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Transesterification of Palm Oil Using Nano-Calcium Oxide as a Solid Base Catalyst

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Abstract: Fatty acid methyl esters (biodiesel) can be produced from the transesterification reaction of vegetables oil with alcohols. In this paper, the comparison of nano-CaO as transesterification catalyst with bulk CaO was studied. The catalysts were characterized using BET, XRD and TEM. A study for optimizing the reaction conditions for the transesterification of palm oil was performed. In this work, the transesterification reaction was studied on four important parameters namely type of catalyst, methanol:oil molar ratio, catalyst wt% and reaction time. From the study it was found that the optimum reaction was at 65 °C, molar ratio oil to methanol of 1:15, catalyst weight percent of 2.5% and reaction time of 2.5 hours with 94% and 90% conversions for nano-CaO and bulk CaO, respectively. The higher conversion also indicated that the nano-CaO catalyst gave stronger activity and better selectivity due to the relatively greater surface area hence higher contact surface with the reactants. Furthermore, the formation of soap and emulsion from the nano-CaO catalysed reaction found to be lower than the bulk catalyst. The biodiesel produced was washed by using citric acid to remove any soap and emulsion contained in the mixture.

Key words: Transesterification · Nano-calcium oxide · Bulk calcium oxide · Fatty acid methyl esters

INTRODUCTION

Due to the fact that the supply of fossil fuels is limited while energy demand continues to rise, research has been directed towards alternative renewable fuels is receiving increasing attention around the world. Biodiesel also known as fatty acids methyl ester (FAME) has the potential as fuels substitution, characterized by excellent properties as diesel engine fuels and thus can be used in compression-ignition (diesel) engines with hardly any modifications necessary [1]. It can be produced from transesterification of vegetable oil catalyzed by bases, acids and enzymes [2-4].

One mole of triglyceride requires three moles of alcohol to produce three moles of fatty acids methyl ester and one mole of glycerol. The transesterification process occurred as shown in Fig. 1. The stoichiometric equation for the reaction is 3:1 alcohol to triglyceride, however in practice this is usually increased to 6:1 or more to increase the product yield. Whether it is a base, acid or enzyme type, the catalyst that is selected to accelerate the reaction has become one of the main contributors where low temperature operations are the most economical.

Calcium oxide (CaO) is one of the well researched heterogeneous catalyst as it has a higher basicity, lower price, non-corrosive, economically benign, lower solubility and easier to handle than homogeneous base catalysts [5,6]. These advantages together with it being safe to the ecosystem made it an interesting choice in the catalysis research.

In this paper, the comparison activity of nano calcium oxide (nano-CaO) and bulk CaO uses as the transesterification catalyst was studied. To achieve high activity, nano-CaO was activated by pretreatment with methanol before it is used as a transesterification catalyst. During the pretreatment stage, a small amount of CaO was converted into $Ca(OCH_3)_2$. It functions as an initiating reagent for the transesterification reaction and

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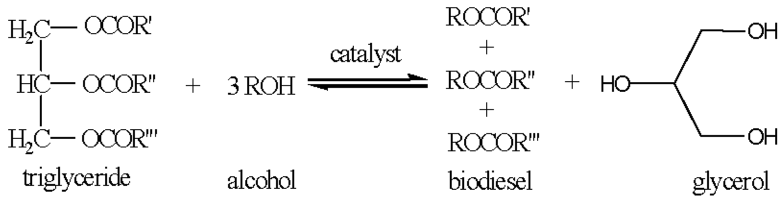

Fig. 1: Transesterification process to produce alkyl esters and glycerol as by product

produces glycerin as a by-product [7]. Subsequently, the calcium-glycerol complex was formed due to the reaction of CaO with glycerol.

MATERIALS AND METHODS

Synthesis of Catalyst: Bulk calcium oxide was synthesized by calcinations of calcium carbonate ($CaCO_3$) at 700 °C for 2 hours. Nano-calcium oxide was purchased from Sigma Aldrich.

Catalyst Characterization: Surface area and pore size of each sample were determined using an instrument type Micromeritics ASAP 2010 and nitrogen physical adsorption at liquid nitrogen temperature 77 K. The BET surface area was then automatically determined using Micromeritics ASAP 2010 software. XRD technique was used to determine the shape of the structure and the crystallinity of materials. XRD diffractogram for the sample analyses employed the diffractometer at the 2θ angle ranging from 20° to 80° and wavelenght, λ=0.154nm. TEM photomicrographs were obtained using Philips 201 Transmission Electron Microscope. The pictures were taken at 100 kV. The samples were ultrasonicated for 20 minutes before they were transferred to the membrane Cu grid coated carbon polymer micro grid (mesh 400). This technique was used to determine the morphology and particle sizes.

