Activated carbon supported CaO for conversion of palm oil to biodiesel: Kinetic experiment

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ABSTRACT

Biodiesel is one of the bio-energies prepared from vegetable oil or animal fat through transesterification reaction with methanol. Because of the separation cost and associated environmental problems of homogeneous catalyzed biodiesel production, utilization of basic heterogeneous catalysts is steadily increasing in recent years. CaO is among the most solid base catalysts which can be used in transesterification reaction. In this study, activated carbon supported CaO catalyst was used for the transesterification reaction of palm oil. The catalyst was prepared according to the conventional incipient witness impregnation method. Kinetic experiment was performed in a batch reactor in the presence of heterogeneous catalyst for a wide range of operating conditions. The progress of the reaction was monitored using the refractive index method. Response surface methodology coupled with the central composite design was used to screen out the operating conditions and optimize the experimental result. A conversion of 34.78% was found at set of optimized conditions (reaction time of 150 min, temperature of 59.5 ^{0}C, methanol to oil molar ratio of 19.40:1, and amount of catalyst loaded of 10.55 (wt.%)). The predicted values of the response surface model were found in a good agreement with the actual experimental values at the aforementioned operating conditions. Moreover, the experimental result demonstrated that a pseudo-first order kinetic model best explains the transesterification reaction. Using graphical method from the Arrhenius equation, the value of activation energy and pre-exponential factor were calculated to be 35.16 kJ mol^{-1} and 731.43 kJ mol^{-1}, respectively.

Keywords: Activated carbon, CaO catalyst, Kinetics data, Palm oil, Refractive index

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INTRODUCTION

Global warming is causing serious climatic changes threatening human nature necessitating greater efforts to reduce green house gas emissions. This is a major reason that much interest has been taken in converting biomass resources, which are generated from carbon dioxide and water with the aid of photosynthesis, into the alternative fuel and chemicals. Biodiesel is an alternative diesel fuel derived from vegetable oils by transesterification reaction (Rios *et al.*, 2012). Transesterification is the reaction of triglycerides with alkyl alcohol to form alkyl ester and glycerol (by-product) (Kokoo, 2008). The type of alcohol and the fatty acid profile of the oil affect the properties of biodiesel product (Yan *et al.*, 2007).

Nowadays, biodiesel is commonly produced by transesterification of triglyceride with mono-

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alkyl alcohols, such as methanol in the presence of homogeneous base or acid catalysts. The base catalysts are most often used commercially due to higher catalytic activity compared to acid catalysts, hich are also more corrosive. Although the reaction is easily performed, subsequent neutralization, separation, and purification steps are time consuming and non-environmental friendly due to the large amount of water required during the washing step (Tongpoothorn *et al.*, 2011). Heterogeneous catalysis are becoming primary candidates to overcome problems associated with homogeneous catalytic conversion of biodiesel. After the reaction has been completed, the heterogeneous catalyst can easily be removed from the produced biodiesel and reused for further reactions (Baroutian *et al.*, 2011).

It has been reported (Wan and Hameed, 2011) that many researches have been conducted in search for heterogeneous catalysts that have high activity, and stability, with reasonable cost for the transesterification reaction. Solid catalysts can be either solid acid to replace strong liquid acids and hence eliminate the corrosion and environmental hazard problems associated with liquid acids or solid base catalysts (Helwani *et al.*, 2009). However, the efforts at exploiting solid acid catalysts for transesterification are limited due to the pessimistic expectations on the possibility of low reaction rates and adverse side reaction. Basic zeolites, hydrotalcites and alkaline earth oxides are among the reported solid catalysts used for the transesterification reaction (Helwani *et al.*, 2009).

Alkaline earth metal oxides are also potential base catalysts for triglyceride transesterification reaction. The origin of basic sites in alkaline earth oxides is due to the presence of M^{2+}– O^{2-}ion pairs in different coordination environments. The basic strength of the group II oxides and hydroxides increased in the order of Mg<Ca<Sr<Ba. Of these, Ca - derived bases are the most promising as they are inexpensive, least toxic and they exhibit low methanol solubility (Helwani *et al.*, 2009). It has been reported elsewhere (Kouzu, 2012) that CaO supported by porous materials could be a potential solid catalyst from the economic and catalytic activity point of view (Yan *et al.,* 2007; Tongpoothorn *et al.*, 2011; Buasri *et al..,* 2012).

In heterogeneous transesterification, rate of reaction is lower than in a homogeneous system due to the diffusion limitations in three phases. One of the ways to overcome this mass transfer problem is using structure promoters or catalyst supports which can provide more specific surface area and pores for active species, where they can be anchored and react with large triglyceride molecules (Baroutian et *al.,* 2010). Different types of supports have been used in heterogeneous transesterification reaction. It has been confirmed elsewhere (Hameed *et al.*, 2009; Baroutian *et al.*, 2010; Wan and Hameed, 2011) that activated carbon which has large surface area over which the catalyst can be dispersed can be used as a catalyst support. In addition to the large surface area of activated carbon, its surface characteristics does not change at high temperature and pressure making it suitable for its use at high temperature or pressure (Baroutian *et al.*, 2010).

Kinetics study of a transesterification reaction provides parameters that can be used to predict the extent of reaction at any time under particular conditions (Zhang *et al.*, 2010). Although many studies have been reported regarding the kinetics of transesterification reactions using homogeneous/ heterogeneous base catalysts (Stamenkovic *et al.,* 2008; Zhang *et al*., 2010; Birla *et al.,* 2012), to the best of our knowledge, no kinetic studies of supported solid base catalyzed transesterification using the refractive index method have been reported. In this work, the transesterification reaction kinetics was investigated using activated carbon supported CaO catalyst and synthesis of biodiesel was optimized using response surface methodology.

MATERIALS AND METHODS

Chemicals and instruments

Calcium nitrate ($Ca(NO_3)_2.4H_2O$, Sigma-Aldrich) Methanol (99%, Sigma-Aldrich), Potassium hydroxide (92%, Sigma-Aldrich), Phenolphthalein indicator, Sodium hydroxide, diethyl ether, sulfuric acid, ethanol, iodine, bromine liquid, sodium thiosulphate, boric acid and hydrochloric acid were used. All chemicals used in this study were of analytical grade.

