Comparison of Homogeneous and Heterogeneous Catalysts in Biodiesel Production from *Pongamia pinnata* Oil

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Biodiesel was prepared by transesterification of *Pongamia pinnata* (*P. pinnata*) oil using potassium hydroxide (KOH) as homogeneous catalyst and synthesized calcium methoxide [$Ca(OCH_3)_2$] as heterogeneous catalyst. The $Ca(OCH_3)_2$ was synthesized from quick lime and characterized by scanning electron microscopy, X-ray diffraction, attenuated total reflection fourier transform, energy dispersive X-ray spectroscopy and BET surface area analysis to evaluate its performance. The parameters affecting the fatty acid methyl ester (FAME) content such as catalyst concentration, methanol to oil molar ratio and reaction time were investigated. Under optimized reaction condition, it was found that the 99.5 % of FAME conversion using KOH catalyst was achieved with 11:1 of methanol to oil molar ratio, 1.50 % wt of catalyst amount and 1 h of reaction time. The $Ca(OCH_3)_2$ catalyst was obtained the 98.04 % of FAME conversion with 15:1 of methanol to oil molar ratio, 3 % wt of catalyst amount, 3 h of reaction time at 65 ± 0.5 °C of reaction temperature and 750 rpm of stirring rate on both catalysts. The result of the % FAME conversion, which determined by ^{1}H NMR, suggested that $Ca(OCH_3)_2$ was the promising heterogeneous catalyst in replacing conventional homogeneous catalyst.

Keywords: *Pongamia pinnata*, Homogeneous catalyst, Heterogeneous catalyst, Calcium methoxide, Biodiesel.

INTRODUCTION

The decreasing of mineral diesel fuel resources, petroleum prices and rising demand of petroleum products encouraged the researchers to develop for the renewable alternative fuels like biodiesel. Biodiesel is produced by transesterification reaction of vegetable oils, animal fats or used cooking oils with methanol and catalyst to produce fatty acid methyl ester and glycerol as a byproduct[1].

Since the prices of edible vegetable oils are higher than diesel fuel, therefore used cooking oils and non-edible oils such as *P. pinnata* are preferred as potential low priced biodiesel sources. *P. pinnata* trees can grow in several countries such as India, Australia, Malaysia and it is traditional plant in the south of Thailand. The trees had 5-10 sub-branches, a circular canopy with branches. Pods with single and two seeds. *P. pinnata* seeds contain about 20-40 % wt of oil content, which can be converted to biodiesel by transesterification method[2,3].

In transesterification reaction, homogeneous catalysts provide much faster reaction rates than heterogeneous catalysts, but it is difficult to separate from the reaction mixture. Recently, heterogeneous catalysts have been renewed interest because these catalysts have many advantages such as noncorrosive,

easier to separate, economically and environmentally friendly. Types of heterogeneous catalyst for transesterification reactions of triglycerides were reported in the literature such as alkali metal oxides, alkaline earth metal oxides, transition metal oxides, mixed metal oxides and derivatives, ion exchange resins, sulfated oxide, waste materials and enzyme[4,5].

Quick lime or burnt lime is calcium oxide obtained by calcination of pulverized lime stone. It was used as the reactant to synthesized calcium methoxide catalyst in this study. The quick lime is nontoxic material, low-cost, environmentally friendly and commercially available in Thailand that makes it suitable active base catalyst for biodiesel production. In addition, calcium methoxide represents a potential base catalyst due to it higher activity and very low solubility compared to calcium oxide catalyst in transesterification of vegetable oil[6].

In previous work, Liu *et al.*[7] synthesized calcium methoxide by direct reaction between calcium and methanol at 65 °C for 4 h and it was used to catalyze in transesterification reaction of soybean oil with methanol to biodiesel. Masood *et al.*[8] synthesized calcium methoxide by using calcium oxide reacted with methanol under reflux condition at 65 °C for 2 h for transesterification reaction between palm oil methyl esters and trimethylolpropane to trimethylolpropane triesters.