Transesterification: Methanol and RBD palm olein (Seri Murni Brand) were purchased from Sigma Aldrich and a local grocery shop, respectively. Characterization of the palm olein properties was shown in Table 1. These two reactants were mixed at a molar ratio of 15:1 over bulk and nano-calcium oxide catalysts. The transesterification process was conducted in a batch reactor that consisted of a 3-neck flask, a condenser and a thermometer at reaction temperature 65 °C. In this work, the transesterification reaction was studied on four important parameters: type of catalyst, methanol:oil ratio, percent mass ratio of catalyst and reaction time. Glycerol yielded from the transesterification was separated from biodiesel by using separator funnel and filtered. Unreacted methanol was removed from crude glycerol using evaporation method. The transesterification products, fatty acid methyl ester (FAME) and glycerol were analyzed using HPLC. The catalysts were regenerated by washing them with hexane and filtered. After that, they were dried at 110 °C before use in the next reaction.

RESULTS AND DISCUSSIONS

Catalyst Characterization: From BET analysis, bulk calcium oxide has a surface area of 15.10m^2/g while the nano calcium oxide has a surface area of 85.0 m^2/g. This could be a good indication of the catalytic performance for the nano-CaO having nearly six times the surface area of the bulk CaO.

From XRD patterns shown in Fig. 2, the bulk CaO showed typical diffraction peaks at 2θ= 28.63°, 34.22°, 47.10°, 50.78°, 54.34°, 62.64°, 64.45° and 71.07°. Nano-CaO showed diffraction peaks at 2θ= 28.65°, 34.25°, 47.15°, 50.80°, 54.29°, 62.57°, 64.48° and 71.75°. Generally, diffractogram for bulk CaO peaks were similar to nano-CaO peaks. It is also important to note that the nano-CaO peaks were broader and wider with lower intensity compared to the bulk CaO. This was due to the lower crystallinity in nano-CaO structure. Nevertheless, the blunt peaks detected in nano-CaO sample indicated a similar sharp peaks trend of the bulk CaO sample. No peaks from any other phases of CaO were observed and this XRD pattern was in agreement with what has been reported by Olga *et al.* [8].

Table 1: Properties of the palm olein

Properties	Palm oil
Density at 27 °C (g/Ml^{-1})	0.923
Viscosity (cp)	68.0
Free fatty acid (%)	1.128