After the oil has been pretreated, the transesterification reactions were carried out in 250 ml round bottom and 500 ml 3- necked round bottom flasks equipped with a reflux condenser, a mechanical stirrer, and a stopper to remove samples for further analysis as shown in Figure 1. The amount of CaO dispersed on activated carbon was determined using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, ULTIMA-2).

Catalyst preparation and characterization

CaO supported on activated carbon catalyst was prepared according to the conventional incipient-wetness impregnation method at a neutral pH by mixing the activated carbon (AC) with an aqueous solution of $Ca(NO_3)_2.4H_2O$ (Hameed *et al.*, 2009). The catalyst was obtained by loading precursor on the AC support in ratio of 1:7.6 (Wan and Hameed, 2011). After stirring (500 rmp) for 4 h, the paste was dried in an oven at 120 ^{0}C overnight. The dried solid was calcined at 450 ^{0}C for 4 h (Tongpoothorn *et al*., 2011) and kept in an inert atmosphere.

The amount of Ca dispressed on activated carbon supported before and after impregnation was determined using Inductively Coupled Plasma Optical Emission Spectrometer.

Oil preparation

In order to remove the water soluble gums, the oil was degummed with hot water at 70- 80 ^{0}C for 15 minutes and allowed to stand inseparating funnel (Kokoo, 2008). Thereafter, the aqueous layer was removed by decantation. The procedure was repeated several times to ensure the removal of most gums. The presence of high Free Fatty Acid (FFA>2.5 mg KOH/g) content in the oil enhances esterification reaction. Neutralization of the oil with strong bases is one mechanism to lower the FFA content. For this, a 250 gram of the degummed oil was poured into a beaker and heated to 80 ^{0}C,after which 167 ml of 0.1 M NaOH was added and stirred toform a uniform solution. 25 gm of sodium chloride was added to help settle-out the soap formed (Baroutian *et al*., 2010). The solution was left in a separating funnel for an 1 h; then, the soap was separated from the oil by decantation. The solution was washed using hot water several times to ensure complete removal of suspended soap.

Calibration of the refractive index measurement

A refractive index method was used to measure the conversion of palm oil to biodiesel during the transesterification reaction. To obtain a correlative equation among the refractive indices and the ester content, mixtures of palm oil with methylic biodiesel at different proportions were prepared, and the refractive index of each sample was measured. The biodiesel used as standard in these mixtures was synthesized by repeating alkaline transesterification reaction twice using 0.6% (w/w) sodium hydroxide catalyst with 100% vol. excess amount of alcohol (Santos *et al.*, 2013). The transesterification reaction was performed in a 500 ml three-neck round bottom flask, equipped with a reflux condenser, a thermometer and magnetic stirrer. The reactor on oil bath was initially charged with 100 g of palm oil and heated to a reaction temperature of 50 ^{0}C. Subsequently, the specified amount of catalyst was dissolved in alcohol and added to the reactor and reaction was started. After the end of the reaction period (1 h), the glycerol phase was separated by using a separating funnel. To insure complete conversion of the palm oil in to methylester, an amount of alcohol and catalyst as in the previous step was added and the reaction was allowed for 30 minutes. Finally, the resulting biodiesel sample was washed using 0.1 N HCl solution to neutralize the alkali catalysts. Then to insure complete removal of remaining catalysts and glycerol, the sample was washed using distilled water. The product was heated to 105 ^{0}C under vacuum for the subsequent analysis.

In the next step, palm oil and biodiesel mixtures were prepared in different weight proportions; B_{0}: 100% palm oil, B_{10}: 10% biodiesel, B_{20}: 20% biodiesel, B_{30}: 30% biodiesel, B_{40}: 40% biodiesel, B_{50}: 50% biodiesel, B_{60}: 60% biodiesel, B_{70}: 70% biodiesel, B_{80}: 80% biodiesel, B_{90}: 90% biodiesel, B_{100}: 100% biodiesel. The blends were prepared by weight because the weight fraction does not significantly change with temperature (Santos *et al.*, 2013). The refractive index of each sample was measured, and the correlation equation for the refractive index with the ester content was fitted and evaluated.

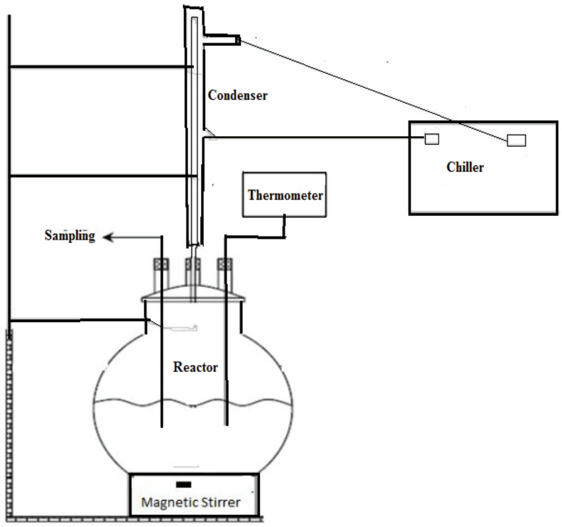

Figure 1 Experimental set up for biodiesel production and kinetics experiment.

Biodiesel fuel characteristics

The refractive index of the biodiesel was measured to an accuracy of 10^{-4} with FRM340 refractometer at 40 ^{0}C, which was thermostatically controlled by water bath to maintain the temperature according to ISO 6320 (Santos et al., 2013). The physicochemical properties of the biodiesel; kinematic viscosity at 40 ^{0}C (ASTMD445-06), specific gravity at 25 ^{0}C (ASTMD 5002-94), acid value (ASTMD 664), saponification value (ASTMD 5558-1995), iodine value (ASTMD 1959), cetane number (ASTMD 613), higher heating value (D2015) were evaluated according toAmerican Societyfor Testing and Materials (ASTM, 1950).