Many researchers studied on homogeneous and heterogeneous catalyst for synthesis of *P. pinnata* biodiesel followed these details. Nail *et al.*[9] and Sharma *et al.*[10] studied the production of biodiesel from high free fatty acid *Pongamia pinnata* oil by two step reactions. The first step was acid-catalyzed esterification by using H_2SO_4 to reduce % free fatty acid lower than 2 %. The next step was alkali-catalyzed transesterification by using KOH, NaOH and CH_3ONa. Biodiesel obtained from high free fatty acid content of *P. pinnata* oil had been observed the high conversion of fatty acid methyl ester. Although *P. pinnata* oil had been taken for synthesis of biodiesel, there were not many reports of it being catalyzed by heterogeneous catalysts. Sharma *et al.*[11] reported that used waste eggshells as heterogeneous catalyst for biodiesel synthesis from *P. pinnata* oil. The result showed that 97.4 % conversion of fatty acid methyl ester was obtained.

Since, there is no report on the comparative production of biodiesel from *P. pinnata* using KOH and synthesized $Ca(OCH_3)_2$ catalyst. In this study, we synthesized $Ca(OCH_3)_2$ from quick lime as catalyst and characterized by XRD, ATR-FTIR, SEM, EDX and BET techniques. *P. pinnata* oil feedstock was decreased % free fatty acid content of oil to less than 2 % by esterification reaction using sulfuric acid. Parameters that influenced in the transesterification reaction (methanol to oil molar ratio, catalyst amount and reaction time) were investigated. The fatty acid methyl ester conversions were investigated by ^{1}H NMR. Finally, both biodiesels were analyzed and compared with biodiesel standards followed ASTM and EN standards.

EXPERIMENTAL

P. pinnata seeds were collected from Ranong province (Thailand). Quick lime was obtained from Panjapol paper industry Co., Ltd. (Thailand). Standard chromatographic grade fatty acid methyl esters (FAME) were purchased from Sigma-Aldrich (Switzerland). Standard methyl heptadecanoate was purchased from Fluka (Switzerland). Analytical grade methanol, sulfuric acid, hexane, *n*-heptane and potassium hydroxide were purchased from Merck (Germany).

Oil extraction: *P. pinnata* seed was ground by Moulinex (type 241, France) and dried in hot air oven at 105 ºC, 5 h for evaluate moisture content before oil extraction. Dried seed was extracted with hexane in Soxhlet Extractor (Buchi B-811, Switzerland) after that hexane was evaporated under vacuum. Then, the yield of extracted oil was calculated by following in eqn. 1.

$$\text{Extracted oil (\%)} = \frac{\text{Weight of extracted oil (g)}}{\text{Weight of dried seed (g)}} \times 100 \quad (1)$$

The fatty acid profile of *P. pinnata* oil was determined by gas chromatography utilizing a Hewlett-Packard (Agilent Technologies, santa clara, CA) 6890 gas chromatograph equipped with flame ionization detector and DB-wax (30 m × 0.32 mm × 0.25 µm) column. The free fatty acid (FFA) content of *P. pinnata* oil (11.90 %) necessitated acid pretreatment (100 g oil treated with 9:1 methanol to oil molar ratio and 1.0 g H_2SO_4 conc. for 2 h at 60 ºC). The free fatty acid content was reduced to 1.5 % after the acid pretreatment. This pretreated *P. pinnata* oil was further used for transesterification reaction.

Synthesis of calcium methoxide catalyst: Quick lime was ground manually using mortar and pestle and passed through 60 mesh screen to obtain fine powder. The quick lime powder was further subjected to heat treatment in furnace at 700 ºC for 3 h. An amount of 4 g calcined product reacts with 160 mL methanol under reflux condition at 65 ºC for 2 h with stirring rate of 1,250 rpm. After the reaction, the mixture was filtered for removing of methanol and then the residue was dried in the oven at 105 ºC for 1 h to obtain calcium methoxide product.

