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Original Article

Calcium oxide based catalysts for ethanolysis of soybean oil

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Abstract

Transesterification of soybean oil and ethanol catalyzed by calcium oxides prepared from the calcinations of CaO, $Ca(OH)_2$, limestone, and $Ca(OH)_2$/CaO as solid base catalysts was investigated. It was found that the catalytic activities significantly depended upon their base site strengths and their structures. Increases in catalytic performance of CaO could be achieved by loading $Ca(OH)_2$ on CaO and calcinations at a high temperature. The catalytic reaction using a 9:1 molar ratio of ethanol to oil at 70 °C, using CaO loaded with 3.7 wt% $Ca(OH)_2$ exhibited the optimal results, where the conversion of soybean oil reached 96.3% after 10 hrs of the reaction.

Keywords: ethyl ester, calcium hydroxide, calcium oxide, heterogeneous catalyst

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1. Introduction

The decrement of petroleum reserves and the increment of environmental problems have stimulated recent interest in alternative sources for petroleum based fuels. Biodiesel is a renewable energy for diesel engines that is biodegradable, non-toxic and has low emission profiles as compared to petroleum diesel. Biodiesel is usually produced by the transesterification reaction between vegetable oils or animal fat with short chain alcohol such as methanol and ethanol. Methanol, however, is at present mainly produced from natural gas. Methanol vapor is toxic and it does not produce a visible flame when burning and can be absorbed through the skin. Any methanol spill can quickly vaporize and form flammable vapor/air mixtures. On the other hand, ethanol is the renewable alternative fuel because it is made from agricultural products. Ethanol has better solvent properties than methanol for solubility of oil (Issariyakul *et al.*, 2007; Kulkarni *et al.*, 2007). In addition, the use of ethyl ester improves the cold start since its cloud and pour points are lower than those of the methyl ester (Al-Widyan and Al-Shyoukh, 2002; Encinar *et al.*, 2007).

The transesterification can be catalyzed by either homogeneous (acids or bases) or heterogeneous catalysts. The homogeneous catalysts, however, have a problem with the separation of catalysts from the product and the formation of stable emulsion and a large amount of waste water. Alternatively, the heterogeneous catalysts are noncorrosive, environmentally benign, and display fewer disposal problems. Meanwhile, they are more easily separated from the liquid products by filtration and can be developed to give higher activity, selectivity and longer catalyst lifetimes. In the recent years, many kinds of heterogeneous (acids, bases) catalysts have been extensively applied for transesterification process, such as alkaline earth metal oxides, various alkali metal compounds supported on alumina or zeolite. The solid super-acid catalysts of sulfated tin, zirconium oxides and tungstated zirconia were reported for the transesterification of soybean oil with methanol at 200-300°C and the esterification of n-octanoic acid with methanol at 175-200°C with the conversion over 90% (Furuta *et al.*, 2004). A heterogeneous base catalyst, $Na/NaOH/\gamma\text{-}Al_2O_3$ was developed for transesterification of soybean oil with methanol using n-hexane as a co-solvent with the maximal biodiesel yield of 94% (Kim *et*

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al., 2004). Alumina-supported potassium iodide was later on, reported as a solid base catalyst in a heterogeneous manner with methyl ester at conversion yield of 96% (Xie and Li, 2006).

CaO has also been applied as a solid base catalyst because of its high catalytic activity at mild reaction conditions, long catalyst lifetimes and low catalyst cost. The possibility of using nanocrystalline calcium oxides under room-temperature was investigated (Reddy *et al.*, 2006). A solid super base of CaO prepared by the treatment with an ammonium carbonate solution and calcinations at a high temperature was used for the transesterification (Zhu *et al.*, 2006). The sequence of catalytic activity of calcium oxides for transesterification were reported in order of $CaO > Ca(OH)_2 > CaCO_3$. The rapid deactivation of CaO catalysts by water and CO_2 was also mentioned (Kouzu *et al.*, 2008). The alkaline and alkaline-earth metals compounds were used for methanolysis of sunflower oil (Arzamendi *et al.*, 2008). Recently, alkali-doped metal oxide catalysts, $Ca(NO_3)_2/CaO$, $LiNO_3/CaO$, $NaNO_3/CaO$, KNO_3/CaO and $LiNO_3/MgO$ were examined for transesterification of vegetable oils (Granados *et al.*, 2007; Kouzu *et al.*, 2008; MacLeod *et al.*, 2008). Although many developments of new and effective solid catalysts for methanolysis of vegetable oils were established, only few studies have been done on ethanolysis of vegetable oils.

