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Production of Biodiesel from Used Vegetable Oil By Using Calcium Oxide Catalyst

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***Abstract*—This research studies the production of biodiesel from used vegetable oil using calcium oxide catalyst from shell. The shell was calcined at 900 °C for 2 hours. Calcium carbonate was changed the structure to calcium oxide for the transesterification catalyst. XRD and FTIR were used to investigate the catalyst structure. Used vegetable oil was determined the free fatty acid before study. The result found that the free fatty acid was less than 2%. This suitable oil for use in transesterification could produce 95.94% of biodiesel by using shell catalyst at 65 °C, 6g of methanol, 5% (w/w) of catalyst and 3 hours of the reaction time.**

***Keywords*— Biodiesel, Calcium Oxide, Transesterification**

I. INTRODUCTION

Today the rising demand of petroleum products, the decreasing of mineral diesel fuel resources and petroleum prices encouraged the researcher 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 as potential low priced biodiesel sources. In Phetchabun, a province of Thailand, has many restaurants that took the vegetable or fat oil for cooking. Used oil should not to use for cooking again that the main objective in this study used the used vegetable oil as a raw material for transesterification.

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 [2].

Shell is calcium carbonate as a main structure. That can calcined to obtain the calcium oxide as a heterogeneous catalyst. The calcium oxide from shell is nontoxic material, cheap, environmentally friendly and commercially available that makes it suitable active base catalyst for biodiesel production. In addition, Phetchabun province has shell in many water resources. Previously, Lui *et al.*[3] studied biodiesel production from soybean oil using CaO as a solid base catalyst. The transesterification reaction was proposed and the separate effects of the molar ratio of methanol to oil, reaction temperature, mass ratio of catalyst to oil and water content were studied. The experimental results showed that a 12:1 molar ratio of methanol to oil, addition of 8% CaO catalyst, 65°C reaction temperature and 2.03% water content in methanol gave the best results, and the biodiesel yield exceeded 95% at 3 h. Viriya-empikul *et al.*[4] also studied biodiesel production using the solid oxide catalysts derived from waste shells of egg, golden apple snail, and meretrix venus from transesterification of palm olein oil. The shell materials were calcined in air at 800 °C with optimum time of 2-4 h to transform calcium species in the shells into active CaO catalysts. All catalysts showed the high biodiesel production activity over 90% fatty acid methyl ester (FAME) in 2 h, whilst the eggshell-derived catalyst showed comparable activity to the one derived from commercial $CaCO_3$. The catalytic activity was in accordance with the surface area of Ca content in the catalysts.

So, in this study, we calcined calcium oxide from shell as catalyst and characterized by XRD and ATR-FTIR techniques. Parameters that influenced in the transesterification reaction (methanol to oil molar ratio, catalyst concentration and reaction time) were investigated. Moreover, this study want to propagate to people in Phetchabun province who can produce the biodiesel by using heterogeneous catalyst with homemade biodiesel kit replace homogeneous catalyst.

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II. EXPERIMENTAL

A. Materials and Instrument

Used vegetable oil was collected from Phetchabun province (Thailand). Shell was obtained from water resource in Phetchabun Province (Thailand). Analytical grade methanol, ethanol, sodium hydroxide were purchased from Merck (Germany).

B. Oil Preparation

Used vegetable oil was collected, filtered and dried in hot air oven at 105 °C, 5 h for evaluate moisture content before put in the bottle. The fatty acid profile of used vegetable oil was determined by gas chromatography utilizing an Agilent Technologies 7890 gas chromatograph equipped with flame ionization detector and column SP-2560 (100 m x 0.25 mm x 0.20 µm) column. The 0.8147±0.0245% of free fatty acid (FFA) content of used vegetable oil that not necessitated acid pretreatment before transesterification reaction.

C. Preparation of Cacium Oxide Catalyst

Shell was ground manually using mortar and pestle and passed through 60 mesh screen to obtain fine powder The Shell as a calcium carbonate powder was further subjected to heat treatment in furnace at 900 °C for 2 h. The XRD and ATR-FTIR techniques were used to investigate the catalyst phase

D. Characterization of Catalyst

XRD was performed to examine the constituents of the synthesized catalyst on Panalytical/Expert diffractometer, USA with Cu kα radiation. The analysis was made over a 2θ range from 5°-50°. Measurement of IR spectrum was performed using attenuated total reflection fourier transform-infrared (ATR-FTIR) on Perkin Elmer spectrum two 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 500-4000 cm^{-1}.

E. Transesterification Reaction

The transestrification 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 °C. The reaction procedure was follows: first, the catalyst was dispersed in methanol under magnetic stirring. Then, the used vegetable oil was added into the mixture and heated by hotplate. After the reaction, calcium oxide catalyst was separated by centrifugation and the excess methanol was distilled off under vacuum evaporator. After removal of the glycerol layer, the biodiesel was investigated the %yield by calculation. Biodiesel was further characterized for %FFA and density properties.

III. RESULTS AND DISCUSSION

A. Properties of Used Oil

The %FFA of used vegetable oil was found to be 0.8147± 0.0245%. The oleic acid (C18:1) was a major fatty acid composition.