Characterization of catalyst: XRD was performed to examine the constituents of the synthesized catalyst on D8 Advance Bruker diffractometer, USA with Cuk_α radiation. The analysis was made over a 2θ range from 5º-40º. Measurement of IR spectrum was performed using attenuated total reflection fourier transform-infrared (ATR-FTIR) on Bruker Equinox 55 FTIR spectrometer, USA to know the surface groups existing on catalyst surface. The catalyst sample in powder form was analyzed over the scanning range of 4000-500 cm^{-1}. Scanning electron microscopy (SEM) was performed on FEI, QUANTA 450 Scanning Electron Microscope, USA to observe the shape of catalyst particles. Energy-dispersive X-ray spectroscopy (EDX) was conducted on Silicon drift detector to know chemical composition of elements inside the catalyst. Finally, the BET surface area, total pore volume and pore diameter were measured with Quantachrome Autosorb 1, USA.

Pretreatment by esterification reaction: The reaction was carried out in a 500 mL round bottom three-necked flask under reflux condenser and the other neck was fitted with a thermometer for control temperature of reaction. The *P. pinnata* oil was dried in a hot air oven (105 ºC for 2 h) before used for each set of experiments. Acid esterification was performed with 1 % wt of H_2SO_4, 9:1 of methanol to oil molar ratio at 60 ºC and maintained speed 750 rpm to reduce the acid value of the feedstock for 2 h. After acid esterification, water that formed in the product was removed by keeping it in a separating funnel.

Transesterification reaction: After lowering of the free fatty acid value, the transesterification reaction was carried out in a 100 mL round bottom three-necked flask under reflux condenser and using a hotplate for control temperature of reaction. The other neck was fitted with a thermometer. Magnetic stirring rate was about 750 rpm at 65 ºC. Methanol was used as alcohol and potassium hydroxide (KOH) and calcium methoxide [$Ca(OCH_3)_2$] were used as catalyst for transesterification. Molar ratio between methanol and oil, catalyst amount and reaction time were investigated. After completed the reaction by using KOH catalyst, the excess methanol was distilled off under vacuum evaporator and glycerin layer was separated in a separation funnel. The fatty acid methyl ester layer was washed with warm water and then removed excess water by heating at 105 ºC. The completed reaction by using $Ca(OCH_3)_2$ catalyst, the $Ca(OCH_3)_2$ catalyst was separated by centrifugation. The biodiesel from the both optimum conditions were investigated the fatty acid methyl ester (FAME) conversion by ^{1}H NMR followed EN 14103 standard.

Determination of fatty acid methyl ester conversion: The fatty acid methyl ester conversion of *P. pinnata* oil was determined by ^{1}H NMR spectroscopy followed the work of Knothe [12]. 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 (R-CH$_2$). An equation to calculate the percentage of fatty acid methyl ester conversion is shown in eqn. 2.

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

where C is the percentage of fatty acid methyl ester conversion, A$_{ME}$ is the integration value of the protons of the methyl esters and A$_{\alpha\text{-}CH_2}$ is the integration value of the methylene protons.

RESULTS AND DISCUSSION

Properties of *P. pinnata* oil: The 30.58 % wt of *P. pinnata* oil was obtained after extraction by hexane. The % free fatty acid was found to be 11.90 %. The oleic acid (C18:1) was the major fatty acid composition in *P. pinnata* oil. Table-1 explained *P. pinnata* oil fatty acid composition by GC analysis.

TABLE-1
FATTY ACID COMPOSITION OF *P. pinnata* OIL

Fatty acids	wt %
Palmitic acid (C16:0)	11.00 ± 0.10
Oleic acid (C18:1)	52.43 ± 0.16
Linoleic acid (C18:2)	13.91± 0.04
Linolenic acid (C18:3)	4.41 ± 0.02
Arachidic acid (C20:0)	1.92 ± 0.01
Behenic acid (C22:0)	9.96 ± 0.04
Erucic acid (C22:1)	0.38 ± 0.02
Lignoceric acid (C24:0)	2.95 ± 0.01

Characterization of synthesized calcium methoxide catalyst: The reaction of the synthesized calcium methoxide by using calcined quick lime (CaO) reacted with methanol under reflux condition at 65 °C for 2 h was followed in eqn. 3.