Kinetic experiment

To study the kinetics of the reaction, 19.50:1 molar ratio of methanol to palm oil and 10% (wt %) amount of catalyst loaded with respect to weight of oil was used in all experiments. To examine the effect of temperature on the conversion of palm oil in to methyl ester and to determine the reaction rate constants at each temparature, the experiments were conducted for a wide range of temperatures (30, 40, 50, 60, and 70 ^{0}C).

The reactor was initially charged with 165.20 ml of a palm oil with FFA lower than 2.5, 143 ml of methanol and 15 g of the activated carbon supported catalyst. The reactor was heated to the desired temperature and the magnetic stirrer was set at 500 rpm in order to have perfect mixing of the reaction mixture. The volume of the reaction mixture during the reaction process was assumed to be constant. Three milliliters of the reaction mixture was collected at 30, 60, 90, 120, 150, 180, 210 and 240 minute in test tubes and immediately centrifuged for 10 minute in order to stop the reaction. The concentration of palm oil to methyl ester were analyzed by RFM340 refractometer at 40 ^{0}C (Santos *et al*., 2013).

Experiments for optimization of biodiesel production

Design expert software, version 7.0.0 (Stat-Ease) was used to design the experiment and to optimize the biodiesel production using activated carbon supported CaO catalyst. Response surface method coupled with central composite design was used to analyze the data obtained from the experiment. The four independent variables considered in this study were reaction time, methanol to oil molar ratio, reaction temperature and catalyst load. The values and levels of the four independent variables considered in this particular study are presented in Table 1. Six replications at a center point of the design were used to determine experimental error (Wan and Hameed, 2011). The response of the transesterification reaction is methyl ester conversion (X). The conversion of methyl ester was monitored by refractometer (Santos *et al*., 2013).

Table 1 Range and levels of the variables for transesterification reaction experiments.

Variables	Code	Unit	Levels				
			-2	-1	0	1	2
Reaction time	A	min	60	90	120	150	180
Methanol to oil molar ratio	B	-	6	10.5	15	19.5	24
Reaction temperature	C	^{0}C	30	40	50	60	70
Amount of catalyst	D	wt.%	5	10	15	20	25

Selection of levels for each factor is based on the literature reports on the applications of homogeneous alkali transesterification reactions (Baroutian *et al*., 2011). The lower level of temperature was 30 ^{0}C since below that the reaction rate is expected as relatively slow and the upper level of temperature, 70 ^{0}C, is limited by boiling point of methanol (Baroutian *et al*., 2010).

Table 2 presents the total experimental run rquired for the optimization of the transesterification reaction based on the output of the design expert software, version 7.0.0 (Stat-Ease). For clearity purpose, the experimental result obtained for each run based on the centeral composite factorial design is presented in the same table.

Table 2 Central composite design matrix of the four independent variables together with thevexperimental result.

			Manipulated variables						Responses	
	A		B		C		D		Y	X
Run	Reaction time (min)	**Level**	Molar Ratio (MeOH:Oil)	Level	Reaction Temp.	Level	Catalyst load (wt.%)	Level	RI	Conversion (%)
1	90	-1	10.5	-1	40	-1	10	-1	1.45595	11.75
2	150	1	10.5	-1	40	-1	10	-1	1.45441	20.35
3	90	-1	19.5	1	40	-1	10	-1	1.45517	16.13
4	150	1	19.5	1	40	-1	10	-1	1.45351	25.32
5	90	-1	10.5	-1	60	1	10	-1	1.45389	23.2
6	150	1	10.5	-1	60	1	10	-1	1.45253	30.75
7	90	-1	19.5	1	60	1	10	-1	1.45315	27.31
8	150	1	19.5	1	60	1	10	-1	1.45195	34.00
9	90	-1	10.5	-1	40	-1	20	1	1.45625	10.11
10	150	1	10.5	-1	40	-1	20	1	1.45496	17.25
11	90	-1	19.5	1	40	-1	20	1	1.45603	11.31
12	150	1	19.5	1	40	-1	20	1	1.45481	18.10
13	90	-1	10.5	-1	60	1	20	1	1.45425	21.24
14	150	1	10.5	-1	60	1	20	1	1.45301	28.11
15	90	-1	19.5	1	60	1	20	1	1.45393	23.00
16	150	1	19.5	1	60	1	20	1	1.45282	29.17
17	60	-2	15	0	50	0	15	0	1.45558	13.84
18	180	2	15	0	50	0	15	0	1.45267	30.00
19	120	0	6	-2	50	0	15	0	1.45379	23.71
20	120	0	24	2	50	0	15	0	1.45251	30.90
21	120	0	15	0	30	-2	15	0	1.45644	9.03
22	120	0	15	0	70	2	15	0	1.45292	32.12
23	120	0	15	0	50	0	5	-2	1.45384	23.50
24	120	0	15	0	50	0	25	2	1.45559	13.78
25	120	0	15	0	50	0	15	0	1.45317	27.22
26	120	0	15	0	50	0	15	0	1.45322	26.93
27	120	0	15	0	50	0	15	0	1.45311	27.57
28	120	0	15	0	50	0	15	0	1.45301	28.11
29	120	0	15	0	50	0	15	0	1.45310	27.59
30	120	0	15	0	50	0	15	0	1.45289	28.78

Statistical analysis

The significance of the obtained experimental data was analyzed using multiple Analysis of Variance (MANOVA). Moreover the valudity of the statistical model (significance of each parameter on methyl ester conversion) was checked by the response surface methodology using the following second-order polynomial equation:

$$y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \beta_{ii} x_i^2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \beta_{ij} x_i x_j \qquad (1)$$

Where y-is the response (methyl ester conversion); x_i and x_j are the coded independent variables and β_0, β_i, β_{ii} andβ_{ij} are intercept, linear, quadratic and interaction constant coefficients, respectively. The response surfaces was developed using the fitted quadratic polynomial equation obtained from regression analysis, holding two of the independent variables at a constant value corresponding to the stationary point and changing the other two variables. Confirmatory experiment was carried out to validate the equation, using combinations of independent variables which are not part of the original experimental design but within the experimental region (Hameed *et al*., 2009).

