



Optimization of Transesterification Reaction for Biodiesel Production from Refined Palm Oil using Calcined Quick Lime Catalyst

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Commercial quick lime was calcined to produce calcium oxide and it was explored as solid catalyst for the transesterification of refined palm oil with methanol. The physico-chemical properties of catalyst were characterized by X-ray diffraction, scanning electron microscopy and Brunauer-Emmett-Teller. The results from characterization showed that calcium oxide was successfully synthesized. In the investigation of catalyst activity for transesterification reaction, a response surface methodology was performed. The design of experiment was made by application of 5-level-3-factors central composite design in order to study the effect of different factors on the percentage of fatty acid methyl ester conversion that determined by ¹H NMR. Quadratic model equation was obtained describing the inter-relationships between dependent and independent variables to maximize the fatty acid methyl ester conversion. Fuel properties of the produced biodiesel were also examined and the results were met well with biodiesel standard.

Keywords: Quick lime, Transesterification, Response surface methodology, Refined palm oil, Biodiesel.

INTRODUCTION

The liquid catalysts, widely used in commercial biodiesel process, have many disadvantages. All of these are: (1) they cannot be reused, (2) they produce large amounts of wastewater and (3) they produce glycerol as by-product with high impurity content. In contrast, the solid catalytic process, offering simplified production and purification process, is expected to be environmental friendly for biodiesel production process [1]. Triglyceride solid catalysts for transesterification reactions, such as alkali metal oxides, alkaline earth metal oxides, transition metal oxides, mixed metal oxides and other derivatives, have been reported in the literature for a variety of application, including ion exchange resins, sulfated oxide, waste materials and enzyme [2].

Quick lime or burnt lime is calcium oxide (CaO) obtained by calcination of pulverized lime stone (CaCO₃). It was used as the raw material to synthesize CaO catalyst in this study. Quick lime is a nontoxic material that is inexpensive, environmentally friendly and commercially available in Thailand.

Refined palm oil (RPO) was obtained from a physical oil refinery plant. The oil passes through three refining steps (degumming, bleaching and deodorizing) to remove impurities in the crude palm oil. Refined palm oil contains a low free fatty acid (FFA) content (around 0.1 wt %); thus, it is suitable

for making biodiesel *via* transesterification without any problems caused by salt formation.

Response surface methodology is a useful statistical technique that has been applied to analyze research involving a complex variable process. Response surface methodology employs multiple regression and correlation analyses to assess the effects of two or more independent factors 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. Response surface methodology has been successfully applied in the study and optimization of biodiesel production from various feed stocks [3-5].

In this study, CaO was prepared from quick lime and its physical and chemical properties were analyzed. The CaO was also tested as a solid catalyst in the transesterification of refined palm oil. Response surface methodology was utilized for process optimization, with the aim to better understand the relationships among three operating variables (catalyst concentration, methanol-to-oil molar ratio and reaction time).

EXPERIMENTAL

Quick lime powder and refined palm oil were kindly supplied by Panjapol Paper Industry Co., Ltd. (Saraburi, Thailand) and Patum Vegetable Oil Co., Ltd. (Pathum Thani, Thailand), respectively. Standard chromatographic grade fatty acid methyl ester (FAME)

were obtained from FLUKA (Switzerland) and Sigma-Aldrich (Switzerland), respectively. Analytical grade methanol and *n*-heptane were purchased from Merck (Germany).

Characterization of refined palm oil: A sample (40 mg) of refined palm oil was placed in a 50 mL three-necked flask with a boiling chip and 5 mL of 0.5 N methanolic sodium hydroxide was added to a sample flask connected to a condenser. The solution was refluxed at 90 °C until the fat globules had disappeared (about 5 to 10 min). Then, 5 mL of boron trifluoride solution (BF₃, 14 % v/v) was added through a condenser and boiling continued for 2 min, after which, 5 mL of *n*-heptane was added followed by boiling for another 1 min. After the reaction completed, the solution was cooled to room temperature and 15 mL of saturated sodium chloride solution were added, followed immediately by 15 s of shaking. The mixture was allowed to rest and separate into two layers. The upper layer of the solution was analyzed by gas chromatography (GC) to determine its fatty acid composition.