$$CaO + 2CH_3OH \longrightarrow Ca(OCH_3)_2 + H_2O \tag{3}$$
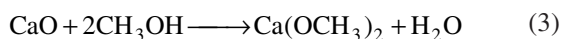
The XRD patterns of the calcium oxide obtained after calcination at 700 °C for 3 h that was removed the impurities (CaCO$_3$ and Ca(OH)$_2$) from quick lime. The obvious two diffraction peaks at 2 values of 32º and 37º attributed to calcium oxide. After reacting with methanol under reflux condition, this calcium oxide was transformed into calcium methoxide as evident from the characteristic peak of calcium methoxide at 2θ value of 11º. These results showed similar result as the reported in the previous studies[7,8]. These results confirmed the successfully synthesized calcium methoxide catalyst of our study.

The ATR-FTIR spectrum confirmed functional groups on synthesized calcium methoxide. The distinct peak observed at around 1070 cm^{-1} was assigned to -C-O stretching vibration of primary alcohol. Other peaks observed at around 3000-2800 cm^{-1} derived from CH$_3$ stretching vibrations and 1465 cm^{-1} concerning -C-H (alkane) bending[6,8].

Fig. 1 showed the shape and morphology of catalyst particles that was observed through SEM. The surface appears to be formed out of the clusters of thin plates and a large number of pores were visible on the surface. The shape of particles gave no indication of the chemical composition of catalyst, so EDX analysis was performed and the spectrum was presented
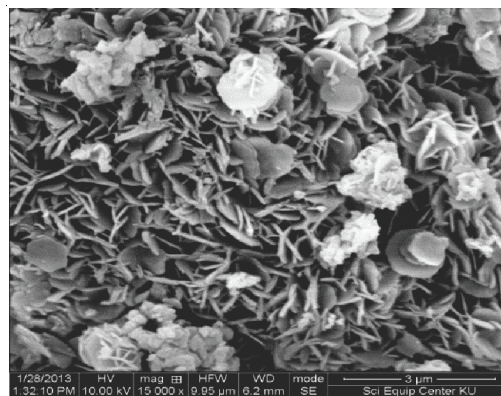

Fig. 1. SEM image of calcium methoxide

in Fig. 2. The atomic % of calcium, oxygen and carbon on a particular area at the surface of synthesized catalyst were 19.23, 61.53 and 19.24 %, respectively. The results for BET surface area, total pore volume and average pore diameter of synthesized catalyst were found to be 38.46 m^2 g^{-1}, 0.33 cm^3 g^{-1} and 34.39 nm, respectively[8].
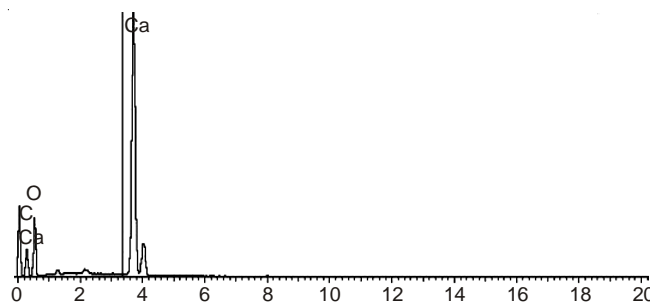

Fig. 2. EDX spectrum of calcium methoxide

Transesterification reaction results: Parameters influenced in the transesterification reaction of *P. pinnata* oil to yield biodiesel (FAME) were methanol to oil molar ratio, catalyst concentration and reaction time.

Effect of methanol to oil molar ratio: The stoichiometry of this reaction requires 3 mol methanol per 1 mol of triglyceride. In this study, an excess of methanol was used in order to obtain a higher biodiesel yield and decreased the impact of glycerol on the retrieve of catalyst. The results were illustrated in Fig. 3a and 3b, respectively which indicated the maximum fatty acid methyl ester conversion about 88.88 % at 1 h of reaction time and 1 % wt of KOH catalyst under excess methanol. Using Ca(OCH$_3$)$_2$ as catalyst, the optimum conversion of fatty acid methyl ester obtained 93.90 % with 15:1 methanol to oil molar ratio at 3 h of reaction time and 3.0 % wt of Ca(OCH$_3$)$_2$ catalyst. Further addition of methanol after optimum condition did not increase the yield on both catalysts. Then, the reaction rate decreased with the increasing of the molar ratio because the catalyst content decreased that result in a hindrance for the access of triglyceride molecules to active sites[8].

