Rapid Biodiesel Production From Palm Kernel Through In Situ Transesterification Reaction Using Cao As Catalyst

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Abstract

Current biodiesel production consist multiple step including extraction and purification oil which consuming 70% of the total production cost and also time consuming. In situ transesterification reaction process has been identified could simplified the biodiesel production. In situ transesterification is a process of producing alkyl ester directly from oil-bearing material which extraction and transesterification reaction proceeds in one single step, with the alcohol acting both as an extraction solvent and a transesterification reagent. This research studies the feasibility of CaO as a catalyst in the production of biodiesel through in situ transesterification reaction of palm kernel seed with methanol. Four parameters were investigated including seed particle size (1 and >1 mm), reaction time (2 – 4 h), catalyst amount (0.5; 1 and 1.5 g) and volume of methanol (100 – 400 mL). It was found that the concentration of biodiesel was affected by the parameters. Using 1 mm seed particle size, 3 h reaction time, 1 g catalyst weight and 200 mL methanol, the optimal concentration of biodiesel was reached. It can be concluded that CaO could facilitate in situ transesterification of palm kernel to biodiesel.

Keywords: in situ transesterification, biodiesel, CaO, palm kernel.

INTRODUCTION

With the increase in fossil oil consumption, particularly for transportation, housing and industry, the fluctuating oil price and environmental concerns have intensified the search for an alternate source of fuel. Thus, the World Energy Forum predicted that oil reserves would be exhausted in less than 100 years if new oil wells are not found [1, 2]. Biodiesel, which is obtained by the transesterification of oil/fat with monohydric alcohols, is one such alternative fuel [3, 4]. Biodiesel gives lower hydrocarbon and carbon monoxide emissions, higher cetane numbers, and less smoke and particulates, provides engine lubricity, and is biodegradable and non-toxic [5-7].

However, currently the price of biodiesel is high compared to petroleum diesel due to the higher costs of biodiesel production [8]. The overall biodiesel cost consists of raw materials, catalyst, energy, consumables, labour, distribution and local taxes [2, 9]. The preparation of the raw material involves the extraction of triglycerides from oilseed using solvents, purification and refining. The preparation of triglycerides procedure is time consuming and expensive, contributing to 70% of the total biodiesel production costs [10]. In addition, the use of hexane as the extraction solvent contributes to the production of atmospheric smog, global warming and is classified as a hazardous air pollutant [10, 11]. Currently, biodiesel can only compete with petroleum diesel if there are tax exemptions and subsidies from governments [12].

To solve this problem, biodiesel manufacturers are focusing their attention on using low cost feedstock such as waste cooking oil. Waste cooking oil is far less expensive than refined vegetable oils and the cost of waste cooking oil is $2 - 3$ times lower than vegetable oil [13]. Unfortunately, waste cooking oil contains $2 - 7\%$ free fatty acids [14] which makes processing exceedingly difficult because soap formation occurs, especially when an alkaline catalyst is used [5]. Soap formation leads to catalyst consumption, lowering the result and making it difficult for them to be separated and purified downstream [15].

Another way to reduce the production cost of biodiesel is by in situ transesterification process reaction. In situ transesterification is a process of producing alkyl ester directly from oil-bearing material, usually ground oilseeds [16, 17]. In situ transesterification differs from the conventional reaction in that the oil-bearing material makes contact with the alcohol and catalyst directly. Therefore, the extraction and transesterification reaction proceeds in one single step, with the alcohol acting both as an extraction solvent and a transesterification reagent [18-20].

Numerous researchers have investigated the performance and feasibility of in situ transesterification since 1985 when Harrington and D'Archy-Evans explored the feasibility of in situ transesterification using homogenized whole sunflower seeds as substrate [21]. Homogeneous alkaline [10, 11, 19, 22-27] and acid [15, 18, 20, 21, 28-32] or a combination of the acid and alkali [33] has been used as a catalyst in in situ

transesterification and has given high yields. Another researcher used dimethoxymethane (DEM) as a co-solvent to increase the reaction time and produce a product containing 97.7% biodiesel within 13 mins [25]. However, all of the work were used a homogeneous substance as a catalyst. To the best of our knowledge, the utilization of heterogeneous substance as the catalyst in in situ transesterification reaction is very rare. Several researchers have conducted in situ transesterification of crops seed and microalgae using heterogeneous substance as catalyst assisted by microwave irradiation [34, 35]. However, microwave irradiation needs a special instrument to be functional and has a higher operational cost.