Preparation and characterization of CaO: Quick lime powder was screened through a 60-mesh screen to obtain a fine powder. The quick lime powder was further subjected to heat treatment in a furnace at 700 °C for 2 h. The calcined catalyst was then stored in a closed vessel to avoid the reaction with moisture in the air and carbon dioxide before used. The catalyst was characterized extensively. X-ray diffraction (XRD) patterns were recorded using a D8 Advance Bruker diffractometer (USA) with Cu K_α radiation. The analysis scanned a 2θ range from 5 to 40°. The textural and physical appearances were imaged using scanning electron microscopy (SEM) on a FEI Quanta 450 SEM (USA). Prior to imaging, the samples were covered with gold and mounted on a carbon film. The total surface area, total pore volume and average pore diameter were determined by the Brunauere-Emmette-Teller (BET) method with a Quantachrome Autosorb 1 (USA). The basic strengths (H₊) were determined using Hammett indicators [6]. The indicators used were phenolphthalein (H₊ = 9.3), 2,4-dinitroaniline (H₊ = 15.0) and 4-nitroaniline (H₊ = 18.4).

Transesterification process: The transesterification reactions were conducted in a laboratory-scale setup using a three-necked 100 mL flask equipped with a reflux condenser and a thermometer on a magnetic, heated stirrer set to 60 °C and 750 rpm. The CaO was added to the flask when the reactants reached the required temperature. After the reaction completed, the product was separated by centrifugation. The top layer consisted of biodiesel and the bottom layer contained a mixture of glycerol and CaO. The excess methanol contained in the biodiesel was further removed in a rotary evaporator at 65 °C. The obtained purified biodiesel was then bottled and stored for characterization.

Experimental design and statistical analysis: Response surface methodology with central composite design (CCD)

was used to optimize the biodiesel production process and to investigate the influence of different process variables on the percentage of FAME conversion. At five levels of independent variables ranging from -1.68 to +1.68, 20 experimental runs were carried out with the three independent variables: catalyst concentration (wt %) (A); methanol-to-oil molar ratio (mol), (B); and reaction time (h) (C). In addition, the 20 runs included 8 factorial points, 6 axial points and 6 replicates at the center point to determine the experimental error in this study.

The experimental data were analyzed using a second order polynomial equation (eqn. 1) to find the relationship between the independent variables and % FAME conversion:

$$Y = \beta_0 + \sum_{i=1}^3 \beta_i X_i + \sum_{i=1}^3 \beta_{ii} X_i^2 + \sum_{i=1}^3 \sum_{j=i+1}^3 \beta_{ij} X_i X_j \quad (1)$$

where Y is the response (% FAME conversion), β_0 is the intercept, β_i , β_{ii} and β_{ij} are the linear, quadratic and interactive coefficients, respectively and X_i and X_j are the independent variables. Statistical analysis of the equation was employed to evaluate the analysis of variance (ANOVA) and Design-Expert 8 software (State Ease Inc., Minneapolis, Mn, USA) was used to design the experiments and carry out the regression and graphical analysis of the data. The coded and uncoded of independent variables for reaction experiment parameter were designed as shown in Table-1.

Determination of the percentage of fatty acid methyl ester (FAME) conversion: The FAME conversion of refined palm oil was determined by ¹H NMR spectroscopy followed the work of Knothe [7]. Briefly explained, the chemical shift at 3.6 ppm represented the methyl ester protons and at 2.3 ppm represented the protons on the carbon next to the glyceryl moiety (α-CH₂). An equation to calculate the percentage of FAME conversion is shown in eqn. 2

$$C = 100 \times (2A_{ME}/3A_{\alpha-CH_2}) \quad (2)$$

where C is the percentage of FAME conversion, A_{ME} is the integration value of the protons of the methyl esters and A_{α-CH₂} is the integration value of the methylene protons.