Effect of catalyst amount: The concentration of KOH catalyst on *P. pinnata* oil was varied within the range of 1-2 % wt. The % fatty acid methyl ester conversion increased with increasing KOH amount and the maximum biodiesel yield was obtained by adding 1.5 % wt KOH. The optimum condition reached 99.50 % at 1 h of reaction time 11:1 of molar ratio of
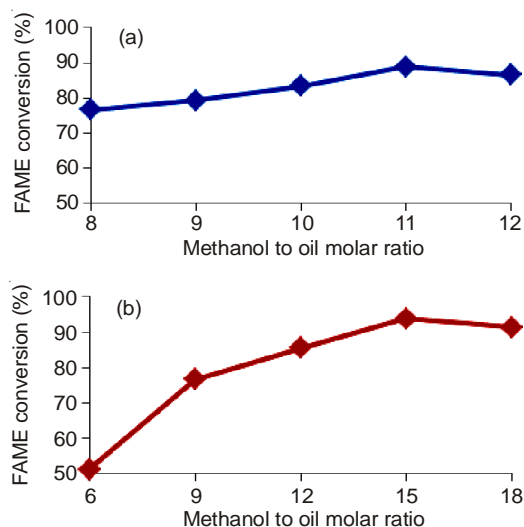
Fig. 3. Effect of methanol to oil molar ratio: a. KOH catalyst and b. Ca(OCH₃)₂ catalyst

methanol to oil (Fig. 4a). Using Ca(OCH₃)₂ as catalyst, the solid catalyst was varied within the range of 1-5 % wt. The % fatty acid methyl ester conversion increased with increasing Ca(OCH₃)₂ and the maximum fatty acid methyl ester conversion was obtained by adding 3 % wt Ca(OCH₃)₂. The optimum condition reached 96.62 % at 3 h of reaction time, 15:1 of molar ratio of methanol to oil (Fig. 4b). The catalyst amount beyond 1.5 % wt of KOH and 3 % wt of Ca(OCH₃)₂ did not showed any increase in the yield of both biodiesels because the mixture were increasing the viscosity from side reaction "saponification" that resulted in soap formation and lowered the yield[13].
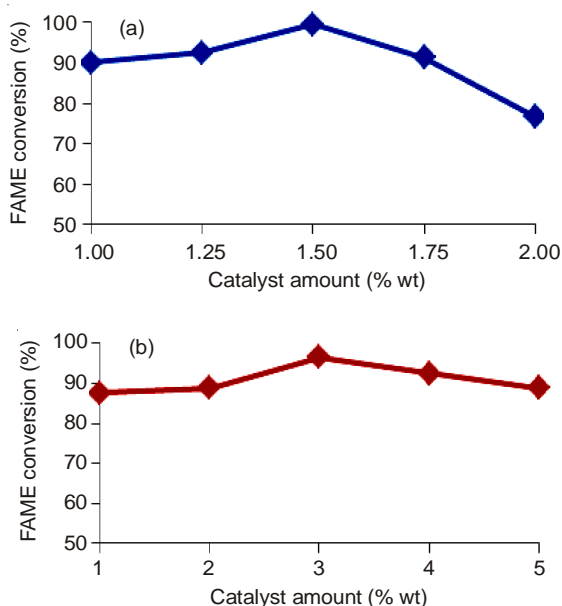