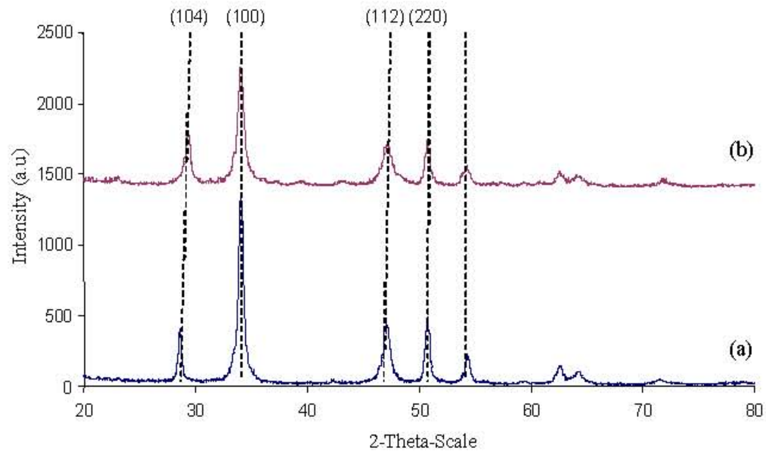

Fig. 2: XRD patterns for (a) bulk CaO and (b) nano-CaO

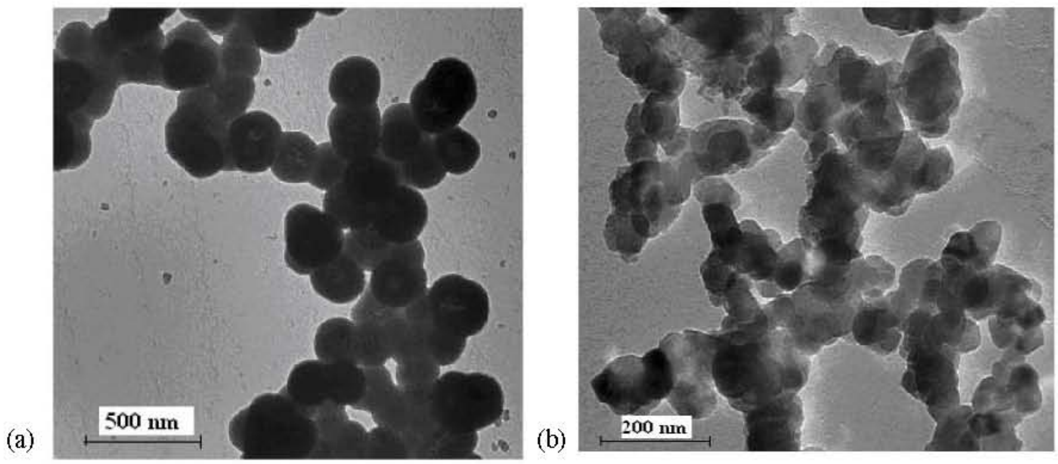

Fig. 3: TEM micrograph of catalyst a) bulk CaO and b) nano-CaO at magnification of 10000x and 35000x, respectively

The TEM of bulk and nano-particles CaO was illustrated in Fig. 3. From Fig. 3, CaO bulk and nano-particles were well dispersed in alcohol at mean size particles of 200 nm and 45 nm, respectively.

Transesterification: Transesterification reaction between triglyceride with methanol had been performed using the procedures as described in materials and methods section. The orthogonal test result of the above reaction is given in Table 2.

Orthogonal Test: The orthogonal test of several reactions with three parameters depicted the catalytic activity of nano-CaO in transesterification as illustrated in Table 2. This technique was used in the interpretation the influential parameters in the transesterification reaction. It was shown that weight percent of the catalyst to oil was the more dominant parameter followed by the molar ratio oil to methanol and the reaction time. The optimum condition for this reaction was as follows: molar ratio oil to methanol of 1:15, catalyst weight (%) of 2.5% and reaction time of 2.5 hours with conversion of 94%.

From the reaction, the three main parameters were used to determine the catalytic activity for bulk CaO and nanopowder CaO. Weight percent catalyst to oil has the most profound effect over the reaction time as shown in Fig. 4. It was found that at 2.5wt% catalyst gave the highest conversion of 94% at 2.5 hours compared to the other wt% catalyst. The effect of percent mass ratio catalyst to oil of bulk CaO and nanopowder CaO on percent conversion were also depicted in Fig. 5. By fixing the 2.5wt% catalyst for the reaction of molar ratio oil to methanol at one to fifteen, higher conversion could well be achieved. After 2.5 hours of the reaction, it was found that nano-CaO reached relatively higher conversion compared to the bulk CaO at 2.5wt% catalyst.

Table 2: Orthogonal test results of transesterification of palm oil using bulk CaO and nano-CaO as a solid base catalyst

Experiment	Oil: MeOH (mol ratio)	Catalyst (wt%)	Reaction Time (h)	Bulk CaO conversion (%)	Nano-CaOconversion(%)
1	1:15	1.0	2	75	84
2	1:15	1.0	2.5	82	90
3	1:15	1.5	2	84	88
4	1:15	2.0	2	85	90
5	1:15	2.5	2.5	90	94
6	1:15	2.0	2.5	86	93
7	1:12	1.0	1.5	72	78
8	1:12	2.0	2	84	90
9	1:12	1.5	2	80	85
10	1:12	2.5	2	87	91
11	1:12	1.5	2.5	84	90
12	1:10	1.0	2	80	82
13	1:10	1.5	1.5	77	80
14	1:10	2.0	2	84	88
15	1:10	2.0	2.5	86	90
16	1:10	2.5	2.5	88	92
k1	62.07	61.43	60.97		
k2	60.56	61.67	61.07		
k3	61.73	62.12	62.24		
k4		60.31			
R	1.51	1.81	1.27		
Rank	2	1	3		
Optimum	1:15	2.5%	2.5 h		