RESULTS AND DISCUSSION

Catalyst characterization

The amount of CaO dispersed on activated carbon was determined using Inductively Coupled Plasma Optical Emission Spectrometer. The result showed that the amount of Ca is two orders of magnitude higher in impregnated activated carbon compared to virgin activated carbon. The amount of Ca before and after impregnation was 752.10, and 4319.88 ppm, respectively. This demonstrates that sufficient amount of Ca is disperesed/supported on the activated carbon framework.

Effect of operating condition on catalyst activity

The conversion of biodiesel was determined through mapping the refractive index measurement of the mixtures of palm oil and biodiesel. Figure 2 shows the linear correlation between the biodiesel and oil wt.% ratios and the refractive index measurement. As it can be seen in Figure 2, the refractive index of the mixture linearly decreases with increasing the amount of biodiesel in the mixture. As biodiesel is more transparent than heavy oil, it absorbs less light. Moreover, the result demonstrated that there is a linear correlation between the fatty acid methyl ester (FAME) oil blends and the refractive index. Such a linear correlation with $R^2 = 0.9994$ further confirms the reliability of the method (Santos *et al.*, 2013).

Effect of catalyst load

The results for conversion of palm oil at different catalyst loading are shown in Figure 3. As it can be seen from the figure, the amount of catalyst loaded has a significant effect on the conversion of palm oil to biodiesel which could be due to the availability of free active sites for the reaction (Arzamendi *et al.,* 2007). However, it decreases beyond 10 wt.% of the catalyst load. This may be due to, higher amount of solid catalyst increases the viscosity of the reaction mixture, which leads to increase the mass transfer resistance (Helwani *et al.,* 2009). The amount of optimum catalyst loaded to achieve the maximum conversion was found to be 10 % (w/w).

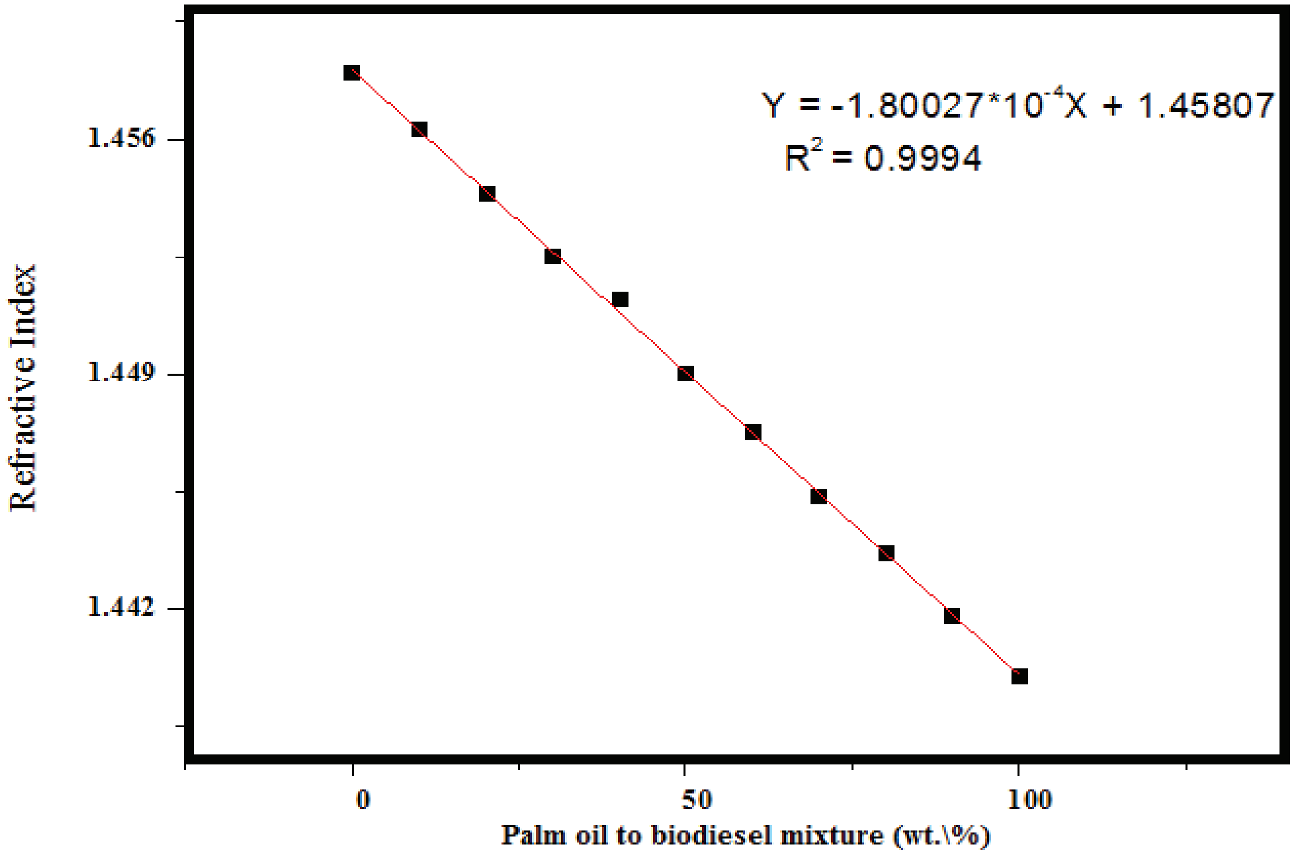

Figure 2 Refractive index measurement of the biodiesel blends at 40 ^{0}C.