RESULTS AND DISCUSSION

Characterization of refined palm oil: The fatty acid profile of the refined palm oil reveals that palmitic acid (42.83 %) and oleic acid (39.59 %) are the two major fatty acids, followed by linoleic acid (9.40 %) and stearic acid (4.43 %). The minor fatty acids are lignoceric acid (1.69 %), myristic acid (0.94 %), arachidic acid (0.35 %), lauric acid (0.32 %), behenic acid (0.16 %), linolenic acid (0.15 %) and palmitoleic acid (0.14 %). The average molecular weight of refined palm oil calculated from the fatty acid profile is 854.45 g/mol. The refined palm oil also contains 1.5 wt % of free fatty acid.

TABLE-1
INDEPENDENT VARIABLES AND LEVELS FOR CCD

Variables	Symbol coded	Range and levels				
		-1.68	-1	0	+1	+1.68
Catalyst concentration (wt %)	A	3.48	4.5	6.0	7.5	8.52
Methanol-oil-molar ratio (mol)	B	8.95	11	14	17	19.04
Reaction time (min)	C	104.32	135	180	225	255.68

Characterization of CaO: The crystal structure and symmetry of each sample are compared with the standard powder diffraction pattern in the database of the International Centre of Diffraction Data (ICDD). The calcium hydroxide impurities was removed from the quick lime by calcination at 700 °C for 2 h in a furnace. The XRD pattern indicates that calcination yields high purity CaO in the calcined quick lime, as shown in Fig. 1. The two diffraction peaks at 2θ of 32.20° and 37.34° are attributed to the CaO phase (ICDD file No. 00-037-1497) as a major component. The presence of calcium oxide hydrate ($\text{CaO}\cdot\text{H}_2\text{O}$, ICDD file No. 01-070-5492) is also observed at 2θ of 18.07°, 34.17°. The presence $\text{CaO}\cdot\text{H}_2\text{O}$ of results from interactions between water molecule in moisture and the surface of the CaO catalyst.

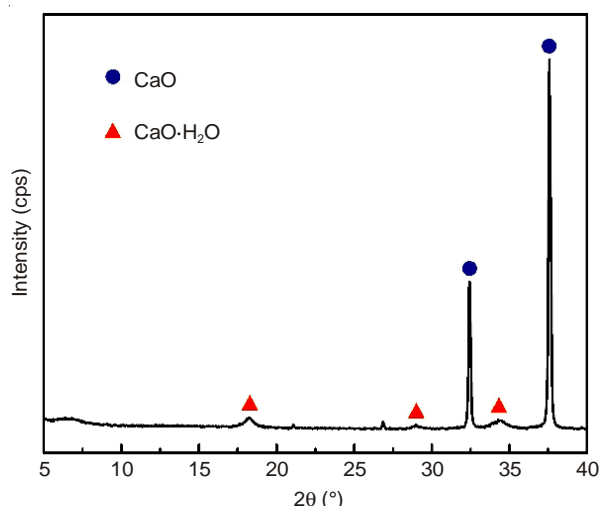


Fig. 1. XRD pattern of calcined quick lime

The shape and topology of the CaO particles are observed by SEM (Fig. 2). The morphology appears to be rod-like particles. A large number of pores are visible on the surface. The BET surface area, total pore volume and average pore diameter of the synthesized CaO were found to be 16.66 m² g⁻¹, 0.18 cm³ g⁻¹ and 44.26 nm, respectively. The surface area of a