The aim of this research is to determine the feasibility of using non-toxic CaO as a catalyst in the in situ transesterification of palm kernel to biodiesel. Of metal oxides, CaO is the most studied due to its lower solubility, higher basicity, lower price and ease of handling [36]. Hence, in this report we used CaO as a heterogeneous catalyst in in situ transesterification and first activated CaO by pre-treatment with methanol according to Kawashima, et al [37]. The effect of some factors, such as seed particle size, reaction time, catalyst weight and methanol volume was systematically investigated to find the suitable operating conditions at which the highest product yield and/or purity can be achieved.

EXPERIMENTAL

Materials and Chemicals

Palm kernel was obtained from PT. Perkebunan Nusantara II (Sumatera Utara – Indonesia). They were milled using a blender to reduce the particle size. A sieve-shaker was then employed to separate the ground seed into 2 different sizes (1 mm and > 1 mm). Methanol (99.8% purity), n-Hexane, CaO, Heptane and Methyl Heptadecanoate were purchased from a local chemical dealer.

Catalyst Characterization

X-ray diffraction (Bruker XRD) was used to determine the crystallinity of CaO while the morphology of the CaO was examined using a FEI F50 Inspect FE-SEM. CaO was mounted on carbon tape and sputter-coated with 2 nm platinum. The SEM image occurred at an accelerating voltage of 10 kV at a working distance of 13.9 mm and at 30,000x magnification for 100ms. The catalyst was examined by thermogravimetric analysis (TGA) using Perkin Elmer TGA and temperature from 30^0C to 1000^0C with 10^0C / min heating rate. The surface area and pore volume of CaO were measured by the Brunauer-Emmett-Teller (BET) method.

Parameter Study

Four parameters were studied in this paper. The effect of the parameter was achieved by changing the parameter interest whilst other parameters were constant. Table 1 summarises the setting of all parameters used in the experiments.

Table 1. The effects of some experiment factors.

Experiments	Parameters			
	Seed Size (mm)	Reaction Time (hour)	Catalyst Weight (g)	Volume of Methanol (mL)
Effect of particle size	1; >1	3	1	200
Effect of reaction time	1	2; 3; 4; 5	1	200
Effect of catalyst amount	1	3	0.5; 1; 1.5	200
Effect of methanol volume	1	3	1	100; 200; 300; 400

In Situ Transesterification Procedure

Water removal pre-treatments of palm kernel milled with the methanol washing method was done first of all in order to reduce moisture [38]. Milled palm kernel (25 g) was mixed with 50 mL of methanol for 10 min; the slurry obtained was vacuum-filtered on a Buchner funnel and the filter cake was used in the in situ transesterification. An activated catalyst was obtained by mixing a given amount of CaO and 200 mL methanol in a 500-ml two-necked flask equipped with a reflux condenser and stirred for 1.5 h at room temperature. Next, 25 g of milled dry palm kernel was added to the mixture; the mixture was stirred using a magnetic stirrer and subsequently heated at 65^0C in an oil bath for 3 h. At the end of reaction, the product was separated from the palm kernel cake and catalyst by vacuum-filtering through a Buchner funnel. The excess methanol was distilled off under vacuum and after the products were centrifuged, it formed two phases whereby the upper layer was biodiesel and the lower layer was glycerol. After removal from the glycerol phase, the biodiesel was collected, weighed, and sent for chromatographic analysis to determine the percentage of methyl ester.

Analysis

The biodiesel samples were analysed in Clarus 500 gas chromatography equipped with a flame ionization detector and capillary column (30 m x 250 mm). The temperature of the oven and the detector was set at 180 and 2300C, respectively. Methyl heptadecanoate was used as the internal standard. The peaks of different methyl esters were identified by comparing the retention time of each component in the reaction samples with the peaks of pure methyl ester standard compound. The concentration (C) of FAME in the samples was calculated as:

$$C = \frac{\sum A - A_{EI}}{A_{EI}} \; x \; \frac{C_{EI} \; x \; V_{EI}}{m} \; x \; 100\%$$

where ΣA is the total peak area from the methyl ester C12 to C20; A_{EI} is the peak area corresponding to methyl heptadecanoate; C_{EI} is the concentration, in mg/ml of the methyl heptadecanoate solution; V_{EI} is the volume, in ml of the methyl heptadecanoate solution being used; m is the mass of the sample (mg).