Fig. 4. Effect of catalyst amount: a. KOH catalyst and b. Ca(OCH₃)₂ catalyst

Effect of reaction time: The reaction times varied from 0.5 to 2.5 h of KOH and 1 to 5 h of Ca(OCH₃)₂ catalysts. Fig. 5a of KOH catalyst revealed that the % fatty acid methyl ester conversion increased from 0.5 to 1 h after that it decreased from 1 to 2.5 h. Fig. 5b of Ca(OCH₃)₂ catalyst revealed that
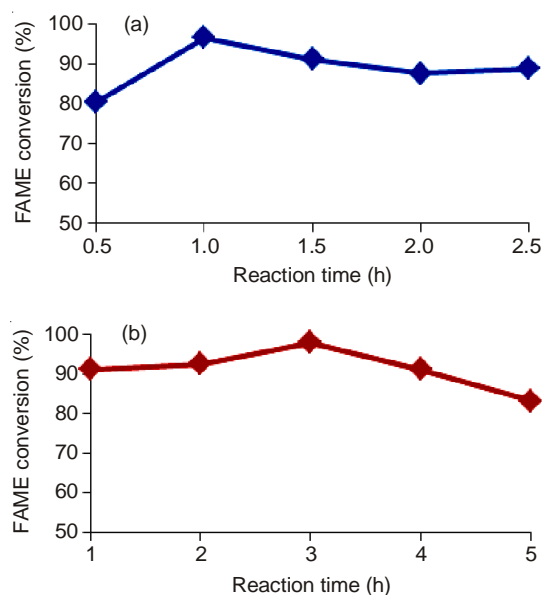

Fig. 5. Effect of reaction time: a. KOH catalyst and b. Ca(OCH₃)₂ catalyst

the % fatty acid methyl ester conversion increased from 1 to 3 h after that it decreased from 3 to 5 h. The optimum conditions for KOH catalysts were 1.5 % wt of catalyst amount, 11:1 mole of methanol to oil molar ratio and 1 h of reaction time. This condition gave 96.62 % of fatty acid methyl ester conversion. For Ca(OCH₃)₂ catalyst, the optimum conditions were 3 % wt of catalyst amount, 15:1 mole of methanol to oil molar ratio and 3 h of reaction time. This condition gave 98.04 % of fatty acid methyl ester conversion. The reason of % fatty acid methyl ester decreasing after the obtained optimum condition on both catalysts was the reversible reaction influenced on this effect[14].

The optimum conditions of *P. pinnata* oil in transesterification reaction was found to be comparable with that obtained from soybean and refined palm oil that are most commonly employed for biodiesel development in the several countries and has been given in Table-2. It can be observed that the % fatty acid methyl ester conversion obtained with all the three oils are high (> 96.5 %). Moreover, the synthesized Ca(OCH₃)₂ has been used for biodiesel production from *P. pinnata* oil with % fatty acid methyl ester similar to that obtained from homogeneous catalysis.

Biodiesel properties: The conversions of triglyceride were quantified along with the fatty acid profile in both biodiesel from the ¹H NMR spectrum in Fig. 6. The conversions were calculated by comparing the integrated peak area of methoxy proton (3.6 ppm) and methylene proton (2.3 ppm).

The values of various properties were tested followed biodiesel standard of USA (ASTM D 6751) and Europe (EN 14214) as exhibited in Table-3. The result showed that both biodiesel properties met the requirement standard. The kinematic viscosities of biodiesel were 5.70 and 5.92 cSt at 40 ℃, which is also within the ASTM specification. The acid values of *P. pinnata* oil biodiesel were determined to be 0.51 and 0.55 mg of KOH/g, which is within the ASTM specification. The flash point values of biodiesel were 186 and 189 ℃, which was well above the minimum ASTM specification (130 ℃) and can be considered safe for storage and transportation.