On our preliminary study, it was found that calcined limestone granules exhibited higher catalytic activity for transesterification reactions of soybean oil and ethyl alcohol than the calcined CaO. The X-ray diffraction (XRD) patterns of the calcined limestone indicated the existence of calcium hydroxide on CaO. In order to investigate catalytic property that can simulate the transesterification reaction, CaO catalysts prepared by the calcinations of CaO, $Ca(OH)_2$, $Ca(OH)_2$/CaO and limestone at a high temperature were used for the transesterification. Catalyst characterizations were then examined by means of XRD, BET surface area, transmission electron microscopy, and temperature-programmed desorption of carbon dioxide (CO_2-TPD). The effects of operational parameters, such as a molar ratio of ethanol to oil, a mass ratio of catalyst to oil, reaction time, and type of catalysts on the transesterification were also examined. The results would be of great benefits for the development of CaO catalysts for the ethanolysis of vegetable oils.

2. Experimental

2.1 Materials and catalyst preparation

Soybean oil used in the experiments was obtained from Thanakorn Vegetable Oil Products Co. Ltd. (Samut Prakan, Thailand), which consisted of linoleic acid 55%, oleic acid 23%, palmatic acid 12%, linolenic acid 6%, stearic acid 3%, and traces of other acids. The acid value of the soybean oil is 0.2 mg KOH/1 g oil with 0.1 wt% of water content. Absolute ethanol of 99.9% purity (J.T. Baker, Selangor, Malaysia) was used for the synthesis of biodiesel. CaO and $Ca(OH)_2$ were purchased from Ajax Finechem (New South Wales, Australia). Limestone was obtained from a local cement factory (Saraburi, Thailand). Seven catalyst samples have been prepared for this study.

Sample 1-3 denote the catalysts in forms of calcined CaO, limestone and $Ca(OH)_2$, respectively. 12 grams of these materials were calcined in a muffle furnace at 800°C for 24 hrs without gas purge.

Sample 4-5 denote the catalysts obtained by wetness impregnation method with different concentrations of $Ca(OH)_2$ solution at 3.7 and 9.3 wt%, respectively on CaO support. All samples were dried in an oven at 100°C overnight, and then the solid was calcined in a muffle furnace at 800°C for 24 h without gas purge.

Sample 6-7 denote the catalysts in form of untreated $Ca(OH)_2$ and CaO.

In the further description, the catalysts under the activation treatment by the calcination in air at 800°C for 24 hrs are identified with "*"; for example, CaO* represents CaO under the activation treatment by the calcination in air at 800°C for 24 hrs. The methods for preparing all catalysts in this study are summarized in Table 1.

2.2 Catalyst characterization

X-ray power diffraction (XRD) patterns were recorded using a Bruker D8 Advance X-ray diffractometer (Baden-Württemberg, Germany) with Cu K_a radiation (l = 0.15064 nm)

Table 1. Methods for preparing all catalysts.

Sample No.	Sample Name	Wt% of $Ca(OH)_2$ loading on CaO	Drying		Calcination	
			Temp. (°C)	Time (hrs)	Temp. (°C)	Time (h)
1	CaO*	-	-	-	800	24
2	CaO* from limestone	-	-	-	800	24
3	$Ca(OH)_2$*	-	-	-	800	24
4	[3.7 wt% $Ca(OH)_2$/CaO]*	3.7	100	12	800	24
5	[9.3 wt% $Ca(OH)_2$/CaO]*	9.3	100	12	800	24
6	commercial $Ca(OH)_2$	-	-	-	-	-
7	commercial CaO	-	-	-	-	-

operating at 40 kV and 30 mA. The spectra were scanned at the rate 0.02 °/step from 2θ = 10° to 80°.