Yield Calculation

Yield, in mass percentage, was calculated from the concentration of biodiesel as analysed by GC and the mass of biodiesel (upper layer) and comparing it with the mass of triglycerides in palm kernel seed[20, 27], as in the equation below:

$$Yield \; (\%) = \frac{Concentration \; of \; Biodiesel \; x \; Mass \; of \; Biodiesel}{Mass \; of \; Triglycerides \; in \; Palm \; Kernel} \; x \; 100\%$$

Characterization of Biodiesel

Biodiesel production from in situ transesterification of palm kernel using CaO as the catalyst was confirmed using infra-red spectrophotometer (Perkin Elmer FT-IR 400) equipped with attenuated total reflectance probe. A 600 MHz Bruker spectrophotometer ^{1}H-NMR was also used to identify the biodiesel production with condition of 64 scans and 1 second D1 delay.

RESULTS AND DISCUSSION

The oil content of the palm kernel seeds was determined as 33.08% and the free fatty acid content calculated to be 0.62%. The amount of oil extracted was found to be in agreement with the values reported in the literature, which range from 4 – 50% [39]. The fatty acid profile of palm kernel oil was determined by GC as lauric acid ($C_{12:0}$;

48.2 wt%), miristic acid ($C_{14:0}$; 15.8 wt%), palmitic acid ($C_{16:0}$; 8.1 wt%) and oleic acid ($C_{18:1}$; 15.9 wt%).

Liu, et al. found that in the presence of a little water (no more than 2.8%), CaO generates more methoxide anions, the transesterification reaction rate can be accelerated and the biodiesel yield is improved within a short reaction time. However, if too much water is present, the fatty acid methyl esters will hydrolyse to generate fatty acid which can react with CaO to form soap [40]. As water content in palm kernel seeds was calculated to be 2.968%, the water content must be lowered before use. Qian and Yun reported the methanol washing method to decrease water content in cottonseed meal is more effective than the vacuum oven drying method. The results obtained with methanol washing suggest that methanol washing removes not only the water, but also other impurities in cottonseed such as free fatty acids, colloid, gossypol and colouring matter, which could inhibit the in situ transesterification reaction[38]. Hence, in this research, the milled palm kernel seeds were initially washed with methanol to decrease the moisture content.

