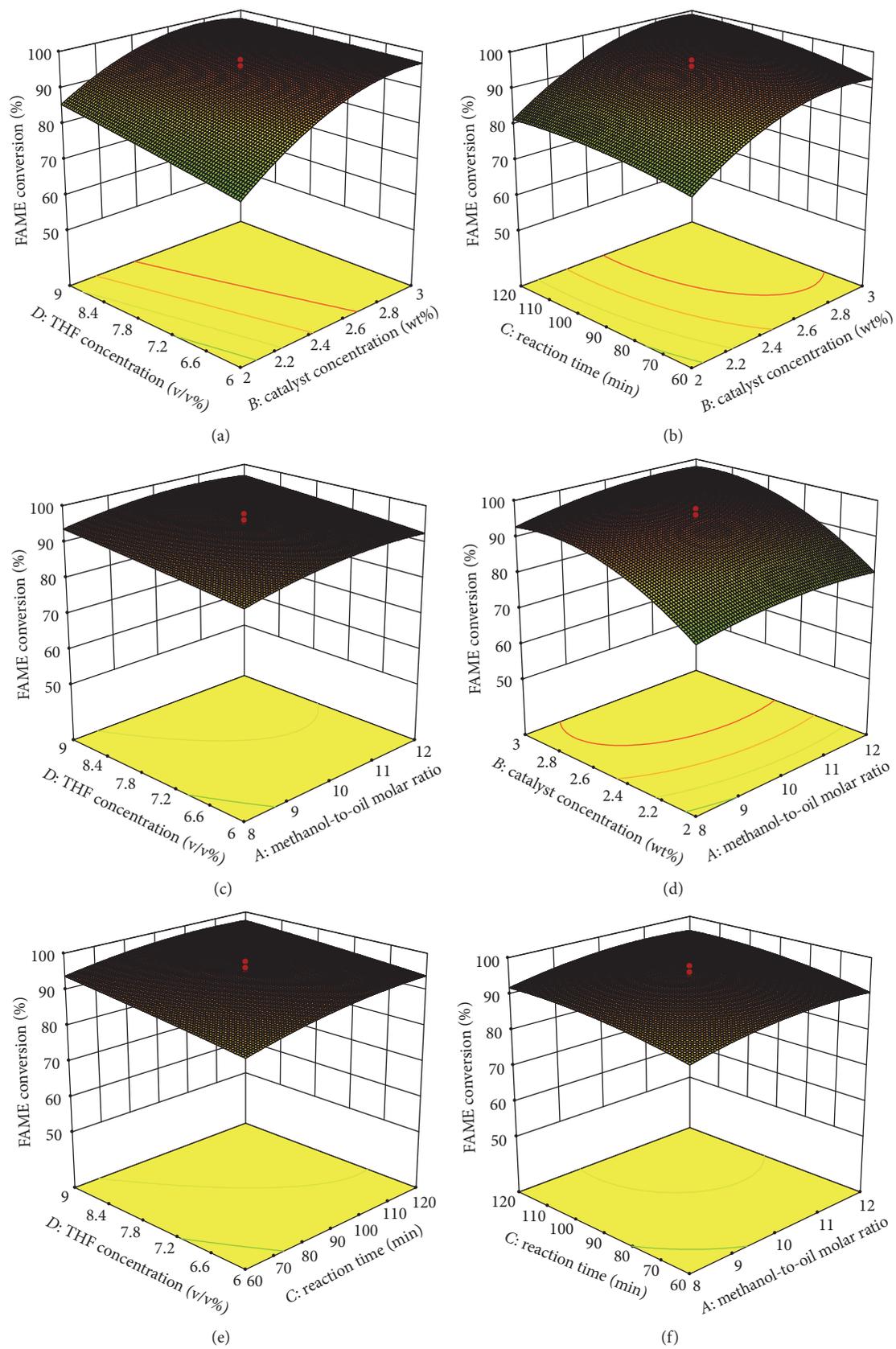


FIGURE 5: Response surface plots elucidating the effects of (a) THF in methanol concentration and catalyst concentration; (b) reaction time and catalyst concentration; (c) THF in methanol concentration and methanol-to-oil molar ratio; (d) catalyst concentration and methanol-to-oil molar ratio; (e) THF in methanol concentration and reaction time; and (f) reaction time and methanol-to-oil molar ratio.