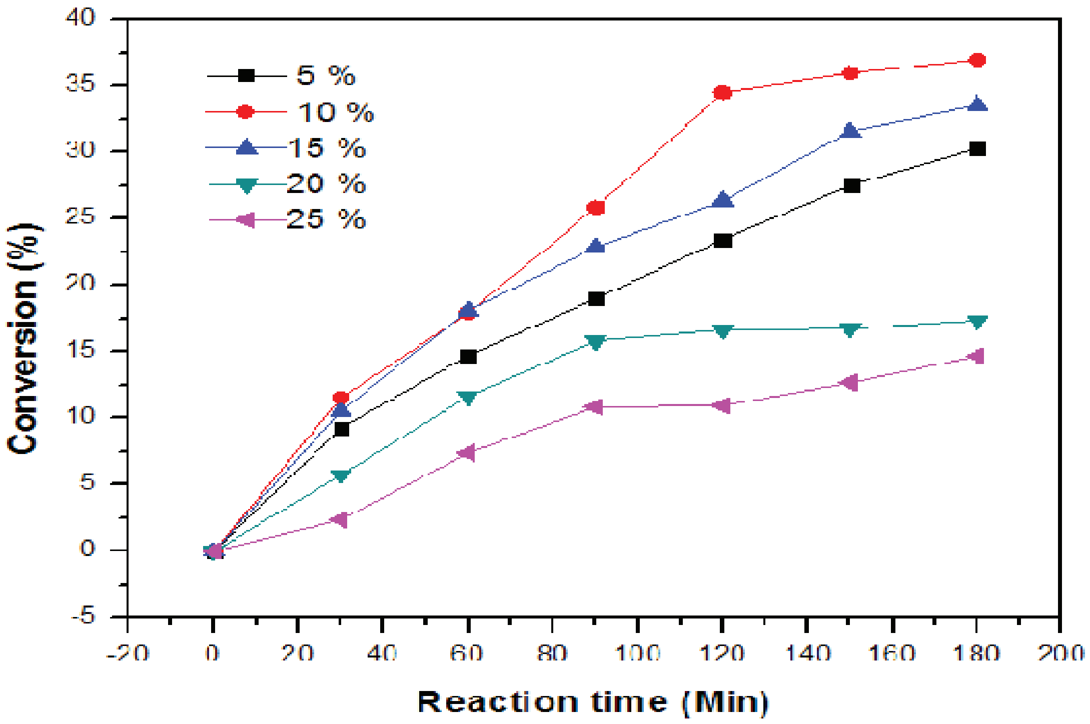

Figure 3 Effect of catalyst load on methyl ester conversion at 19.50:1 methanol to oil molar ratio and 60 ^{0}C reaction temperature.

Effect of reaction temperature

To study the effect of reaction temperature on the conversion of palm oil, the reaction was carried out for a wide range of temperature (30 to 70 ^{0}C). Figure 4 presents the effect of reaction temperature on methyl ester conversion. As it can be seen from the figure, the methyl ester conversion increases with temperature. This is due to the fact that the intrinsic rate constants are strong functions of temperature. Therefore, high temperature promotes the kinetic energy of the molecules and hence increases the methyl ester conversion (Zhang *et al*., 2010). It is also noted that the conversion tends to decrease beyond 70 ^{0}C suggesting that the transesterification reaction takes place mainly in the liquid phase. Above the temperature of 70 ^{0}C, the formation of methanol bubbles due to its boiling point limits the mass transfer on the three phase interface (Baroutian *et al.,* 2010). Thus, due to the mass transfer limitation of three phases (catalyst, methanol and oil) interphase the reaction is expected to be slowdown. Moreover, since methanol vaporize above the specified temperature, the reactant methanol exist in gas phase where as the oil and the catalyst are still in the liquid phase. Thus, due to the limited amount of methanol (below the stoichemetric amount) in the liquid phase the reaction may be halted ultimately decrease the conversion.

