Original Article

Use of calcium oxide in palm oil methyl ester production

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Abstract

Introducing an untreated calcium oxide (CaO) as a solid heterogeneous catalyst for biodiesel production from palm oil by transesterification was studied in this work. The four studied parameters were methanol to oil molar ratio, CaO catalyst concentration, reaction time, and water content. The results for palm oil show that when the water content is higher than 3%wt and the amount of CaO greater than 7%wt soap formation from saponification occurs. A higher methanol to oil molar ratio requires a higher amount of CaO catalyst to provide the higher product purity. The appropriate methanol to CaO catalyst ratio is about 1.56. Commercial grade CaO gives almost the same results as AR grade CaO. In addition, reusing commercial grade CaO for about 5 to 10 repetitions without catalyst regeneration drops the percentage of methyl ester purity approximately 5 to 10%, respectively.

Keywords: biodiesel, palm oil, heterogeneous catalyst, methyl ester, transesterification, calcium oxide

1. Introduction

Biodiesel has shown great potential worldwide as a clean alternative fuel for diesel engines because of its reduced emission pollutants, sustainability, biodegradability, and usability in conventional diesel engines without significant modifications (Hai-xin *et al*., 2009; Mueanmas *et al*., 2010). The most common processes for biodiesel synthesis involve homogeneous base catalysts such as sodium hydroxide (NaOH) or potassium hydroxide (KOH) which allows complete transesterication in a few hours (Liu *et al*., 2008). The oil containing high fatty acid can be used to produce biodiesel by a two-stage process (Prateepchaikul *et al*., 2007). However, the common processes still have side reactions such as saponification from free fatty acid (FFA) and/or methyl ester with base catalyst (Bournay *et al*., 2005) and hydrolysis reaction of methyl ester with water. Besides that, it is technically difficult to remove homogeneous catalysts from biodiesel product. This finally increases operating costs (Huaping *et al*., 2006). To avoid these problems, several types of biodiesel production processes have been studied, such as heterogeneous catalysts, acid catalysts, supercritical processes and enzymatic processes.

Since heterogeneous base catalysts have many advantages on reactions, for example, noninvasive, stable, easily separable and reusable (Liu *et al*., 2008). Additionally, calcium oxide (CaO) is inexpensive. It can be used in biodiesel production which requires 6 to 24 hours to obtain high conversion (Abeti *et al*., 2009; Hai-xin *et al*., 2009). Therefore, the purpose of this study was to discover the use of untreated CaO as a heterogeneous catalyst in palm oil biodiesel production by transesterication. The effects of methanol to oil molar ratio, CaO catalyst concentration, reaction time and water content were studied.

2. Material and Methods

2.1 Material

Palm oil (MW ~841 g/mol) containing 0.3-0.6% free fatty acid and less than 1% moisture content (data from Specialized R&D Center for Alternative Energy from Palm Oil

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and Oil Crop, Songkhla, Thailand) was used with a commercial grade methanol (from Sigma) as reactants. Analytical reagent (AR) grade CaO and commercial grade of CaO with surface areas of 0.38 and 0.59 m^2/g, respectively, and methyl heptadecanoate solution were also purchased from Sigma.

2.2 Methods

2.2.1 Experimental conditions

The experiment consisted of three parts. First, a study of the use of AR grade CaO under the experimental conditions as shown in Table 1. Second, an investigation of the conditions for using commercial grade CaO by a response surface method (Five level-three factor central composite design, CCD), The experimental conditions were shown in Table 2 and the experimental results of this part were statistically analyzed by Design-Expert (version 7.0) to determine the fit model for the percentage of fatty acid methyl ester (FAME) as a function of the studied parameters. The last part of the experiment focused on reusing commercial grade CaO. The experiment was conducted under the optimal condition found from the analysis in the second part and was to observe the effect of using CaO repetition without catalyst regenerating on methyl ester purity.

2.2.2 Reaction and product preparation

Transesterification reaction was carried out in a 250-ml two-neck glass flask connected with a methanol reflux condenser. Some modification in comparison to Kawashima *et al.* (2009) were done, first, the palm oil was put into the reactor and was heated up to 65°C while CaO, methanol and water were mixed and stirred at room temperature (30°C) for 30 minutes. Then the mixture was added to oil in the reactor and stirred at rate of 750 rpm for the desired time. At the end of the reaction, the product of each part was filtrated to remove the catalyst and evaporated under vacuum in order to get rid of the excess methanol. After that the product was washed to eliminate the remaining base catalyst and evaporated the water at 120°C for 24 hours.