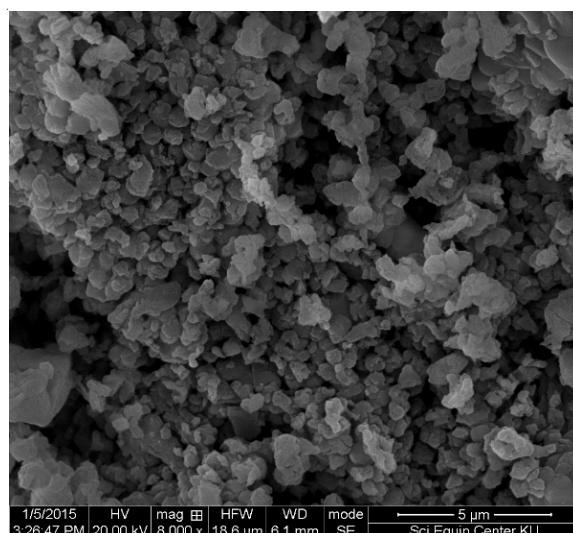


Fig. 2. SEM image of calcined quick lime

solid catalyst has direct impact on its catalytic activity and hence the higher surface area catalyst is expected for higher catalytic [8].

The calcined CaO changed the colour of phenolphthalein ($H_- = 9.3$) from colourless to pink and most of the CaO changed the colour of 2,4-dinitroaniline ($H_- = 15.0$) from yellow to mauve. A few CaO samples failed to change the colour of these indicators due to $\text{CaO}\cdot\text{H}_2\text{O}$ contamination while the colour of 4-nitroaniline ($H_- = 18.4$) remained unchanged. Thus, the basic strength (H_-) of CaO is between 9.3 and 18.4 and can be considered as a strong bases for conducting transesterification.

Optimization of transesterification reactions by response surface methodology: In this research, the relationships between the response (% FAME conversion) and the three reaction variables (catalyst concentration, methanol-to-oil molar ratio and reaction time) were evaluated using response surface methodology. The results at each point based on the experimental CCD are presented in Table-2. Twenty experiments were performed in duplicate.

TABLE-2
EXPERIMENTAL DESIGN WITH OBSERVED AND PREDICTED VALUE FROM TRANSESTERIFICATION OF REFINED PALM OIL

Run	Catalyst concentration (wt %)	Methanol-to-oil molar ratio (mole)	Reaction time (min)	Observed FAME conversion (%)	Predicted FAME conversion (%)
1	4.50	11.00	135.00	60.93	66.07
2	7.50	11.00	135.00	70.71	75.15
3	4.50	17.00	135.00	69.67	73.51
4	7.50	17.00	135.00	77.52	81.38
5	4.50	11.00	225.00	87.72	87.61
6	7.50	11.00	225.00	93.89	93.80
7	4.50	17.00	225.00	88.89	88.20
8	7.50	17.00	225.00	94.56	93.17
9	3.48	14.00	180.00	80.32	77.26
10	8.52	14.00	180.00	91.32	89.08
11	6.00	8.95	180.00	86.58	82.82
12	6.00	19.04	180.00	90.09	88.55
13	6.00	14.00	104.32	74.91	66.45
14	6.00	14.00	255.68	91.32	94.48
15	6.00	14.00	180.00	95.97	95.36
16	6.00	14.00	180.00	96.62	95.36
17	6.00	14.00	180.00	95.24	95.36
18	6.00	14.00	180.00	94.26	95.36
19	6.00	14.00	180.00	93.90	95.36
20	6.00	14.00	180.00	95.24	95.36

Regression analysis was employed to fit the empirical model with the generated response variable data. The response obtained in Table-2 was correlated with the three independent variables using a polynomial equation (eqn. 1). The observed and predicted values of % FAME conversion obtained at the design points of different reaction conditions are shown in Table-2. The % FAME conversion varies between 60.93 and 96.62 %. The minimum % FAME conversion (60.93 %) was obtained at 4.50 % catalyst concentration, 11:1 methanol-to-oil molar ratio and 135 min reaction time, while the maximum (96.62 %) was produced at 6 % catalyst concentration, 14:1 methanol-to-oil molar ratio and 180 min reaction time.