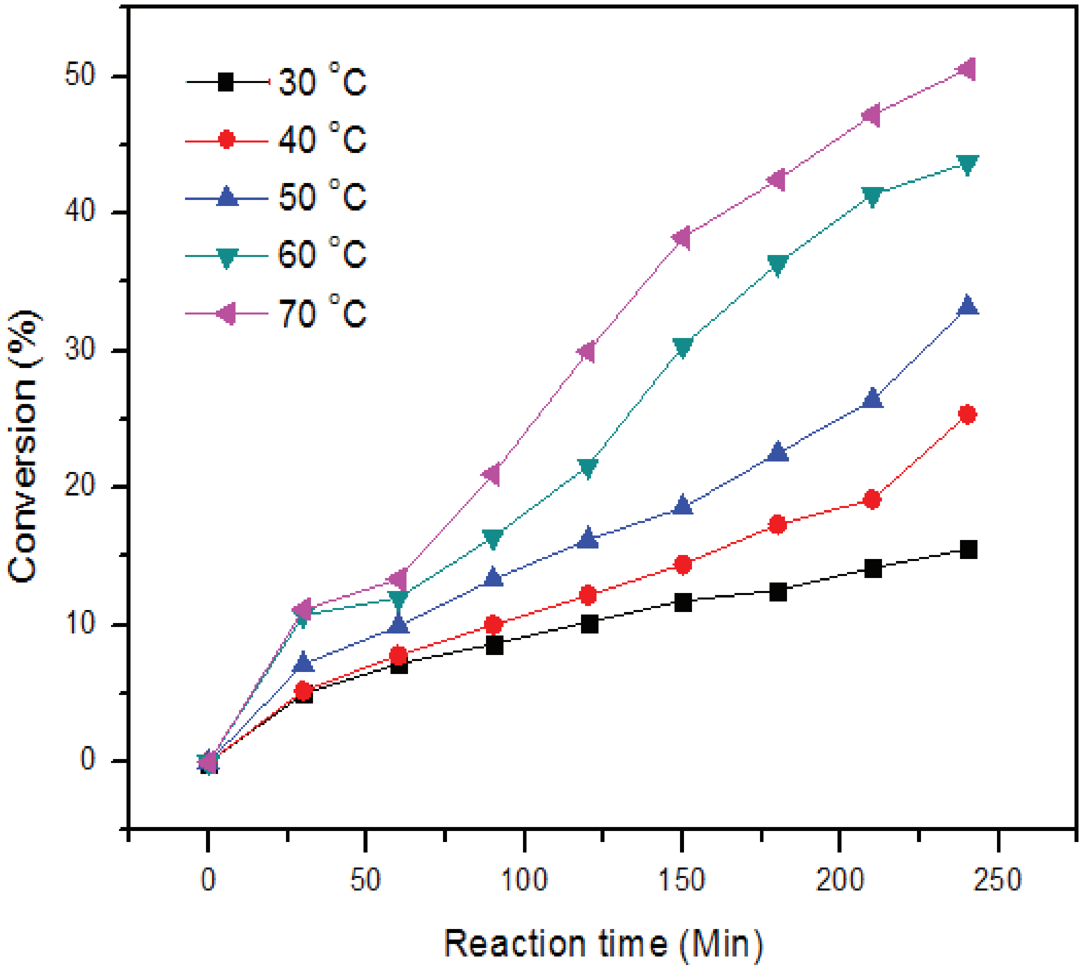

Figure 4 Effect of reaction temperature on methyl ester conversion at 19.50:1 methanol to oil molar ratio and 10 wt. % catalyst load.

Optimization of process parameters

Central composite design coupled with response surface methodology was used to optimize the experimental parameters for the desired response of the system on the basis of the model obtained and input criteria. Four reaction parameters were optimized using responses surface methodology by fitting the experimental data obtained using design expert 7.0.0 software.

Analysis of variance (ANOVA) was performed to investigate fitness and the significance of the model parameters. It can also present the effects of individual parameters and interaction of variables on the responses. Summaries of the analysis of variance (ANOVA) are presented in Table 3. Values of ”p >F” and/or less than 0.0500 indicate the model terms are significant. The ANOVA table shows that the four parameters of reaction time (A), Methanol to oil molar ratio (B), reaction temperature (C), the amount of catalyst loaded (D), the interaction of methanol to oil molar ratio amount of catalyst loaded (BD) and quadratic terms of reaction time (A^2), reaction temperature (C^2) and amount of catalyst loaded (D^2) significantly affect the measured response of the reaction conversion.

Table 3 ANOVA results for model regression.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob >F	
Model	1498.8780	14	107.0627	194.3462	<0.0001	significant
A-Reactiontime	347.4726	1	347.4726	630.7515	<0.0001	significant
B-methanoltooil	53.8801	1	53.8801	97.8061	<0.0001	significant
C-Reactiontemp.	733.05707	1	733.0571	1330.6858	<0.0001	significant
D-Amoutofcatalyst	104.0001	1	104.0001	188.7867	<0.0001	significant
AB	0.1089	1	0.1089	0.1977	0.6629	
AC	1.2321	1	1.2321	2.2366	0.1555	
AD	1.6002	1	1.6002	2.9048	0.1089	
BC	0.0930	1	0.0930	0.1689	0.6869	
BD	8.7616	1	8.7616	15.9045	0.0012	significant
CD	0.5776	1	0.5776	1.04849	0.3221	
A^2	62.9028	1	62.9028	114.1847	<0.0001	significant
B^2	0.7753	1	0.7753	1.4074	0.2539	
C^2	93.9377	1	93.9377	170.5210	<0.0001	significant
D^2	149.4667	1	149.4667	271.3202	<0.0001	significant
Residual	8.2633	15	0.5509			
LackofFit	6.0765	10	0.6076	1.3894	0.3766	not significant
Pure Error	2.1868	5	0.4374			
CorTotal	1507.1413	29				

The calculated optimum values of the parameters were; reaction time of 150 min, methanol to oil molar ratio of 19.40:1, reaction temperature of 59.5 ^{0}C and amount of catalyst loaded with respect to oil 10.55%. The model predicts that the biodiesel conversion under the optimum reaction conditions is 34.78%. The validity of the statistical model used to optimize the reaction parameters was confirmed through conducting practical experiments under these predicted optimal values. The result of the experiment is shown in Table 4 and as it can be seen from the table, the error between the experimental and predicted value is about 2.29%.

Table 4 Results of model validation.

Experiment	Reaction time	Methanol to oil molar ratio	Reaction Temp.	Amount of Catalyst (Wt.%)	Conversion (%)	
					Experimental	Predicted
Optimum	150	19.4	59.5	10.55	34	34.78