B. Characterization of Calcium Oxide Catalyst

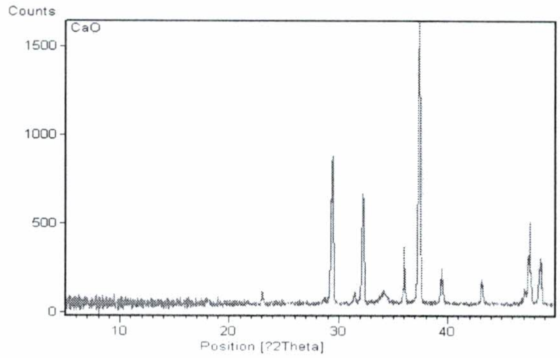

Figure 1. XRD patterns of calcined calcium oxide

The XRD patterns of the calcium oxide obtained after calcination at 900 °C for 2 h that was removed the impurities ($CaCO_3$ and $Ca(OH)_2$) from shell. The obvious two diffraction peaks at 2θ values of 32° and 37° in Fig. 1 was attributed to calcium oxide.

From Figure 1, the calcium carbonate and calcium hydroxide showed peaks at 2θ values of 29° and 18°, 28°, 34°, respectively. Because the calcined calcium oxide could be easily to absorb moisture.

The ATR-FTIR spectrum confirmed functional groups on calcined calcium oxide as shown in Fig. 2.

Figure 2 FTIR spectrum of calcined calcium oxide

The distinct peak not observed at around 1,600-1,700 cm^{-1} was assigned to -C-O stretching vibration of CO_3 in $CaCO_3$ structure. So, this technique could be confirm $CaCO_3$ phase change to CaO after calcination.

C. Transesterification Results

Parameters influenced in the transesterification reaction of used oil to yield biodiesel (FAME) were methanol to oil molar ratio, catalyst concentration and reaction time.

1) Effect of methanol to oil molar ratio

In this study, an excess of methanol was used in order to obtain a higher biodiesel yield. The results were illustrated in Fig 3, which indicated the equilibrium biodiesel yields were about 77.12% at 3 h of reaction and 3% wt of catalyst under methanol 6 g. Then, the reaction rate decreased with the increasing of the molar ratio because the catalyst content decreased to result in a hindrance for the access of triglyceride molecules to active sites [5].

2) Effect of catalyst concentration

A CaO catalyst possessing stronger basic sites than $CaCO_3$ should exhibit high activity. In Fig. 4, the biodiesel yield (%) slightly increased with increasing the catalyst concentration from 1.0 to 5.0 %wt. After that, the FAME (%) slightly decreased from 7.0 to 9.0 %wt. Increasing concentration of catalyst made a slurry mixture of catalyst and reactant that resulted in mixture problem [5]. The catalyst concentration at 5%wt was selected that gave 95.94% of biodiesel yield.

3) Effect of reaction time

Fig. 5 showed the influence of reaction time at 2 to 4.5 h. From the result obtained, The biodiesel yield (%) slightly increased with increasing the reaction time from 2 to 3 h. The biodiesel yield (%) gradually decreased from 3 to 4.5 h. The reversible reaction in transesterification reaction influenced on this effect [6]. The reaction time at 3 h was selected as the best condition.

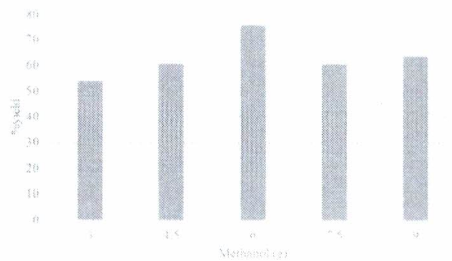

Figure 3. Effect of methanol, reaction time: 3 h;catalyst amount: 3%wt.

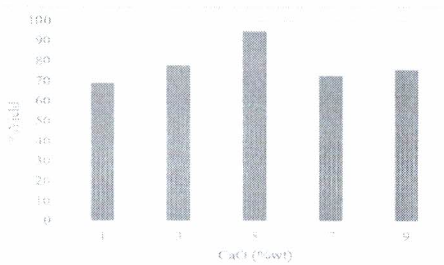

Figure 4. Effect of catalyst amount, reaction time: 3 h; methanol 6 g.

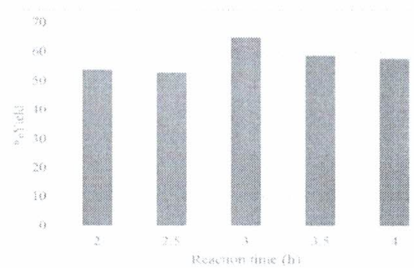

Figure 5. Effect of reaction time, methanol 6 g; catalyst amount: 5% wt.

D. Biodiesel Properties

The biodiesel properties were tested followed biodiesel standard of USA (ASTM D 6751) and Europe (EN 14214) as exhibited in Table 1. The results showed that the biodiesel properties met the requirement standard. The next experiment, we will investigate the optimum condition to use in homemade biodiesel kit.

TABLE I. Properties of Used Oil Biodiesel Using CaO Catalyst

Parameter	Testing method	Limits	Value
Density at 15 °C (g/cm^3)	EN14214	0.86-0.90	0.8702
Acid value (mgKOH/g)	ASTM D664	0.80 max	0.5554
Water and sediment (%v)	ASTM D2709	0.050 max	<0.050

IV. CONCLUSION

The optimized condition in transesterification of used oil were 6 g of methanol, 5.0 % wt of CaO catalyst, and 3 h reaction time at 65°C, which produced biodiesel yield 95.94 %. The XRD and ATR-FTIR results showed that the catalyst was successfully calcined with sufficient purity from shell in Phetchabun province.

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