Design-Expert 8 software was employed to determine and evaluate the coefficients of the full regression model equation and their statistical significance. The second polynomial model for the % FAME conversion was regressed, as shown in eqn. 3:

$$Y = -236.92 + 28.2A + 13.9B + 1.36C - 0.07AB - 0.01AC - 0.01BC - 1.92A^2 - 0.38B^2 \quad (3)$$

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

The obtained data were then analyzed using ANOVA for fitting a second order response surface model by the least squares method and to assess the quality of the fit. The terms of the significant quadratic model for all responses are shown in Table-3. At the 95 % confidence level, $F_{\text{model}} = 10.71$ with a very low probability value ($p < 0.05$) that the null hypothesis is correct, indicating the high significance of the fitted model and showing the reliability of the regression model for predicting the % FAME conversion [9]. In addition, the factors of A, C, A^2 , B^2 and C^2 were found to be significant at the 95 % confidence level according to the computed F-values (high) and the p -value at the 5 % level. These statistical tests indicate that the selected model is satisfactory for predicting the % FAME conversion within the scope of the studied variables and also shows that the quadratic model is valid in the present study. The smaller the p -value for a parameter, the more significant the parameter [10].

The suitability of the model was also tested using the regression equation (eqn. 3) and determination coefficient (R^2).

The high value of R^2 (0.9060) indicates that the fitted model can be used to predict reasonably precise outcomes [11].

Fig. 3 shows that the response predicted from the empirical model is in agreement with the observed values in the range of the experimental variables. The value of the adjusted determination coefficient ($R^2_{\text{adj}} = 0.8214$) is signifying the high significance of the model. A high value of the determination coefficient ($R^2 = 0.9060$) justifies the excellent correlation between the independent variables. On the other hand, a relatively low value of the coefficient of variation ($CV = 5.12$ %) reveals better precision and reliability for this fitted model [3].

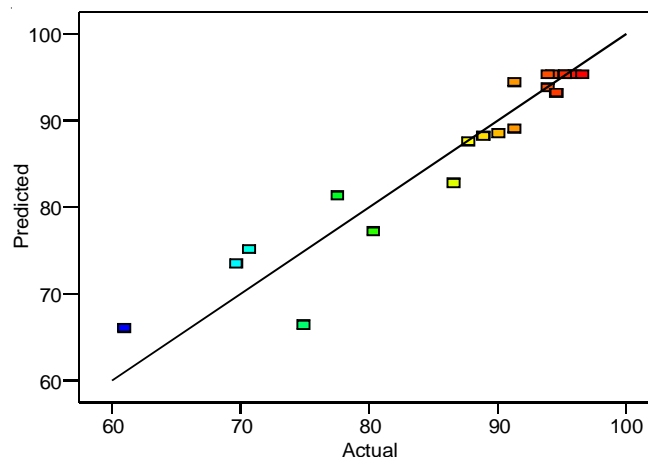


Fig. 3. Predicted % FAME conversion versus actual % FAME conversion plot

The response surface plot of % FAME conversion from various combinations of catalyst concentration, methanol-to-oil molar ratio and reaction time was shown in Fig. 4. It represents the graphical three-dimension surface plot of the regression equation (eqn. 3). Fig. 4(a) represents the effect of varied methanol-to-oil molar ratio and catalyst concentration at fixed reaction time on the % FAME conversion. It is obvious that the increase in % FAME conversion occurred with the increase in catalyst concentration and methanol-to-oil molar ratio. In general, the amount of heterogeneous catalyst had a significant positive effect on the transesterification of vegetable oil to

TABLE-3
ANOVA FOR THE RESPONSE SURFACE QUADRATIC MODEL

Source of variation	Sum of squares	Degree of freedom	Mean square	F-value	p -Value ^a	Significant at 5 % level
Model	1889.48	9	209.94	10.71	0.0005	Yes
A	168.49	1	168.49	8.59	0.0150	Yes
B	39.73	1	39.73	2.03	0.1850	No
C	948.74	1	948.74	48.39	<0.0001	Yes
AB	0.74	1	0.74	0.038	0.8500	No
AC	4.19	1	4.19	0.21	0.6537	No
BC	23.50	1	23.50	1.20	0.2993	No
A^2	267.62	1	267.62	13.65	0.0041	Yes
B^2	168.58	1	168.58	8.60	0.0150	Yes
C^2	399.59	1	399.59	20.38	0.0011	Yes
Residual	196.06	10	19.61			
Lack of Fit	190.87	5	38.17	36.81	0.0006	Yes
Pure Error	5.19	5	1.04			
Total	2085.54	19				