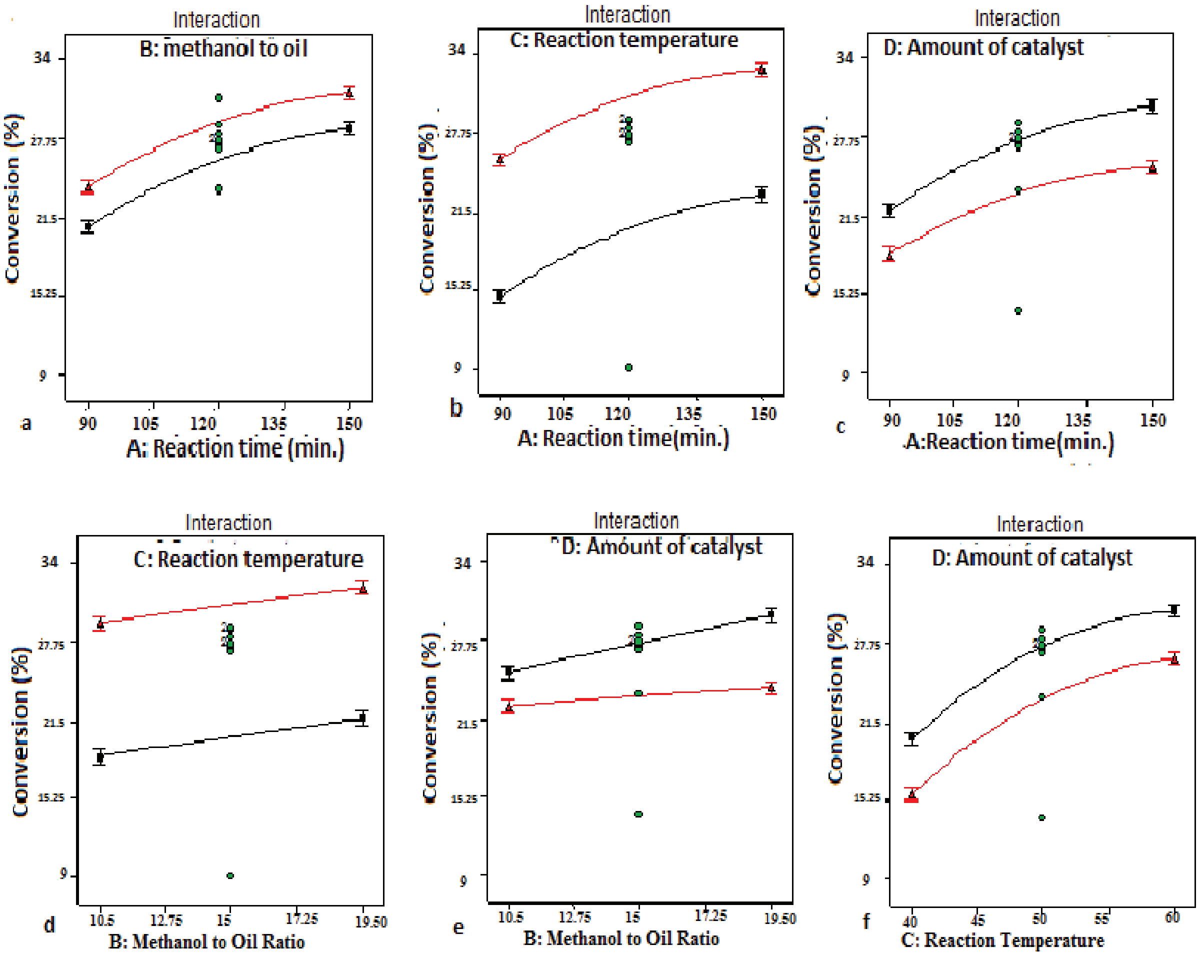

Figure 5 Interaction effect of reaction parameters of transesterification reaction.

Figure 5 shows the interaction effects of the four independent reaction parameters. As it is shown from the graphs in Figure 5 (a, b, c, d, and f), the curvatures indicate that the interaction effect of the terms are not significant. Where as the graph of Figure 5 (e), the curvatures are non–parallel; which indicates the presence of signiificant interaction effect of methanol to oil molar ratio and amount of catalyst loaded.

Physico-chemical characteristics of biodiesel

The biodiesel produced under the optimum conditions via transesterification reactions using activated carbon supported CaO catalyst was characterized for its physical and chemical properties. The result of these physicochemical properties is presented inTable 5, which also present the comparisons of the obtained palm FAME with the ASTM limits. As it can be seen from the table, the physicochemical properties of the produced biodiesel are all within the range of ASTM standard limits (Buasri *et al.,* 2012).

Table 5 Physico-chemical properties of the prepared biodiesel.

Property	Unit	Test Method	Biodiesel	
			Std limit	Exp'tal result
Specific gravity at 25 ^{0}C	Kg/m^3	ASTM D 5002-94	890	890
Kinematic viscosity at 40 ^{0}C	mm^2 /s	ASTM D 445	1.9-6.0	5.21
Refractive index at 40 ^{0}C				1.451
Acid value	mgKOH/g	ASTM D 664	max 0.8	0.221
Saponification value	mgKOH/g	ASTM D 5558 - 1995		190.1
Iodine value	g/100g	ASTM D 1959	max 120	50.15
Ester value	%(mol/mol)	EN 14103	min 96.5	189.879
Higher heating value	MJ/kg	ASTM D 6751		42.388
Cetane number		ASTM D 613	min 47	63.73

Determination of kinetic parameters

The amount of methanol used was sufficiently excess with respect to weight of oil to shift the reaction equilibrium towards the formation of fatty acid methyl ester. Thus, the reverse reaction could be ignored and change in concentration of the catalyst during the course of the reaction can be assumed to be negligible (Zhang *et al*., 2010). Thus, the overall reaction law for the forward reaction can be expressed by equation 2 (Birla *et al*., 2012).

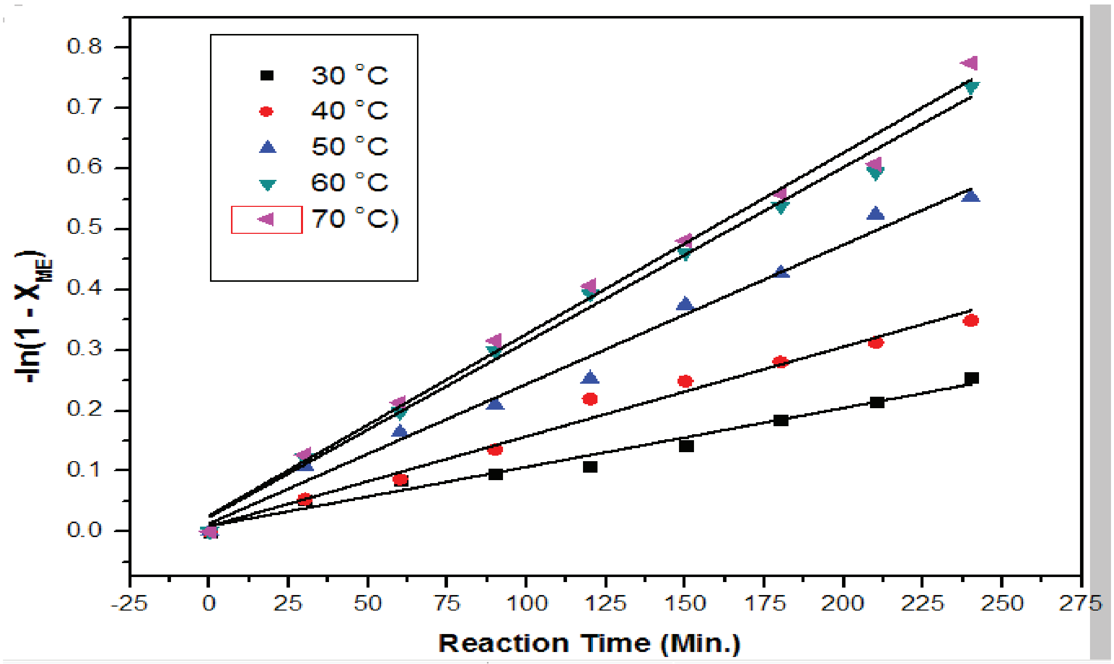

Figure 6 Plots of -ln(1 - X_{ME}) *versus* time (min) at temperatures of 30, 40, 50, 60 and 70 ^{0}C.