Effect of Particle Size

The oil and water contained in the milled palm kernel seed made particle separation difficult because the milled seeds usually stuck to each other. In addition, Kaul et al. reported the medium seed size of Jatropha curcas (>0.85 to <2,46 mm) achieved better results than a <0.85 mm seed size [11]. Other researchers also reported that no significant difference was determined between the yield for the smallest two particle size ranges, <0.5 mm and 0.5 − 0.71 mm [32]. Qian et al. also achieved the same results with cottonseed [24]. As a result, in this study only 2 particle sizes were used (1 mm and >1 mm). There is a decrease in the biodiesel yields as particle size increases with 67.51% and 45.44% for particle size 1 mm and >1 mm, respectively (fig. 1A). Furthermore, the concentration of biodiesel showed the same result with only a small difference in the concentration (fig. 2A). Shuit et al. explained that particles with a smaller size have a larger surface area and have more contact with the methanol and catalyst; however, for seeds with a larger particle size, there will be a stage where mass transfer limitation limits the extraction of oil trapped deep inside the seed core [20]. These results are consistent with those reported by other researchers [11, 24, 27].
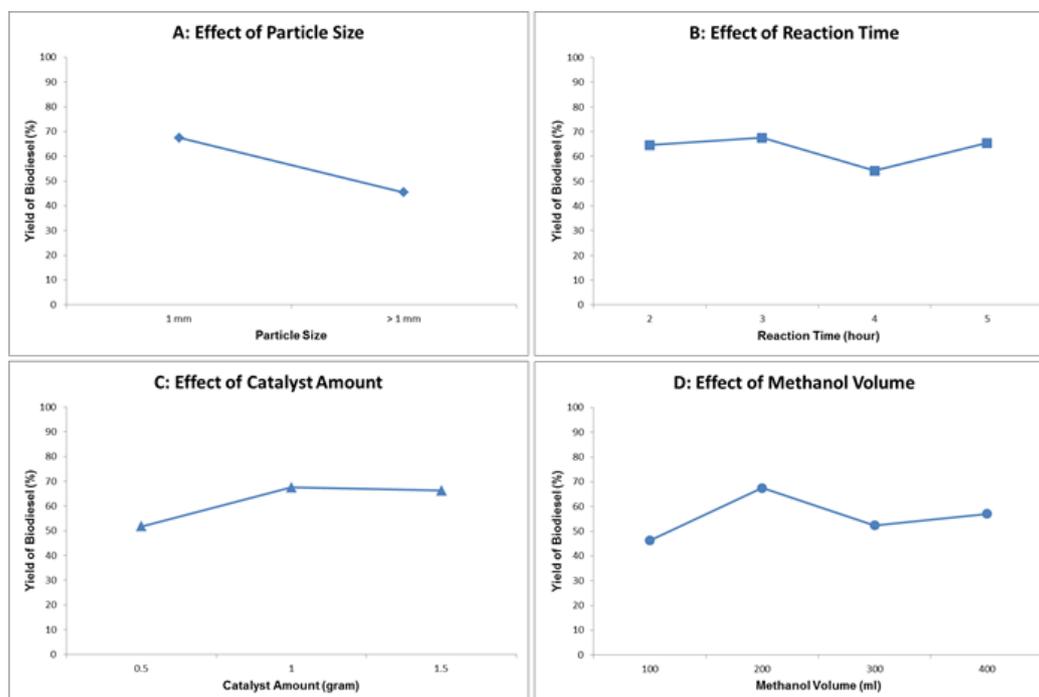
Fig. 1. The yield of biodiesel vs process variables: **(A)** particle size (reaction time of 3 h using 1 g CaO and 200 ml methanol); **(B)** reaction time (1 mm particle size, 1 g CaO and 200 ml methanol); **(C)** catalyst amount (reaction time 3 h, 1 mm particle size and 200 ml methanol); **(D)** methanol volume (reaction time 3 h, 1 mm particle size and 1 g CaO).

Effect of Reaction Time

Reaction time is one of the most important factors which affect in situ transesterification [38]. The efficiency of biodiesel formation and the quality of biodiesel products were also affected by reaction time. To study the effect of reaction time in the in situ transesterification of palm kernel using CaO as the catalyst, reaction time was varied from 2 to 5 hours. Figure 2B shows the effect of the reaction time on palm kernel seed oil conversion by in situ transesterification reaction with 200 mL methanol, 1 g CaO and 25 g of 1 mm particle size at reflux condition. The biodiesel yield increased in each increment of reaction time. A 3 hour reaction produced the highest yield as showed in figure 1B and concentration of biodiesel. Further increases in the reaction time from 3 - 5 hours did not affect either the yield or the concentration. It was found that there was a slight decrease of biodiesel from 3 - 5 hours. Eevera et al. predicted that hydrolysis occurred in the prolonged reaction time as the reaction reversed rendering free fatty acids [41]. Therefore, a 3 h reaction time can be chosen as the most suitable reaction time for the in situ transesterification reaction.
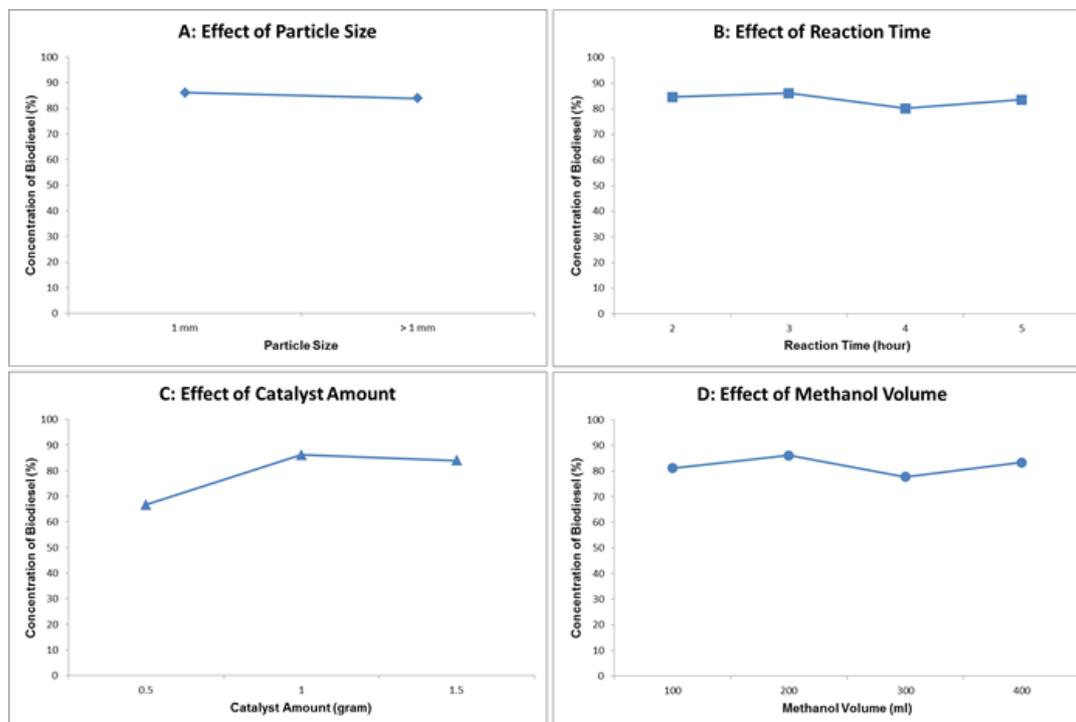
Fig. 2. The concentration of biodiesel vs process variables: **(A)** particle size (reaction time of 3 h using 1 g CaO and 200 ml methanol); **(B)** reaction time (1 mm particle size, 1 g CaO and 200 ml methanol); **(C)** catalyst amount (reaction time 3 h, 1 mm particle size and 200 ml methanol); **(D)** methanol volume (reaction time 3 h, 1 mm particle size and 1 g CaO).