^a $p > 0.05$ is not significantly different at the 5 % level

methyl ester due to the number of active site available for the reaction [12] and the high amount of methanol helped to promote the reversible reaction forwards and the result in a better % FAME conversion [13]. Then, the % FAME conversion decreased with excess methanol due to the catalyst content decreased that result in a hindrance for the access of triglyceride molecule to active sites [14]. Fig. 4(b) shows the effect of reaction time and catalyst concentration while methanol-to-oil molar ratio was kept constant. It revealed the increased % FAME conversion with increasing the catalyst concentration and reaction time. However, the % FAME conversion slightly decreased with increasing concentration of catalyst made a slurry mixture of catalyst and reactant that resulted in mixing problem [15]. Fig. 4(c) represent the effect of reaction time and methanol-to-oil molar ratio on % FAME conversion at constant catalyst concentration. The % FAME conversion increased with increasing methanol-to-oil molar ratio and reaction time.

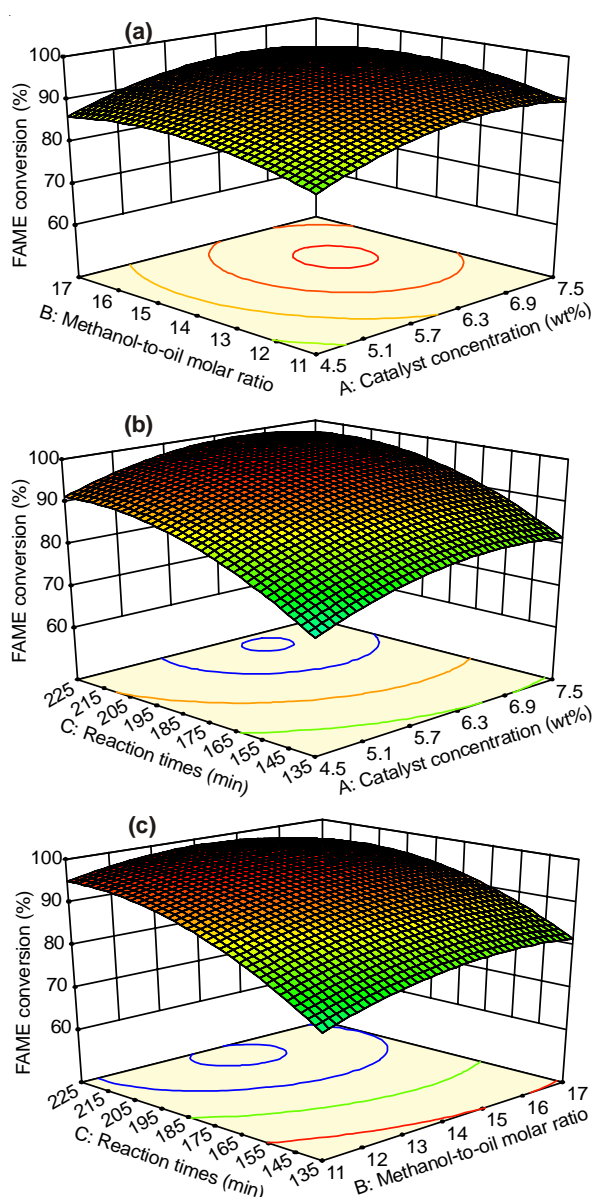


Fig. 4. Response surface plots elucidating the effects of: (a) methanol-to-oil molar ratio and catalyst concentration; (b) reaction time and catalyst concentration; and (c) reaction time and methanol-to-oil molar ratio

The optimum transesterification condition was predicted by applying numerical optimization of Design Expert software using response surface methodology. Optimization criteria were set for all variables including independent variables and the response. The range of the optimization for the response was 96.5 % FAME conversion to 100 % FAME conversion.