2.2.3 Quantitative analysis of fatty acid methyl ester content

The biodiesel or fatty acid methyl ester (FAME or ME) content in product was analyzed by a GC-7890 gas chromatography (Agilent HP7890A). Its column was a Select™ Biodiesel for FAME (capillary column, length 30 m x 320 μm I.D. x 0.25 μm film thickness and Varian Part No. CP-9080). The initial column temperature was set to 210°C and retained for 12 minutes at this temperature. Then, the column temperature was raised up to 250°C at the rate of 20°C/min and maintained for 8 minutes at this temperature. The temperature of the injector and the flame ionization detector (FID) were 290 and 300°C, respectively. The FAME content was quantitatively determined by using the concentration of methyl heptadecanoate (C17:0, internal standard).

For a sample preparation, approximately 250 mg of sample was filled in a 10 ml vial. Then 5 ml of methyl heptadecanoate solution (10 mg/ml) was added. The quantitative analysis in each condition of the experiments performed on the average value of three samples.

2.2.4 Statistical analysis

The experimental data were analyzed via response surface regression procedure using a second-order polynomial as shown in Equation 1 and Design-Expert program.

Table 1. Conditions of using AR grade CaO for biodiesel production by transesterification of palm oil.

Experiment	Reactiontime (h)	Water content (%wt)	Methanol to oil molar ratio	CaO to oil mass ratio (%wt)
1	0-14	3	12:1	4
2	Optimum	0-4	12:1	4
3	Optimum	Optimum	3:1-21:1	4
4	Optimum	Optimum	Optimum	0.5-14

Table 2. Five level-three factor central composite design for transesterification process of palm oil.

Variable	Symbol	Level				
		-2	-1	0	+1	+2
Methanol to oil molar ratio	M	9:1	11:1	15:1	19:1	21:1
CaO to oil mass ratio (Catalyst concentration, %w/w)	C	1	3	6	8	10
Reaction time (min)	RT	120	217	360	503	600

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \left[\sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta_{ij} x_i x_j \right]_{i<j} \quad (1)$$

where y is the response variable, x_i and x_j are the coded independent variables. b_o, b_i, b_{ii} and b_{ij} are the intercept, linear, quadratic and interaction coefficients, respectively, and k is the number of studied factors.

3. Results and Discussion

3.1 Use of AR grade CaO catalyst

3.1.1 Effect of reaction time on purity of methyl ester

The effect of reaction time on transesterification of palm oil with methanol is shown in Figure 1. With adding water, the percentage of ME purity reaches approximately 80%wt within the first six hours whereas without adding water, the reaction spends 12 hours to reach a comparable level of percentage ME purity. After 12 hours, the percentage ME purity decreases as a result of diglyceroxide (Kouzu *et al.*, 2008) and the soap production as shown and explained in the next part.

3.1.2 Effect of water content in methanol on purity of methyl ester

Figure 1 also shows the effect of water content on transesterification reaction. The reaction with water content in methanol provides faster reaction than the reaction without water content. Additional experimental results showing the effect of water content on the percentage ME purity as shown in Figure 2. The percentage of water content in methanol at 0, 1, 2, 3 and 4%wt with respect to oil were investigated. The ME product purity increases from 50 to 82%wt as ratio of water content increases from 0 to 3% because the alkaline catalyst or CaO requires a small amount of water to dissolve and to produce O^{2-} ion which is attracted by H^+ from water to form OH^- ion (Liu *et al.*, 2008; Kouzu *et al.*, 2009). In addition, the surface of OH^- ion continuously attracts the H^+ ion from methanol to generate methoxide anion which is the catalyst for transesterification (Gryglewicz, 1999). Although this anion is a weak base, it still has activity in transesterification. However, at 4% water content, %wt of ME decreases because the hydrolysis reaction of ME with water may occur. Additional soap formation can occur at high water content condition (Ma *et al.*, 1998). The results show that the optimum water content in this study is 3%wt.