The BET surface area, pore size and pore volume were measured by N_2 physisorption at liquid N_2 temperature (-196°C) on a Micromeritics ASAP 2020 automated instruments (Atlanta, USA). 0.3 g of sample was degassed at 150°C under vacuum. After degassing the sample was run at -196°C for 3 hrs.

Transmission electron microscopy (TEM) was performed to study catalyst crystal size and the diffraction pattern using a JEOL JEM-2010 (Tokyo, Japan) transmission electron microscope operated at 200 kV with an optical point to point resolution of 0.23 nm. The sample was dispersed in ethanol prior to the TEM measurement.

Temperature-programmed desorption of carbon dioxide (CO_2-TPD) was used to determine the base properties of catalysts. TPD experiments were carried out using a flow apparatus. The catalyst sample (0.1 g) was treated at its calcination temperature (800°C) in a helium flow for 1 h, and saturated with a pure CO_2 flow (50 mL min^{-1}) after cooling to 100°C. After that, it was purged with the helium at 100°C for 1 h to remove weakly physisorbed CO_2. The TPD of CO_2 was carried out at temperature between 100°C and 800°C under a helium flow (10°C min^{-1}, 30 mL min^{-1}). The areas of desorption profiles were obtained from a Micromeritics ChemiSorb 2750 pulse chemisorption system analyzer (Atlanta, USA). For the broad desorption peak, it was separated into many sub-peaks by using the Fityk program for peak fitting. All areas of sub-peaks were summed to calculate the total amount of base sites.

2.3 Transesterification reaction

The transesterification reactions were carried out in 250 ml one-necked glass flask containing the mixtures of soybean oil/ethanol and 1.38 wt% of catalyst in water bath shaker under stirring (150 rpm) and reaction temperature at 70°C. The samples were taken out from the reaction mixture every 2 hrs. After the sample was centrifuged, it formed two phases. The upper layer was primarily composed of biodiesel, glycerol and excess ethanol, and the lower layer was a mixture of solid catalyst and glycerol. Once the mixture in the upper layer was separated, the biodiesel was purified by washing with warm water to remove glycerol and excess ethanol. Then, all contents were decanted to separate biodiesel from the mixture.

The biodiesel samples were analyzed by gas chromatography (GC) (Shimadzu 14B, Tokyo, Japan) with consist of a column (Rtx 5, 30 m, 0.25 mm ID, 0.25 μm) and flame ionization detector (FID). The parameters for the oven temperature program consisted of: start at 150°C, ramp at 5°C/min to 250°C. The sample for the GC was prepared by adding 0.1 ml of biodiesel sample to 4.9 ml of n-hexane. The sample of 2 μL was injected into column for the analysis. The biodiesel conversion was calculated by the following expression:

$$\text{Conversion} = \frac{\text{consumed oil}}{\text{total oil}} \times 100\%$$

Consumed oil was calculated based on ethyl ester produced, which was determined by GC–FID.