TABLE-2
OPTIMUM CONDITIONS OF % FAME CONVERSION USING HOMOGENEOUS AND HETEROGENEOUS CATALYSTS

Oil	Catalyst	Methanol to oil	Reaction time	FAME conversion (%)	References
P. pinnata	1.2 % wt KOH	8:1 (mol)	1 h	96.80	10
P. pinnata	0.8 % wt NaOH	8:1 (mol)	1 h	100.00	10
P. pinnata	1.0 % wt CH_3ONa	8:1 (mol)	45 min	98.28	10
Soybean	2 % wt $Ca(OCH_3)_2$	1:1 (v/v)	2 h	98.00	7
Refined Palm	3 % wt $Ca(OCH_3)_2$	12:1 (mol)	3 h	97.00	14
P. pinnata	1.5 % wt KOH	11:1 (mol)	1 h	99.50	Present study
P. pinnata	3 % wt $Ca(OCH_3)_2$	15:1(mol)	3 h	98.04	Present study

TABLE-3
PROPERTIES OF *P. pinnata* OIL BIODIESEL USING KOH AND $Ca(OCH_3)_2$ CATALYSTS

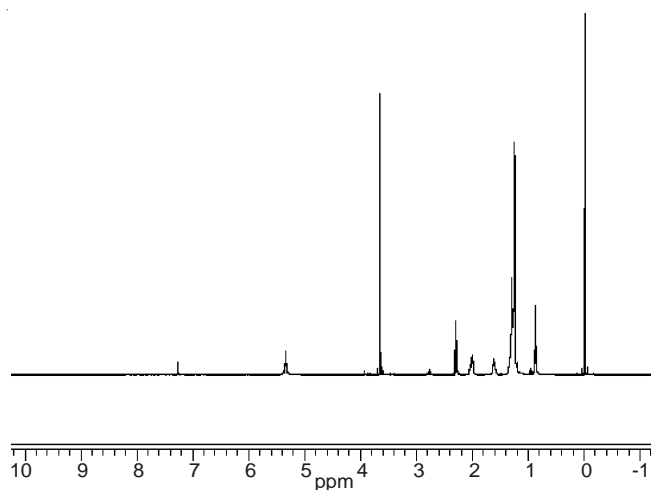| Parameter	Testing method	Limits	Value	
			KOH	$Ca(OCH_3)_2$
Viscosity at 40 ºC (cSt)	ASTM D445	1.9-6.0	5.70	5.92
Density at 15 ºC (g/cm³)	EN14214	0.86-0.90	0.877	0.886
Flash point (ºC)	ASTM D93	130 min	186 ºC	189 ºC
Acid value (mg KOH/g)	ASTM D664	0.80 max	0.51	0.55
Water and sediment (% v)	ASTM D2709	0.050 max	<0.050	<0.050
Methyl ester (% wt)	EN 14103	96.50	99.50	98.04

Fig. 6. ^{1}H NMR spectrum of biodiesel from KOH and $Ca(OCH_3)_2$ catalyst

The density at 15 ºC values were 0.877 and 0.886 and the water and sediment value was less than the maximum specification. The EN standard reports the conversion of oil to fatty acid methyl ester to be at least 96.5 %. The high % fatty acid methyl ester conversions were observed 99.50 and 98.04 % for KOH and $Ca(OCH_3)_2$ catalyst, respectively.

Conclusion

Biodiesel was produced from non-edible oil, *P. pinnata*, using KOH as homogeneous and synthesized $Ca(OCH_3)_2$ as heterogeneous catalyst. The *P. pinnata* oil possessing a high free fatty acid value underwent acid esterification with H_2SO_4 using the optimized parameters. The free fatty acid value became 1.5 % (lower than 2 %) and was followed by transesterification with KOH and synthesized $Ca(OCH_3)_2$ catalyst. The XRD, ATR-FTIR and EDX results showed that the $Ca(OCH_3)_2$ catalyst was successfully synthesized with sufficient purity and the synthesized catalyst was also found to acquire mesoporous surface and high surface area through SEM and BET characterizations. A high conversion of *P. pinnata* oil to

biodiesel was achieved by optimizing parameters such as the methanol to oil molar ratio, catalyst amount and reaction time at constant temperature and stirring rate. Using the optimized reaction conditions, a high % fatty acid methyl ester conversion (> 96.5 %) was obtained from both the catalysts. The biodiesel properties of both the catalysts showed nearly similar characteristics and met the requirement standard. These result implied that $Ca(OCH_3)_2$ as heterogeneous catalyst possibly substituted KOH as homogeneous catalyst to avoid the waste water problem of biodiesel plant in the future.

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