3.1.3 Effect of molar ratio of methanol to oil on purity of methyl ester

Figure 3 shows the effect of methanol to oil ratio on purity of ME in the product. The ME purity in the product increases from 35 to 88%wt as the methanol to oil molar ratio increases from 3.0:1 to 15.0:1. However, a ratio higher than

15.0:1 without increasing the catalyst decreases ME purity because higher methanol content dilutes the concentration of methoxide anion catalyst, see also Modi *et al.* (2007), Liu *et al.* (2008) and Watcharathamrongkul *et al.* (2010).

3.1.4 Effect of mass ratio of CaO to oil on purity of methyl ester and soap content

A mass ratio of CaO to oil of up to 2%wt of CaO can improve the purity of methyl ester as shown in Figure 4a. The purity of methyl ester reaches 85%wt when the CaO is 2%wt.
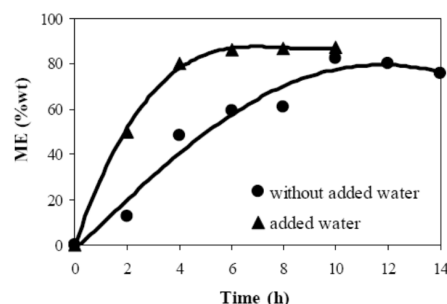

Figure 1.   Effect of reaction time on purity of methyl ester at 12:1 methanol to oil molar ratio, 4% wt. CaO to oil and reaction temperature of 65°C.
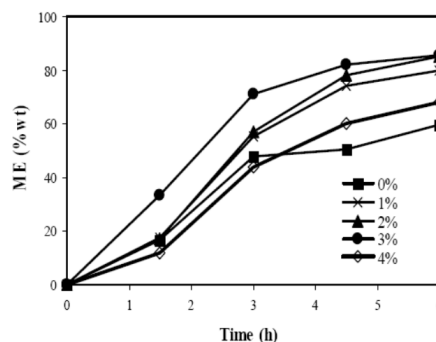

Figure 2.   Effect of water content in methanol on purity of methyl ester at 12:1 methanol to oil molar ratio, reaction temperature of 65°C and 4%wt. CaO to oil.
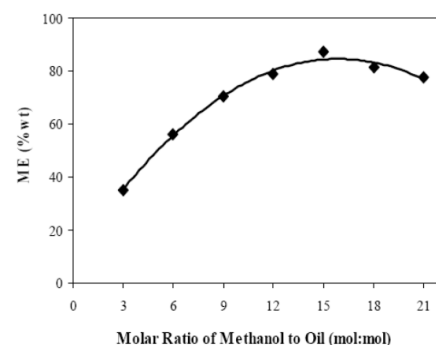

Figure 3.   Effect of molar ratio of methanol to oil on purity of methyl ester at 4% wt. CaO to oil, reaction temperature of 65°C, 3%water content and reaction time six hours.
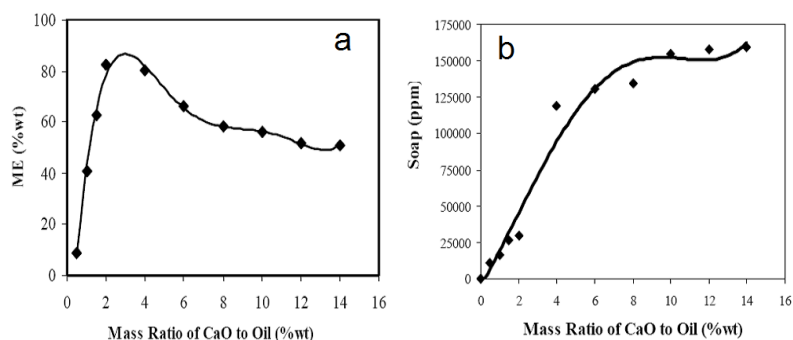
Figure 4.   Effect of mass ratio of CaO to oil on purity of methyl ester (a) and soap content (b) at 15:1 Methanol to oil molar ratio, reaction temperature of 65°C, 3% water content and reaction time 6 hours.

However, for a higher value than 2%wt of catalyst a higher concentration of alkaline base supports the side reactions (saponification) which increases soap content in the product as shown in Figure 4b.

3.2 Use of commercial grade CaO

For the commercial grade CaO, the response surface method was introduced to the experiment design and to determine the effects on %ME purity. The results and discussion in this part are shown as follows.