3. Results and Discussion

3.1 Catalyst characterizations

The XRD patterns of commercial CaO, CaO*, commercial $Ca(OH)_2$, $Ca(OH)_2$*, CaO* from limestone and modified CaO* catalysts with different amount of $Ca(OH)_2$ loading are shown in Figure 1. The diffraction peaks at 32.3°, 37.4°, 54.0°, 65.2°, and 67.5° were those of calcium oxide being similar to those from previous reports (Zhu *et al.*, 2006; Granados *et al.*, 2007; Kouzu *et al.*, 2008; Ngamcharussrivichai *et al.*, 2008). The diffraction peaks at 18.1°, 28.8°, 34.1°, 47.1°, and 50.8° in all catalyst series represented calcium hydroxide (Granados *et al.*, 2007). No peak of calcium carbonate was observed in any of these XRD patterns. $Ca(OH)_2$ is an ionic solid that is slightly soluble in water. By loading $Ca(OH)_2$, which was dispersed in water on CaO particles, the CaO particles was soaked in a saturated $Ca(OH)_2$ aqueous solution and was covered with a thin layer of $Ca(OH)_2$. It was suggested that due to the interaction of CaO and $Ca(OH)_2$ in the granular, it was relatively more difficult to oxidize $Ca(OH)_2$. The XRD result indicated the existence of $Ca(OH)_2$ dispersed on CaO catalysts prepared by the calcinations of limestone and $Ca(OH)_2$/CaO, but not the one from $Ca(OH)_2$. However, the $Ca(OH)_2$ peaks were considerably smaller than those of the CaO. Therefore, in these particles, $Ca(OH)_2$ might not be completely decomposed to CaO.

The BET surface area, pore volume, average pore diameter, crystallite size and base sites of all catalysts are presented in Table 2. The BET surface areas of the [$Ca(OH)_2$/CaO]* were 6.2-7.4 m^2/g, which was about 3 folds that of CaO* owing to the deposit of $Ca(OH)_2$ on the surface areas. Since the pore volume of them was all less than 0.03 cm^3/g, the materials appeared to have nonporous structures. The

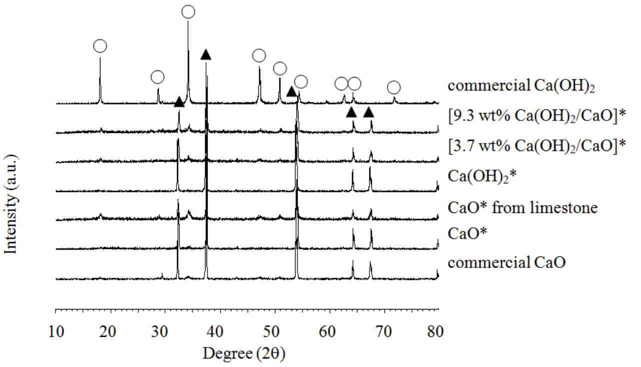

Figure 1. XRD patterns of the employed catalysts. [CaO (▲), $Ca(OH)_2$ (○)]

Table 2. Comparison of BET surface area, pore volume, average pore diameter, crystallite size, and base sites of various types of catalysts. The symbol'*'indicates the catalysts under the activation treatment by the calcination at 800°C in air for 24 hrs.

Catalyst	Total surface area[a] (m^2/g)	Pore volume[a] (cm^3/g)	Average pore diameter[a] (nm)	Crystallite size[b] (nm) CaO	Crystallite size[b] (nm) $Ca(OH)_2$	Base sites[c] (mmole/g)
CaO*	2.4	0.006	10	39	0	1,129
CaO* from limestone	5.9	0.016	11	33	15	2,966
$Ca(OH)_2$*	6.2	0.019	13	36	0	2,868
[3.7 wt% $Ca(OH)_2$/CaO]*	7.4	0.027	14	37	19	2,590
[9.3 wt% $Ca(OH)_2$/CaO]*	6.2	0.021	14	38	40	3,145
commercial $Ca(OH)_2$	5.5	0.020	15	0	36	10,611

[a] Calculated by BET method.
[b] Determined by XRD patterns using Scherrer's equation.
[c] Measured by CO_2 -TPD.

detected pore size and pore volume should belong to the interparticle voids. From the previous reports, the BET surface areas of CaO were 6-13 m^2/g, (Zhu *et al.*, 2006; Arzamendi *et al.*, 2008; Kouzu *et al.*, 2008) whereas, those of $CaCO_3$ were 0.6-10 m^2/g (Arzamendi *et al.*, 2008; Kouzu *et al.*, 2008) and that of $Ca(OH)_2$ was 16 m^2/g (Kouzu *et al.*, 2008). The variations in the values could be according to individual differences in material source and treatment.