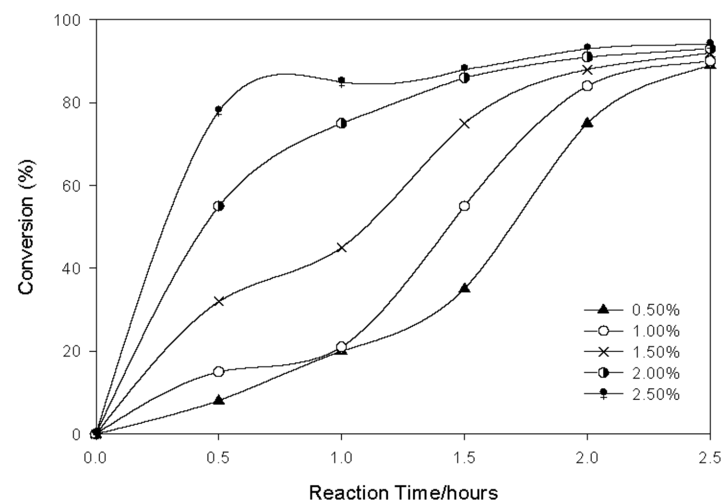

Fig. 4: Effect of percent mass ratio catalyst (nan0-CaO) to oil (%) and reaction time (hours) of nano-CaO to oil on percent conversion where molar ratio oil to methanol: 1:15 and reaction temperature: 65 °C

The former catalyst performance was also investigated at three different molar ratio of oil to methanol as shown in Table 2 over a range of wt% catalyst where the optimum conditions aforementioned prevailed yet again.

On the product treatment, once the biodiesel was separated from the other products and washed, some emulsion was formed. This was due to the reaction of the catalyst and the glycerol that still existed in biodiesel. When most of the triglyceride has been converted to biodiesel, less glycerol was produced. Subsequently, only a smaller amount of the emulsion formed in biodiesel. In order to remove the emulsion, a few drops of citric acid were added.

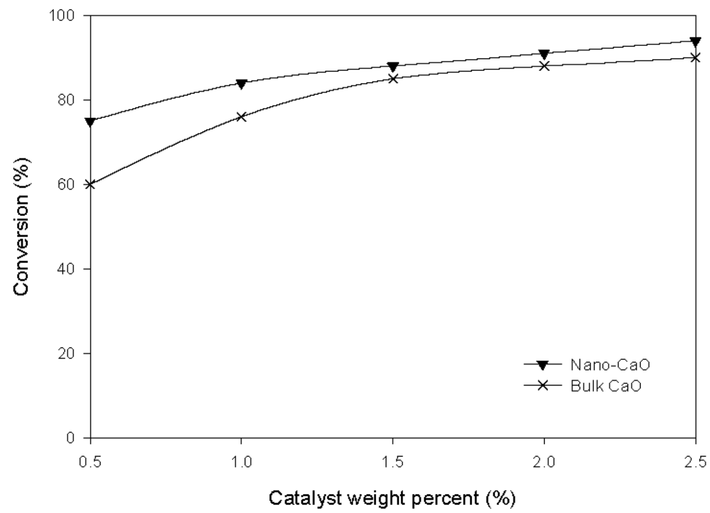

Fig. 5: Effect of percent mass ratio catalyst to oil (%) of bulk CaO and nano-CaO on percent conversion where molar ratio oil to methanol: 1:15, reaction time: 2 hours and reaction temperature: 65 °C

Table 3: Quality of biodiesel and glycerol

Properties	Value	Standard Test method
Biodiesel:		
Acid value (mg/KOH g^{-1})	0.30	EN 14104/14214
Density at 15 °C	0.892	EN ISO 3675
Viscosity at 40 °C	4.32	EN ISO 3104
Glycerol:		
Acid value (mg/KOH g^{-1})	0.62	ASTM D 1093-98
Density at 15 °C	1.23	EN 14104/14214
Viscosity at 40 °C	50.2	EN 14104/14214
Heat of combustion (cal/g)	3820.2	ASTM D0240-02

Characterization of Products: The products of transesterification were separated and characterized using various standard test methods such as European Standard test method and American Standard Test method (ASTM). The properties of biodiesel and the glycerol as a by-product included acid value, viscosity, density and heat of combustion. Characterization of transesterification products was shown in Table 3.

CONCLUSION

The optimum conditions for reaction were found to be as follows: molar ratio oil to MeOH (1:15), catalyst wt % (2.5%), reaction time (2.5h). Biodiesel conversion of 94% and 90% over nano-CaO and bulk CaO have been achieved at the same optimum condition. Another important advantage of using nano-CaO was that it contributed less emulsion than bulk CaO which can be removed by adding citric acid.

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