Effect of Catalyst Amount

Methanol is a poor solvent for lipid extraction as there is only a 9.44% extraction rate if it is used as a solvent [25]. Therefore, catalysts will help to break oilseed cell walls and make the methanol react with the oil. The effect of the amount of catalyst on the in situ transesterification reaction was studied using three different amounts, 0.5; 1 and 1.5 g of CaO that were activated with 200 mL methanol for 1.5 h at room temperature. From figure 2C, it is clear that there is a significant increase in percentage conversion from 0.5 to 1 g observed. However, conversion decreases slightly from 86.17% to 83.95% if the catalyst amount increases from 1 to 1.5 g. Yang et al. suggested the reason for this downward trend was due to the formation of soap in the presence of high amount of catalysts, which increased the viscosity of the reactants and lowered the yield [42]. Another researcher suggested that when the amount of the catalyst is too great, more products are adsorbed and the biodiesel yield decreases [43]. Therefore, a 0.1 g catalyst amount was optimal in the reaction of this study.

Effect of Methanol Volume

To conduct the transesterification reaction, theoretically 3 mole of alcohol are required for 1 mole of triglyceride to produce 3 mole of biodiesel and 1 mole of glycerol. Triglyceride transesterification is a reversible reaction and an excess of methanol is used to drive the reaction towards the completion of biodiesel formation. In the in situ transesterification reaction, methanol acts both as an extraction solvent and a transesterification reagent [18, 20, 44]. Therefore, a suitable amount of methanol is needed to conduct the in situ transesterification reaction. In this study, the volume of methanol was varied from 100 to 400 mL. A high volume of methanol was required in the in situ transesterification reaction to increase the amount of lipid extracted from seed [45]. As shown in Figure 4C, by increasing the volume of methanol from 100 to 200 mL, the conversion to methyl ester was increased from 81.21% to 86.17%. Further excess in methanol does not increase the yield; however an undesirable result is that the concentration of biodiesel decreases, increasing the downstream processing cost [27]. Excess methanol presumably would dilute the concentration of reactants rendering decreasing contact among them and lowering conversion yield. Hence, 200 mL of methanol was selected for optimum biodiesel conversion of palm kernel using CaO as the catalyst.
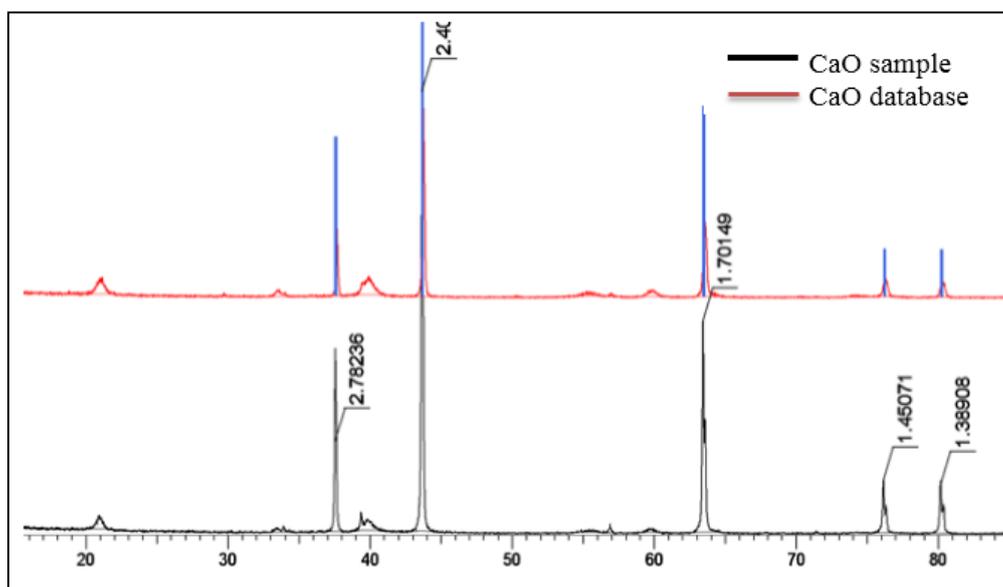
Catalyst Characterization