The TEM micrographs of all catalysts are demonstrated in Figure 2. The TEM images showed that all of the applied catalysts were in sizes of 30-300 nm. It was found that the crystal sizes of CaO* and $Ca(OH)_2$* were considerably larger than the untreated ones and the crystal size of [$Ca(OH)_2$/CaO]* was much larger than that of CaO*. After loading calcium hydroxide on CaO, the morphologies of the particle became similar to the calcined CaO* from limestone

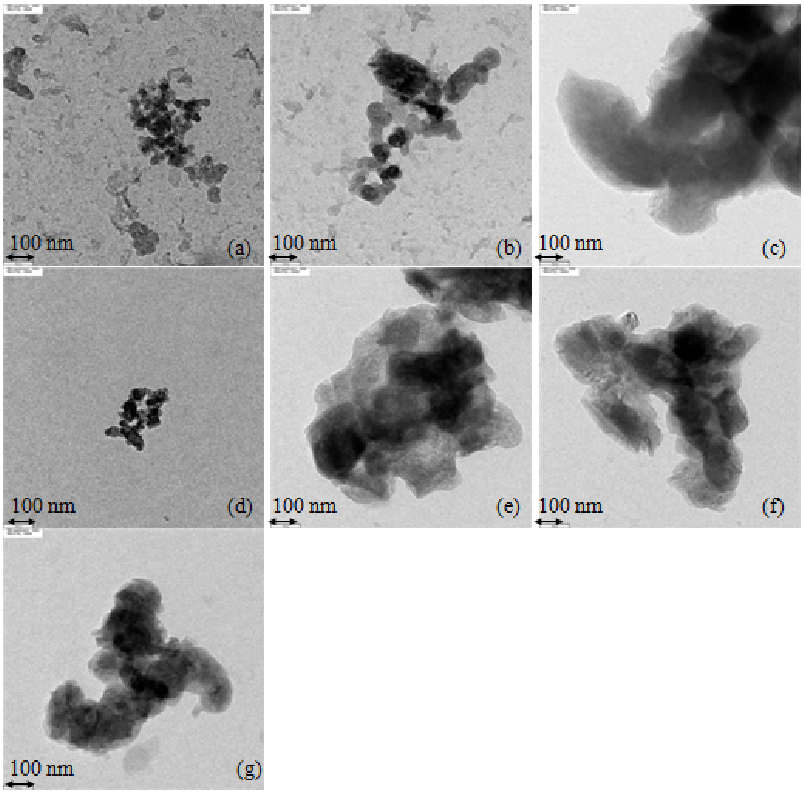

Figure 2. TEM micrographs of catalyst : (a) commercial CaO, (b) CaO*, (c) CaO* from limestone, (d) commercial $Ca(OH)_2$, (e) $Ca(OH)_2$*, (f) [3.7 wt% $Ca(OH)_2$/CaO]*, (g) [9.3 wt% $Ca(OH)_2$/CaO]*.

and $Ca(OH)_2$*. The crystallite sizes determined by XRD patterns of CaO* from limestone, $Ca(OH)_2$* and [$Ca(OH)_2$/CaO]* were all in the range of 30-40 nm. When compared the crystallite sizes calculated from XRD line broadening with those obtained from TEM micrographs, it was found that the crystallite sizes obtained from TEM were much larger due to the accumulation of single crystals.

The base properties of the catalysts could be measured by using CO_2-TPD techniques (Albuquerque *et al.*, 2007; Kouzu *et al.*, 2008). The CO_2-TPD profiles of catalysts are shown in Figure 3. The amounts of base sites summarized in Table 2 are calculated from the area below the curve of TPD profiles. The characteristic peaks of these profiles are assigned to their desorption temperatures indicating the strength of basic sites. For CO_2-TPD profiles (Figure 3), the CO_2 desorption peaks at high temperature (500-650°C) (Albuquerque *et al.*, 2007) appear in all profiles, suggesting that all catalysts have strong base sites. The order of base sites of the catalysts after calcinations are: CaO* < [3.7 wt% $Ca(OH)_2$/CaO]* < $Ca(OH)_2$* < CaO* from limestone < [9.3 wt% $Ca(OH)_2$/CaO]*. The basicity of [$Ca(OH)_2$/CaO]* increased with the amount of $Ca(OH)_2$ loading. The untreated $Ca(OH)_2$ was more base sites than its oxide (about 3.7 folds). The basic sites could be either Bronsted or Lewis bases, which could not be differentiated by CO_2 TPD technique.