TABLE 4: Numerical optimization of the reaction conditions using RSM.

Solution number	A	B	C	D	% FAME conversion	Desirability	
1	11.60	2.83	100.14	8.65	99.43	0.999	<i>Selected</i>
2	11.61	2.82	100.14	8.65	99.42	0.998	
3	11.61	2.83	100.14	8.63	99.42	0.998	
4	11.61	2.82	100.14	8.64	99.42	0.997	
5	11.58	2.83	100.14	8.34	99.39	0.974	

TABLE 5: Optimum reaction conditions and validation test.

Exp. number	A	B	C	D	Observed FAME (%)	Predicted FAME (%)	Error
1	11.60	2.83	100.14	8.65	98.70	99.43	0.73
2	11.60	2.83	100.14	8.65	99.57	99.43	0.12
3	11.60	2.83	100.14	8.65	99.12	99.43	0.31

TABLE 6: Optimum conditions using $\text{Ca}(\text{OCH}_3)_2$ with and without THF as cosolvent for WCO biodiesel production.

Method	Temperature ($^{\circ}\text{C}$)	Methanol-to-oil molar ratio	$\text{Ca}(\text{OCH}_3)_2$ Catalyst (wt%)	Time (min)	FAME	
					Conversion	Purity (%)
Without THF	65 $^{\circ}\text{C}$	12:1	3	180	99.06	97.00
With THF	65 $^{\circ}\text{C}$	11.60:1	2.83	100.14	99.43	97.13

conversion increases with increasing catalyst concentration and THF concentration. For the amount of catalyst, there is a significant positive effect on the transesterification of vegetable oil to methyl ester due to the number of active sites available for the reaction [15]. The 3D response curve indicates that the interaction of catalyst concentration and THF concentration is significant in the reaction.

Figure 5(b) exhibits the effect of the catalyst concentration and reaction time at 10:1 methanol-to-oil molar ratio and 7.5% THF concentration. The % FAME conversion increases with increasing catalyst concentration and reaction time. Then, there is a slight decrease when the reaction period is too long due to the influence of the reversible reaction in transesterification [16]. The 3D response curve reveals that there is no significant interaction effect between the catalyst concentration and reaction time on the % FAME conversion.

Figure 5(c) shows the effect of the methanol-to-oil molar ratio and THF concentration at a 90 min reaction time and 2.5% catalyst concentration. The % FAME conversion increases with the increasing methanol-to-oil molar ratio and THF concentration. In general, a high molar ratio results in a higher rate of methyl ester formation and ensures completion of the reaction. However, overloading of methanol would inactivate the catalyst and reversed the reaction since transesterification is a reversible reaction [17]. The 3D response curve under this condition indicates no significant interaction effect between methanol-to-oil molar ratio and THF concentration on the % FAME conversion.

Figures 5(d)–5(f) illustrate the effect of the methanol-to-oil molar ratio and catalyst concentration, the effect of reaction time and THF concentration, and the effect of methanol-to-oil-molar ratio and reaction time, respectively. The interaction effect of two independent variables was studied by keeping the other variables at their central (0) level. The

results demonstrate that the % FAME conversion increased with an increase in all variables. The 3D response curves in Figures 5(d)–5(f) show no significant interaction effect of the methanol-to-oil molar ratio and catalyst concentration, reaction time, and THF concentration including the methanol-to-oil molar ratio and reaction time on % FAME conversion.