The commercial CaO used as catalyst in this study was characterized using X-ray diffraction, thermogravimetric analysis, scanning electron microscope and BET surface. The XRD pattern of CaO is shown in Figure 3. The diffraction peaks at 37.5^0, 43.5^0, 63.5^0, 76.5^0 and 80.5^0 were those of CaO being similar to those from database. This result indicated that CaO was the main component in the sample and no $Ca(OH)_2$ detected.

The SEM micrograph of commercial CaO particle is shown in figure 4. It can be seen that an irregular shape with different sizes in nano dimension were observed. The exfoliated morphology with larger pores were detected which was confirmed by BET surface analysis. The specific surface area, pore volume and average pore diameter of CaO are presented in Table 2. The BET result showed that CaO was expected to have high catalytic activity due to the higher surface area they have.

Table 2. The BET result of CaO

Catalyst	CaO
Surface area (m^2/g)	3.2
Total pore volume (cm^3/g)	26
Average pore diameter (nm)	200

Fig. 3. The XRD pattern of CaO
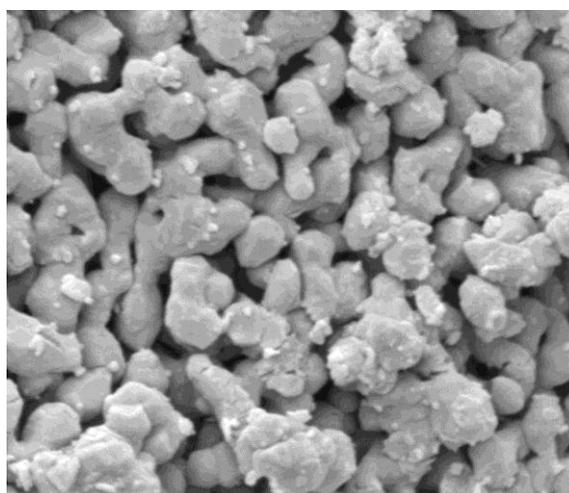
**Fig. 4.** SEM image of commercial CaO

Biodiesel Characterization

FT-IR and ^{1}H-NMR spectrophotometers were used to identify the biodiesel formation. The FT-IR spectra of all biodiesel samples showed a similar pattern. The FT-IR spectrum of biodiesel was different with triglyceride in peak area of 1200 cm^{-1}, which is specified of the functional groups of methoxy (-OCH$_3$) as shown in Figure