3.2 Effect of parameters on biodiesel yield

3.2.1 Molar ratio of ethanol to oil

The effects of molar ratio of methanol to oil on transesterification were presented previously (Xie and Li, 2006; Zhu *et al.*, 2006; Yang and Xie, 2007; Liu *et al.*, 2008). Similarly, the conversion of ethyl ester could be improved by introducing excess amounts of ethanol to shift the equilibrium to the right-hand side. In order to determine the effect of molar ratio of ethanol to oil on the reaction rate without interference by mass transfer, the transesterification was performed by using CaO* at low concentration (1.4 wt% of catalyst in oil). The result as shown in Figure 4 indicated that the molar ratio of ethanol to oil has a significant impact on the conversion yield. After 21 hrs at the reaction temperature of 70°C, the ethyl ester yield increased from 7.0% to 14.7% with the increase of the molar ratio from 3:1 to 9:1. However, the conversions were steady when the ratio further increased up to 12:1 and 15:1 and comparatively decreased when the ratio was up to 18:1. From the previous reports, high excessive amounts of ethanol could cause a negative effect on the conversion rate as it diluted the concentration of catalyst in the system and might cause the catalyst deactivation (Modi *et al.*, 2007; Liu *et al.*, 2008). In this system, the optimal molar ratio of ethanol to soybean oil was 9:1, which corresponded to three times of the stoichiometry.

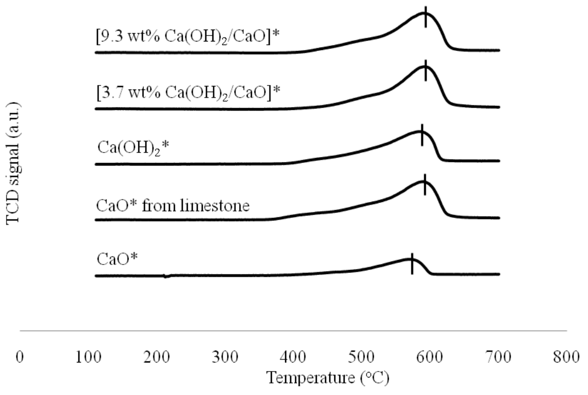

Figure 3. CO_2 -TPD profiles of catalysts.

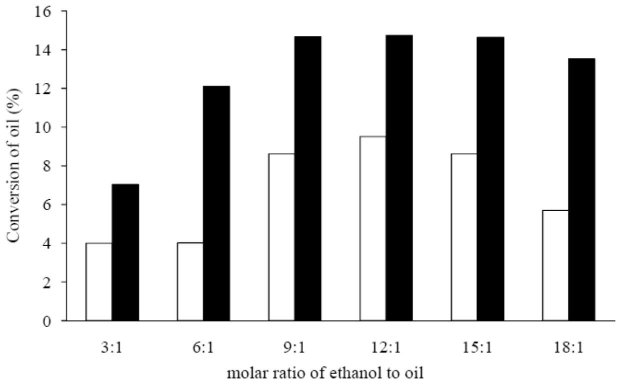

Figure 4. Effect of molar ratio of ethanol to oil on the conversion of soybean oil using 1.38 wt% of CaO*, reaction temperature at 70 °C and reaction time of 10 hrs (☐) and 21 hrs (■).