The optimum condition for producing % FAME conversion (98.69 %) was found as 6.32 %wt of catalyst, 14.12:1 of methanol-to-oil molar ratio and 213.57 (about 214) min of reaction time. The predicted value of 98.69 % was approximately equal to the observed average value of 97.58 % (repeated three times). Therefore, the experimental values were in acceptable agreement with the predicted values and the errors between the two values were small (< 5 % error for the % FAME conversion).

Confirmation and properties of produced biodiesel:

Fig. 5 exhibits the ^1H NMR spectrum of refined palm oil biodiesel. The characteristic peaks of methoxy protons as a singlet at 3.66 ppm and α -methylene protons as a triplet at 2.28 ppm were observed. These two peaks are the distinct peaks for the confirmation of methyl esters [7]. The other peaks observed were at 0.87 ppm due to terminal methyl protons, a strong signal at 1.30 ppm arises from the methylene proton of carbon chain, a multiplet at 1.60 ppm related to β -carbonyl methylene protons and a signal at 5.34 ppm due to olefinic hydrogen [16].

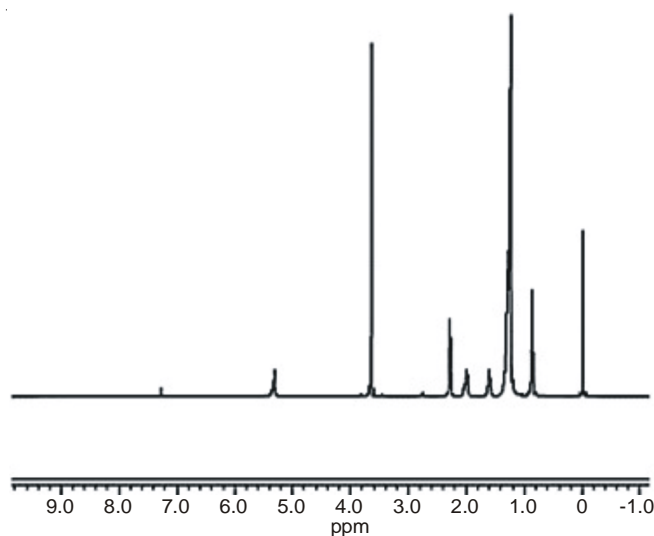


Fig. 5. ^1H NMR spectrum of refined palm oil biodiesel

The values of various properties were tested following the biodiesel standards of the USA (ASTM) and Europe (EN), as exhibited in Table-4. The results show that all biodiesel properties meet the standards.

TABLE-4
PROPERTIES OF REFINED PALM OIL BIODIESEL

Parameter	Testing method	Specifi- cation	Biodiesel in this study
Viscosity at 40 °C (cSt)	ASTM D445	1.9-6.0	5.64
Density at 15 °C (g/cm ³)	EN ISO 3675	0.86-0.90	0.882
Flash point (°C)	ASTM D93	130 min.	154
Acid value (mg KOH/g)	ASTM D664	0.80 max.	0.66
Water and sediment (% v)	ASTM D2709	0.050 max.	0.04

Conclusion

The calcium oxide was successful synthesized when the results were met with the database of the international centre of diffraction data. Response surface methodology technique was applied in transesterification reaction between refined palm oil and methanol using CaO as solid catalyst. A quadratic model, obtained from response surface methodology was suggested for the prediction of FAME conversion, with an ANOVA, revealing that 90.60 % of the observed was explained by the model. The optimum condition obtained from response surface methodology was 6.32 wt % of catalyst concentration, 14.12:1 methanol-to-oil molar ratio and 214 min of reaction time with observed average value of 97.58 % FAME conversion. The CaO provided high catalytic activity for transesterification in term of FAME conversion. The result suggested that quick lime powder was one of the potential solid catalyst to be used in replacing liquid catalysts.

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