5a. In addition, Tariq et al. presented that the formation of biodiesel was recognized in the appearance of peaks at 1435 and 1195 cm^{-1}.[46]　Figure 5b shows the ^{1}H-NMR spectra of both triglyceride and biodiesel. As is clear from that image, the only significant change in the spectra was the appearance of a new singlet peak at 3.6 ppm, which is related to the methoxy group.
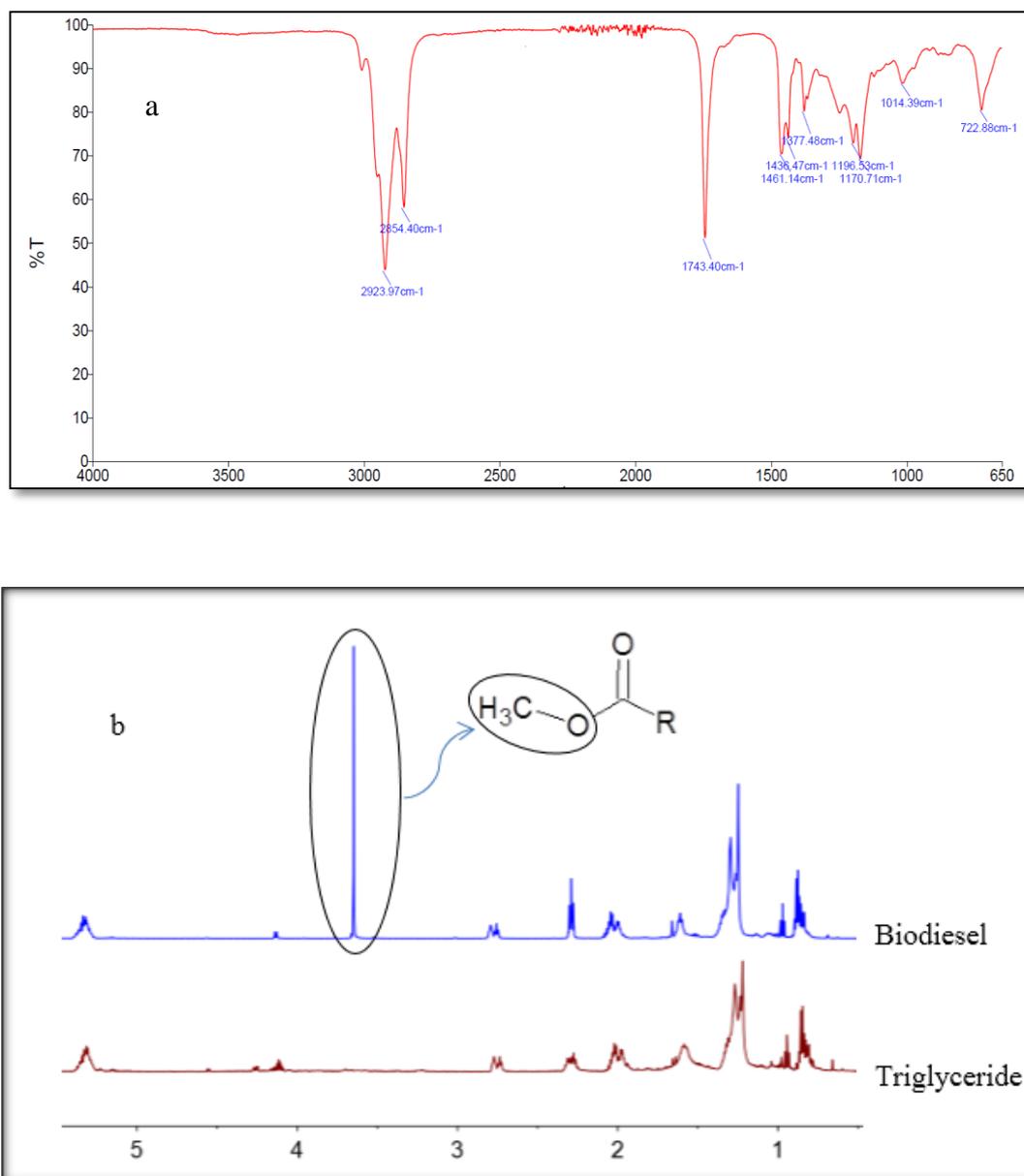
Fig. 5. (a) The FT-IR spectra of biodiesel and (b) ^{1}H-NMR spectra of triglyceride and biodiesel

CONCLUSION

It has been demonstrated that CaO, a heterogeneous catalyst, can be used as a catalyst in in situ transesterification reaction to produce biodiesel. The concentration of biodiesel from palm kernel seed was found to be significantly affected by seed size, reaction time, catalyst weight and volume of methanol. Optimal conditions in this study were approximately < 1 mm seed particle size, a 3 h reaction time, 1 g catalyst weight and 200 mL volume of methanol.

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