The statistical combination of the independent variables by central composite design (CCD) along with the experimental response is presented in Table 3. The statistical significance of this model was evaluated by using the F-test as shown in Table 4. It indicates that this regression is statistically significant (95% probability level) with the correlation

coefficients of determination R-Squared (R^2) and adjusted R-Squared of 0.96 and 0.93, respectively.

The predicted model for %ME purity (y) in terms of the coded factors is shown in Equation 2. Although the catalyst concentration (x_2) has the greatest coefficient in this equation, its numeric value is much smaller than that of reaction time. Therefore, the reaction time played a great effect on %ME purity.

$$y = -33.84 + 19.76x_2 + 0.24x_3 - 0.17x_1^2 - 2.12x_2^2$$
$$-0.0005x_3^2 + 0.53x_1x_2 + 0.008x_1x_3 \qquad (2)$$

where $9:1 \le x_1 \le 21:1$, $1 \le x_2 \le 10$, $120 \le x_3 \le 600$,

y = % (wt) ME purity,
x_1 = methanol to oil molar ratio,
x_2 = catalyst concentration, and
x_3 = reaction time (min).

Table 3.   Experimental matrix for the factorial design and center points.

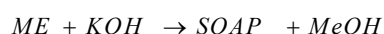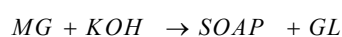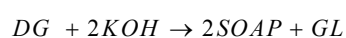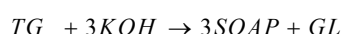| Run	Factors			%wt ME purity
	Methanol to oil molar ratio	Catalyst concentration (%wt)	Reaction time (min)	
1	11:1	8	503	54.00
2	15:1	6	360	82.00
3	11:1	3	503	44.00
4	9:1	6	360	64.30
5	11:1	8	217	65.00
6	21:1	6	360	85.00
7	19:1	8	503	78.00
8	15:1	6	360	82.00
9	19:1	3	503	44.00
10	19:1	3	217	44.00
11	15:1	10	360	64.32
12	19:1	8	217	68.00
13	15:1	6	120	50.20
14	15:1	6	600	55.00
15	11:1	3	217	55.00
16	15:1	6	360	82.00
17	15:1	1	360	15.00

Table 4.   Analysis of variance (ANOVA) of quadratic polynomial model.

Source	Sum of squares	% sum of squares	Mean square	F	df
Regression	5692.7	96	813.24	32.35	7
Residual	226.27	4	25.14		9
Total	5918.9	100			16

A statistical model in Equation 2 predicts that the highest percentage of ME purity is 86.94% at the optimal condition (methanol to oil molar ratio of 21:1, 7.35 %wt of catalyst and a reaction time of 407 minutes) while the experiment provides 84.78% ME purity. This result shows the methanol to oil molar ratio can increase more than 15:1 (see results in Section 3.1.3, Figure 3) because of a higher catalyst concentration (7.35% in this part and 4% CaO in Section 3.1.3). This is shown in Figure 5b. The higher methanol to oil molar ratio with the higher amount of CaO offers the higher methoxide catalyst using in transesterification.

By taking the derivative of Equation 2 with respect to methanol to oil (x_1) molar ratio and setting its derivative equal to zero, it was found that the optimum ratio of methanol to CaO (x_1 to x_2) is 0.53/0.34=1.56. Values higher and lower than this ratio causes %ME purity reduction. In case of a higher ratio, a higher amount of methanol reduced the catalyst concentration whereas in the case of a lower ratio, a higher amount of CaO caused soap formation.

Since CCD in RSM was used to optimize the conditions and study the interaction of the factors affecting to %ME purity in the presence of commercial grade CaO catalyst, response surface plots in Figure 5 were developed by using the fitted quadratic polynomial equation obtained by the regression analysis. Figures 5a-c show the effect of methanol to oil molar ratio and reaction time, the catalyst concentration and methanol to oil molar ratio, and the effect of reaction time and catalyst concentration, respectively. Those figures exhibit the same tend as the AR grade CaO. Possible reasons of the % ME purity reduction when the reaction time is longer than six hours are the saponification reaction from reactants (triglyceride, diglyceride and monoglyceride) or products (methyl ester, ME) and catalysts as shown in Equation 3 and the reaction of the by-product glycerol and CaO forming diglyceroxide (Kouzu *et al.*, 2008). Additionally, a catalyst concentration greater than 6% also provides the saponification from either reactants or product with catalyst as shown in Equation 3. The effects of CaO and reaction time in this work relates to the work of Vicente *et al.* (2007).