3.2.2 Mass ratio of catalyst to oil

In the case of homogeneous catalysts, it has been reported that the amount of catalysts in the system has a strong influence on the conversion to methyl esters (Ma and Hannab, 1999; Yang and Xie, 2007). The effect of CaO* concentration in the range of 1.4%-34.5%wt of oil was investigated at a 9:1 molar ratio of ethanol to oil at the reaction temperature of 70°C for 21 hrs. As demonstrated in Figure 5, the conversion of soybean oil to ethyl ester was strongly enhanced with the increase of CaO* up to 13.8% wt. The transesterification reached a steady state with the biodiesel conversion of 64.8% after 10 hrs of the reaction time. The effect of catalyst concentration on the conversion of oil was negligible when the mass ratio of CaO* to oil was increased above 13.8 wt%. As a result of increasing catalyst concentration, the mixture of catalyst and reactants could become too viscous leading to a mixing problem and a demand of higher power consumption for enough stirring. On the other hand, when the catalyst loading amount was not enough, the maximum production yield could not be reached (Kim *et al.*, 2004). The external mass-transfer resistance becomes more important at high amount of catalyst. It was found that, the optimal catalyst concentration was 13.8 %wt of oil.

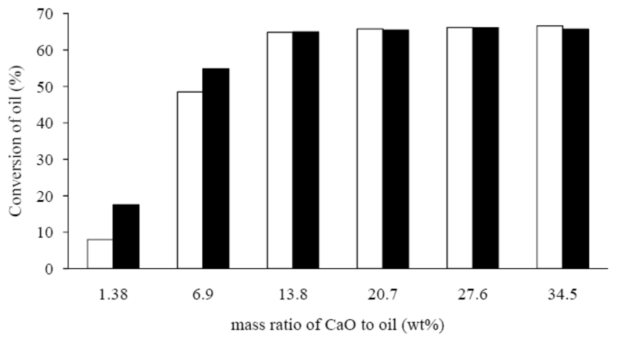

Figure 5. Effect of mass ratio of CaO* to oil on the conversion of soybean oil using molar ratio of ethanol to oil of 9:1, reaction temperature at 70°C and reaction time of 10 hrs (☐) and 21 hrs (■).

3.2.3 Reaction time

The optimum reaction time for the biodiesel production was determined by performing reactions up to 10 hrs. Compared to a homogeneous reaction, the transesterification using a heterogeneous reaction presented relatively slow reaction rate (Zhu *et al.*, 2006; Liu *et al.*, 2008). The experimental results as reported in Figure 6 indicated that the conversion of soybean oil to ethyl ester was very low in the first 4 hrs, however, the conversion increased rapidly during the reaction time of 4-8 hrs. The conversion remained almost constant or gradually increased as a result of a nearly equilibrium conversion after 8 hrs.

3.2.4 Type of catalysts

The set of CaO* from different preparation and the CaO loaded with $Ca(OH)_2$ were examined for the transesterification at 9:1 ethanol to soybean oil molar ratio, 13.8 wt% of catalyst in water bath shaker under stirring (150 rpm) and reaction temperature at 70°C. It was previously reported that calcium hydroxide was much less active in the transesterification of oil with methanol than calcium oxide (Kouzu *et al.*, 2008). In this study (Figure 6), the catalytic activities of catalysts were in the following order: [3.7wt% $Ca(OH)_2$/CaO]* > [9.3wt% $Ca(OH)_2$/CaO]* > $Ca(OH)_2$* > CaO* from limestone > CaO*> commercial $Ca(OH)_2$. It was found that [3.7 wt% $Ca(OH)_2$/CaO]* showed the highest catalytic activity among other samples and obtained the highest ethyl ester conversion at 96.3% after 10 hrs, whereas the untreated $Ca(OH)_2$ showed the lowest catalytic activity. The untreated CaO also exhibited a low activity (not shown). It has been previously reported that the active surface sites of CaO could possibly poisoned by the atmospheric H_2O and CO_2, and it catalytic activity could be improved by activation treatment at high temperature ($\geq$ 700 °C) (Granados *et al.*, 2007; Kouzu *et al.*, 2008). In this study, the catalytic activity could also be improved by loading $Ca(OH)_2$ on CaO to form basic sites on CaO*. It is important to note that the characteristic similarities among the most active catalysts in this study ([$Ca(OH)_2$/CaO]* and $Ca(OH)_2$*) are: base sites of 2,590-3,145 µmole/g with crystal size between 36 to 38 nm.