$$-r = -\frac{d[TG]}{dt} = K[TG][ROH]^3 \qquad (2)$$

Where [TG] is the concentration of triglycerides and [ROH] that of methanol and K is the reaction rate constant. However, due to high methanol to oil molar ratio, the change in methanol concentration can be considered as constant. This means the concentration of methanol does not change during the course of the reaction and it behaves as pseudo first order chemical reaction (Vujicic *et al*., 2010). Then the rate expression can be written as:

$$-r = -\frac{d[TG]}{dt} = -K'[TG] \qquad (3)$$

Where K' is modified rate constant and $K' = K[ROH]^3$.

By assuming the initial concentration of triglyceride was [TG_o] at time t=0, and at time t it falls down [TG_t]. Integration of equation 3 for t=0, [TG] = [TGo] and at t= t, [TG]= [TGt] gives equation 4.

$$\ln TG_0 - \ln TG = K'.t \qquad (4)$$

From a mass-balance

$$X_{ME} = 1 - \frac{[TG]}{[TG_0]} \qquad (5)$$

Or

$$[TG] = [TG_0](1 - X_{ME}) \qquad (6)$$

Where $X_{ME}X_{ME}$is conversion of methyl ester obtained from refractive index measurement. In terms of conversion the rate expression is given as:

$$\frac{dX_{ME}}{dt} = K'(1 - X_{ME}) \qquad (7)$$

Integration and rearrangement of equation 7 gives equation 8.

$$-\ln(1 - X_{ME}) = K'.t \qquad (8)$$

Based on this mathematical model and the experimental data, the conversion of methyl ester at different time interval was determined and the rate constants at each temperature were determined by plotting $-\ln(1-X_{ME})$ *versus* t using equation 8. The calculated values of the rate constants at each temperature and their corresponding correlation coefficient are presented in Table 6.

The kinetic data were collected using refractometer, which can provide real time monitoring of the reaction. The reaction temperatures of 30, 40, 50, 60 and 70 ^{0}C were used to study the kinetics of transesterification using 10 wt.% of catalyst load to oil and 19.50:1 methanol to oil molar ratio. As it is shown in figure 6, linear relationship was obtained which supports the hypothesis of pseudo-first order reaction (Vujicic *et al*., 2010; Zhang, *et al*., 2010).

Table 6 Reaction rate constants at the given temperature.

Temp.	K' (min^{-1})	R^2
30	0.0006306	0.946
40	0.00107	0.967
50	0.00149	0.969
60	0.00244	0.977
70	0.00303	0.989

The activation energy of the transesterification reaction was determined from the linearized plot of Arrhenius equation ($\ln K'$ Vs $1/T$). From the plot, the value of activation energy and pre-exponential factor was found to be 35.16 kJmol^{-1} and 731.43 kJmol^{-1}, respectively. The activation energy for base catalyzed transesterification of oil is in the range of 33.6 – 84 kJmol^{-1} (Zhang *et al*., 2010; Santos *et al*., 2013). Therefore, the activation energy obtained from the transesterification reaction using activated carbon supported CaO as a solid base catalyst is within the range reported in literatures (Zhang *et al*., 2010; Santos *et al*., 2013).

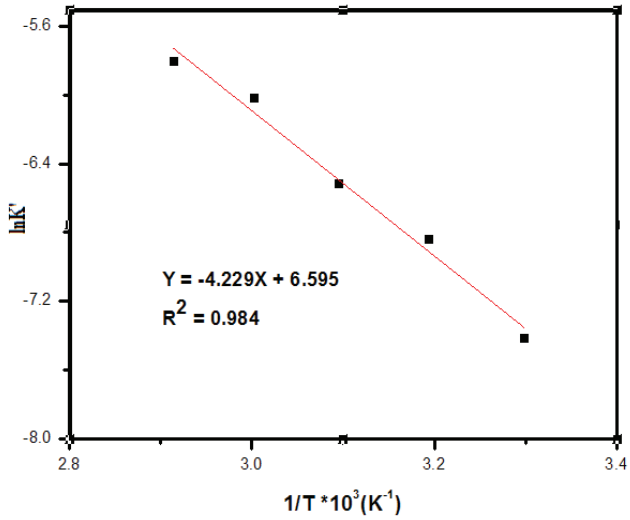

Figure 7 Plot of lnK' *versus* 1/T for transesterification reaction of palm oil.

$$K' = Ae^{-E/RT} \Longrightarrow \ln K' = \ln A - \frac{E}{RT} \qquad (9)$$

$$\ln K' = 6.595 - 4.229/T \qquad (10)$$

CONCLUSION

The catalytic activity of activated carbon supported CaO catalyst for biodiesel production was investigated. A central composite design coupled with response surface methodology was used to study the effect of reaction parameters on the transesterification reaction. An optimal conversion of 34.78% was obtained in reaction time of 150 min., methanol to oil molar ratio of 19.40:1, reaction temperature of 59.5 ^{0}C and amount of catalyst loaded with respect to oil 10.55 wt.%. Based on the experimental result obtained, it can be concluded that the refractive index method could be used to monitor reaction progress of a transesterification reaction using supported solid catalysts. Further experimentation to determine the free fatty acid profile of the transesterification is required to explicitlyexplain the phenomenological kinetic model of the transesterification reaction.

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