The optimal transesterification conditions were predicted by applying numerical optimization with the Design-Expert software using RSM. The results are shown in Table 4. The optimal conditions for the maximum value of % FAME conversion are as follows: 11.60:1 methanol-to-oil molar ratio, 2.83 wt% of catalyst, 100.14 min of reaction time, and 8.65% of THF in methanol concentration. Experiments were also conducted to verify the accuracy of the predicted model, and the experiment at the selected optimal conditions was performed with three replicates to confirm the experimental results as shown in Table 5. The predicted conversion value of 99.43 was approximately equal to the average observed value of 99.13. Therefore, the experimental (obtained) value showed acceptable agreement with the predicted values. The errors values between the predicted and the observed results were less than 1% FAME conversion indicating that the regression model was satisfactory.

3.3. Comparison of WCO Biodiesel Production Using $\text{Ca}(\text{OCH}_3)_2$ and without THF as Cosolvent. In the authors' previous work (Chumuang and Punsuvon, 2016) [18], the production of WCO biodiesel using $\text{Ca}(\text{OCH}_3)_2$ without THF as cosolvent was studied and the results of the optimum conditions were compared with THF as a cosolvent as shown in Table 6.

For production without THF as cosolvent, the optimum conditions were 12:1 methanol-to-oil-molar ratio, 3% $\text{Ca}(\text{OCH}_3)_2$ catalyst concentration, 180 min reaction time,

TABLE 7: Optimum condition of difference catalyst assisted with THF as cosolvent for biodiesel production.

Method	Temperature (°C)	Methanol-to-oil molar ratio	Amount of catalyst (wt%)	THF in methanol (%v/v)	Time (min)	FAME Purity (%)
Present work	65°C	11.60 : 1	2.83	8.65	100.14	97.13
Reference work	65°C	12 : 1	5.00	10.00	90.00	98.5 ± 1.5

TABLE 8: Biodiesel properties.

Parameters	Testing method	Specification	WCO biodiesel
Viscosity at 40°C (cSt)	ASTM D 445	1.9–6.0	4.78
Density at 15°C (g/cm ³)	EN ISO 3675	0.86–0.90	0.89
Acid value (mg KOH/g)	ASTM D 664	0.80 max	0.53
Water and sediment (v%)	ASTM D 2709	0.05 max	<0.05
Methyl ester purity (wt%)	EN 14103	≥96.5	97.13

and 65°C reaction temperature resulting in 99.06% FAME conversion and 97.00% FAME purity. On the other hand biodiesel production with THF as a cosolvent was able to decrease the methanol-to-oil molar ratio (12 : 1 to 11.60 : 1), Ca(OCH₃)₂ catalyst concentration (3 to 2.83 wt%), and reaction time (180 to 100.14 min) while still maintaining the % FAME conversion and % FAME purity at nearly the same levels. The results indicated that THF can accelerate the catalyzed reaction by improving the mixing between the methanol, WCO, and Ca(OCH₃)₂ catalyst. Thus, our discovery can solve the problem of phase separation between hydrophilic methanol, hydrophobic oil, and a solid catalyst that is generally accepted to be major problem in using a heterogeneous catalyst in biodiesel production [5].

3.4. Comparison of Biodiesel Production between Ca(OCH₃)₂ Catalyst Assisted with THF and CaO Catalyst Assisted with THF as Cosolvent. In the work [5], the transesterification for palm oil biodiesel production was studied using CaO catalyst assisted with THF as cosolvent. The optimum condition between the reference work and our present work is shown in Table 7.

For the reference work, the optimum conditions were 65°C reaction temperature, 12 : 1 methanol-to-oil molar ratio, 5% wt CaO catalyst concentration, 10% v/v THF in methanol concentration, and 90 min reaction time resulting in 98.5 ± 1.5% FAME purity. On the other hand, our present work using Ca(OCH₃)₂ assisted with THF as cosolvent was able to decrease the methanol-to-oil molar ratio (12 : 1 to 11.60 : 1), amount of catalyst (5 to 2.83% wt), and THF in methanol concentration (10 to 8.65% v/v), while still maintaining the % FAME purity at nearly the same levels (97.13 and 98.5 ± 1.5%) on the same reaction temperature (65°C). The reaction time was only one variable of our present work that had longer time than the reference work (100.14 and 90 min). Thus, the result indicated that both Ca(OCH₃)₂ and CaO assisted with THF as cosolvent could produce both biodiesels with high purity of FAME but Ca(OCH₃)₂ catalyst was better than CaO catalyst in terms of catalyst concentration, methanol-to-oil

molar ratio, and THF in methanol concentration except reaction time.