3.2.5 Amount of $Ca(OH)_2$ loading

The effect of the amount of $Ca(OH)_2$ loading on CaO on the catalytic activity of the transesterification is shown in Table 3. It was demonstrated that the conversion was over 90% with the use of the calcined CaO loading with 0.9-4.6 wt% $Ca(OH)_2$. Although the catalytic activity was extremely attractive by alkalinity, however, further increasing in the amount of loaded $Ca(OH)_2$ beyond 5 wt%, led to a decrease in the ethyl ester yield. It could be possibly explained that the excessive load of $Ca(OH)_2$ could cover the surface area, and thus cause the decreased catalytic activity. When the

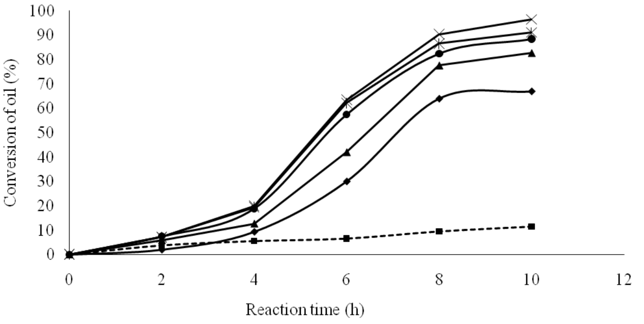

Figure 6. Effect of the reaction time on the conversion of soybean oil using 13.8 wt% of catalyst, molar ratio of ethanol to oil of 9:1, reaction temperature at 70°C: commercial $Ca(OH)_2$, (■); CaO*,(♦); CaO* from limestone, (▲); $Ca(OH)_2$*, (●); [9.3 wt% $Ca(OH)_2$/CaO]*, (*); [3.7 wt% $Ca(OH)_2$/CaO]*, (×).

Table 3. Effect of the amount of $Ca(OH)_2$ loading on CaO on the conversion of soybean oil using 13.8 wt% of catalyst, molar ratio of ethanol to oil of 9:1, reaction temperature at 70°C and reaction time of 10 hrs.

	The amount of $Ca(OH)_2$ loading on CaO (wt%)					
	0	0.9	2.3	3.7	4.6	9.3
Conversion of oil (%)	67.8	93.7	96.2	96.3	95.7	88.9

active sites are inaccessible to incoming reactants, it is accountable for the decrease in the conversion. The highest ethyl ester conversion of 96.3% was obtained after 10 hrs of the reaction at 70 °C with the use of [3.7 wt% $Ca(OH)_2/CaO$]* as the catalyst.

4. Conclusion

For developing a process of ethyl ester production, the present study has been focused on the use of solid base catalysts prepared by the calcinations of CaO, $Ca(OH)_2$, limestone and $Ca(OH)_2/CaO$ for the transesterification of soybean oil. The increase in CaO* catalytic performance was achieved by loading $Ca(OH)_2$ on CaO. The ethanolysis activities of the applied catalysts were in the following order: [3.7 wt% $Ca(OH)_2/CaO$]* > [9.3wt% $Ca(OH)_2/CaO$]* > $Ca(OH)_2$* > CaO* from limestone > CaO* > commercial $Ca(OH)_2$. The catalytic activity was dependent upon their base site strength and their structure. The maximum ethyl ester conversion at 96.3% was obtained after 10 hrs of the reaction at 70°C using [3.7 wt% $Ca(OH)_2/CaO$]* as the catalyst at a 9:1 molar ratio of ethanol to oil. To our best knowledge, this is the first report for the transesterification of vegetable oil and ethanol catalyzed by $Ca(OH)_2$-doped CaO.

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