$$TG + 3KOH \rightarrow 3SOAP + GL$$

$$DG + 2KOH \rightarrow 2SOAP + GL$$

$$MG + KOH \rightarrow SOAP + GL \quad (3)$$
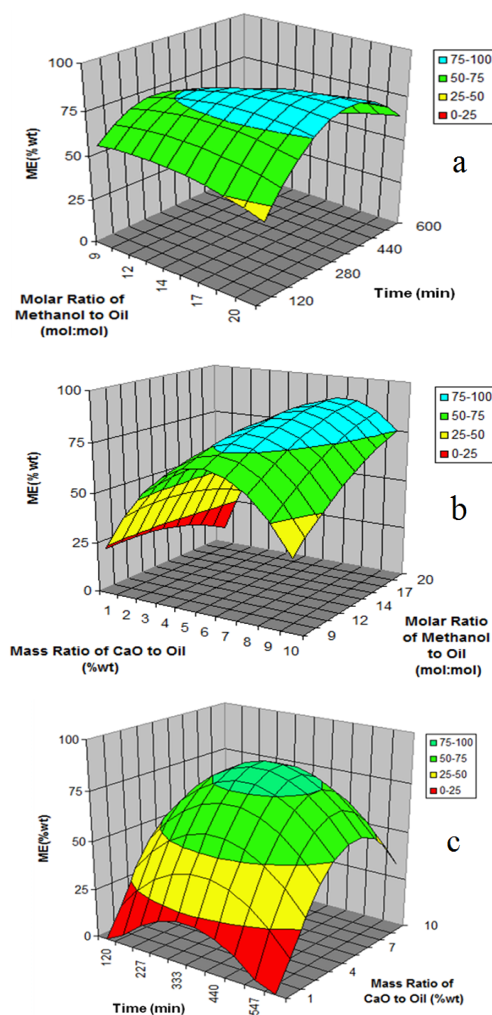
$$ME + KOH \rightarrow SOAP + MeOH$$

Figure 5.   Respond surface of a) time-molar ratio of methanol to oil at 5.5%wt. CaO, b) mass ratio of CaO to Oil-Molar ratio of methanol to oil at reaction time 360 min, and c) reaction time-mass ratio of CaO to oil at 15:1 methanol to oil on predicted % ME purity.

where TG, DG, MG, ME, GL and MeOH are triglyceride, diglyceride, monoglyceride, methyl ester, glycerol and methanol, respectively.

3.3 Use of reusing CaO

The result of reusing CaO is shown in Figure 6. It is found that the % ME purity drops approximately 5 to 10% when using the commercial grade CaO without catalyst

regeneration about 5 to 10 repetition, respectively, because of the catalyst deactivation.

4. Conclusion

In summary, this work shows the water content has significant impact on the % ME purity in transesterification of palm oil with using CaO as a solid base catalyst although the % ME purity is not high due to lower surface area of CaO. A small amount of water content increases the reaction rates in comparison to the anhydrous condition. A higher molar ratio of methanol to oil requires a higher amount of CaO catalyst to provide a higher amount of methoxide catalyst. The appropriate methanol to CaO catalyst ratio is about 1.56. In contrast, only a higher molar ratio of methanol to oil or only a higher amount of catalyst concentration drops the % ME purity. In addition, a longer reaction time drops the %ME purity. Finally, reused CaO can be introduced to the process.

Acknowledgments

Figure 6. Number of repetitions of using CaO at the optimal condition.

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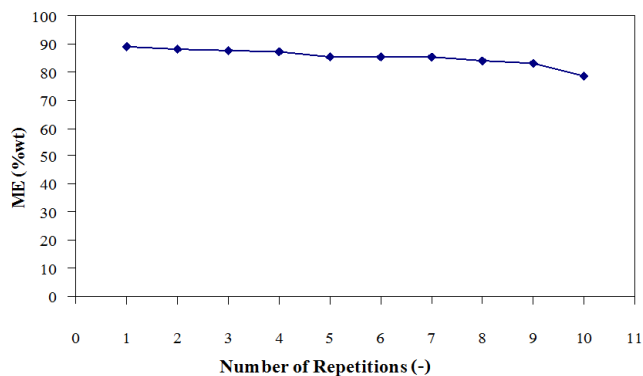
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