3.5. Biodiesel Properties. The biodiesel properties were tested following the biodiesel standards of the USA (ASTM) and Europe (EN), as exhibited in Table 8.

While the result on viscosity result (at 40°C) of this WCO biodiesel is slightly lower (4.78 cst), the value is still within the range of ASTM D445 (1.9–6.0 cst). The density of WCO biodiesel falls in the range of the EN ISO 3675 specifications (0.86–0.90 g/cm³). The acid value of this biodiesel was also found to be 0.53 mg KOH/g which is within the range of ASTM D664 specifications (≤0.80 mg KOH/g). The amounts of water and sediment produced in the biodiesel were less than 0.05% by volume which is in the range of the ASTM D2709 specification (≤0.05% v). The methyl ester purity was determined using the GC method and it was found to be 97.13% which falls in the range of the EN 14103 specification (≥96.5%).

3.6. Reusability of the Catalyst. One of the most important advantages of employing a heterogeneous catalyst is its reusability. Ca(OCH₃)₂ was separated from the reaction mixture by centrifugation followed by washing with hexane and methanol to remove the adsorbed stains. Then, Ca(OCH₃)₂ was collected by filtration and finally dried overnight at 105°C in an oven. The dried catalyst was further reused under the obtained optimal transesterification condition for biodiesel production. Figure 6 shows the relationship between the number of reused times and the % FAME conversion and indicates that a high % FAME (higher than 80%) was still obtained with five times of reuse.

4. Conclusion

RSM was applied to the transesterification reaction between WCO and methanol using a Ca(OCH₃)₂ catalyst assisted with THF as a cosolvent. The significant merit of THF as cosolvent is the short reaction time, low concentration of

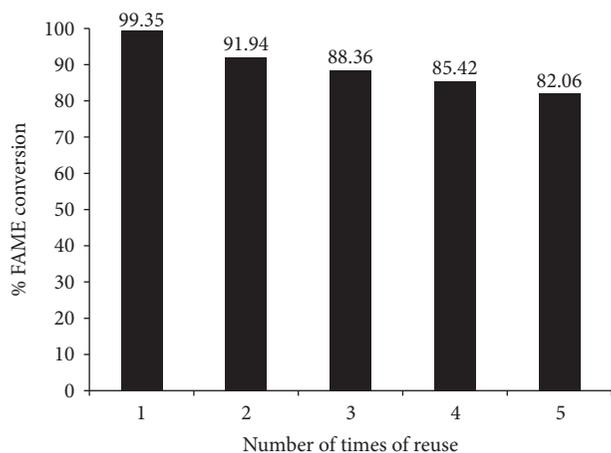


FIGURE 6: $\text{Ca}(\text{OCH}_3)_2$ catalyst reusability testing.

the catalyst, and the low value of the methanol-to-oil-molar ratio compared to the reaction without THF as a cosolvent. The synthesized $\text{Ca}(\text{OCH}_3)_2$ provides high catalytic activity for transesterification in terms of % FAME conversion and % FAME purity and reusability. These results indicate that $\text{Ca}(\text{OCH}_3)_2$ and THF as a cosolvent are both capable of improving the transesterification of WCO for biodiesel production.

Conflicts of Interest

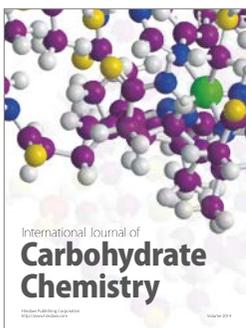
The authors declare that there are no conflicts of interest regarding the publication of this paper.

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