Effect of TiO_2 Mixed CaO Catalyst in Palm Oil Transesterification

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Abstract. Biodiesel is a promising alternative fuel. In this study, production of biodiesel from cooking oil (CO) was carried out via transesterification method. Heterogeneous catalyst, calcium oxide-titanium dioxide (CaO-TiO2) was selected as the best catalyst. The effects of CaO-TiO2 catalyst on catalyst amount and calcined temperature of catalyst towards the percentage conversion of oil to biodiesel were investigated. The catalysts were analyzed using Brunauer, Emmett and Teller (BET) test method. The results obtained showed that 76.67 % of oil was successfully converted into biodiesel using 800˚C calcined CaO-TiO2 catalyst. This indicates that the CaO-TiO2 has potential as a future heterogeneous catalyst for biodiesel production. Catalyst dosage of 0.5 w/w% with molar ratio oil to methanol is 3:5, stirring speed of 250 rpm and temperature of 65˚C in 1 hour reaction time are the best condition for the conversion of oil to biodiesel. It was found out that, methanol to oil molar ratio and catalyst amount gave significant effect on the conversion of oil.

Introduction

As the world is experiencing rapid social, economic and environmental transformation, it is indeed timely that researchers study on topic of biodiesel production and development. Biodiesel fuel (BFD) is one of the most substituted energy resources which is also called fatty acid methyl ester (FAME) or fatty acid ethyl ester (FAEE), which can be produced from vegetables oils or animal fats[1, 2]. In addition, biodiesel could be converted by any type of feedstock that contains free fatty acids and/or triglycerides such as algae, waste oil and waste grease [3].

Biodiesel has many advantages over petroleum diesel fuel, as it is nontoxic and produce less air pollutants, with a lower smoke, airborne particles, carbon monoxide and hydrocarbon emission. Furthermore, it is a biodegradable and renewable fuel [4]. Biodiesel can be produced by transesterification of triglycerides with monoalcohol in the presence of either an alkaline or acidic catalyst. Catalysts can be chosen depending on the amount of free fatty acids (FFA) in the oil.

Numerous investigations have been conducted on the BDF production using heterogeneous base catalysts as they offer higher catalytic activity than solid acid catalysts [3]. CaO has been rapidly studied as an important solid base catalyst in biodiesel production. Even though atomic mass of Magnesium (Mg) is half of Calcium (Ca), its density is higher than CaO. Although the Ca atoms are larger, they are more spread apart than the smaller Mg atoms [5, 6]. Cubic lattice structures allow slippage to occur more easily than non-cubic lattices, so hexagon close packed structure (hcp) metals (Mg atoms) are not as ductile as the face centered cubic structure (fcc) metals (Ca atoms) [7].

As the valence of Ti ion (+4) is higher than that of the Ca ion (+2), Ti addition may theoretically bring about defects on the CaO surface; hence, improve the activity and stability of the catalyst [8]. However, there are rarely reports on biodiesel production using CaO with Ti addition, where a few of them are about MgO with Ti.

In this study, the effect of CaO-TiO_2 for biodiesel production from palm oil has been investigated by studying the amount of catalyst. Besides, calcination temperature of the catalyst is also studied because it gives largely affects the structural and catalytic properties and biodiesel yield [8].

Methodology

Material. Palm oil was bought from AEON shopping mall located at Taman Universiti, Skudai Johor Malaysia. CaO and TiO_2 catalyst was purchased from Sigma-Aldrich and methanol with purity of 99.8% was purchased from Fluka.

Catalyst Preparation. 3g of CaO and TiO_2 catalyst respectively were mixed using solid-solid phase. The mixture was calcined in a furnace at temperature of 200, 400. 600, or 800 ºC for 5 hours to activate the catalyst.

Transesterification Study. First, cooking oil (30ml) was preheated to the reaction temperature before methanol (50ml) and catalyst was added into the reaction beaker. The reaction was carried out at atmospheric pressure with stirring speed of 250 rpm and reaction temperature of 65˚C for 1 hour. Thermometer was attached to retort stand and the beaker to monitor the reaction temperature respectively. After reaction has completed, the solid catalyst was filtered off by funnel with paper filter and the filtrate mixture was transferred into a separating funnel and allowed to stand overnight. The bottom layer was drain off and the top layer was collected and rinsed with hot distilled water until a clear wash water is observed. The parameters to be investigated were effect of methanol to oil molar ratio (1:1 to 5:4), effect of catalyst calcined temperature (200 to 800˚C) and effect of catalyst dosage (0.1 to 2 wt %).

Catalyst Characterization. Surface area of CaO-TiO_2 was analyzed by Brunauer, Emmett and Teller (BET) test method.

Result and Discussion

Effect of Catalyst Dosage on Percentage Yield. The effect of the catalyst loading on yield of biodiesel was investigated with CaO-TiO_2 by varying the concentration from 0.1 to 2.0 wt% of palm oil. The reaction was carried out at 65˚C for 1 hour with 3:5 methanol to oil and 250 rpm stirring speed. Figure 1 illustrates the effect of catalyst CaO-TiO2 on percentage yield of biodiesel. As indicated in Figure 1, when the catalyst amount was increased from 0.1 to 0.5 wt% correspondingly biodiesel conversion was gradually increased and attained a maximum yield of 87.78% at 0.5 wt% CaO-TiO_2. However, further increases in the catalyst dosage, a decreased conversion was observed and slightly increases from 1 to 2 wt% of amount of catalyst.

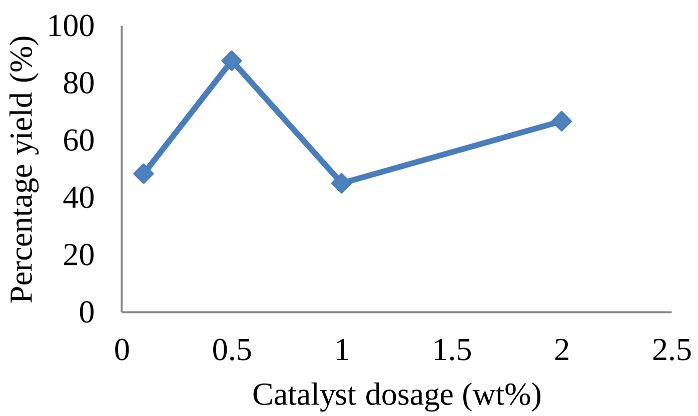

Fig. 1: Effect of catalyst dosage on percentage yield. (Conditions: oil to methanol ratio 3:5, reaction temperature 65 ºC, reaction time 1 hour, stirring speed 250 rpm).

This trend is due to the total number of active sites for reaction that can speed up the reaction rate. After the equilibrium state, the increasing of percentage yield would be insignificant. When the catalyst was excessively used, the reactants and produces can be absorbed by the catalyst powder, and the excess of catalyst powder can reunite together, which reduced the number of active centers [1]. From the result, 0.5 wt% of CaO-TiO2 was used for the other catalyst study.

Effect of Calcination Catalyst Temperature on Percentage Yield. The effect of the calcined catalyst temperature on yield of biodiesel was investigated by varying the temperature of the furnace from 200 to 800˚C. After complete calcined for 5 hr and cooled down, the reaction was carried out at 65˚C for 1 hour with 3:5 methanol to oil, 0.5 wt% catalyst dosage and 250 rpm stirring speed.

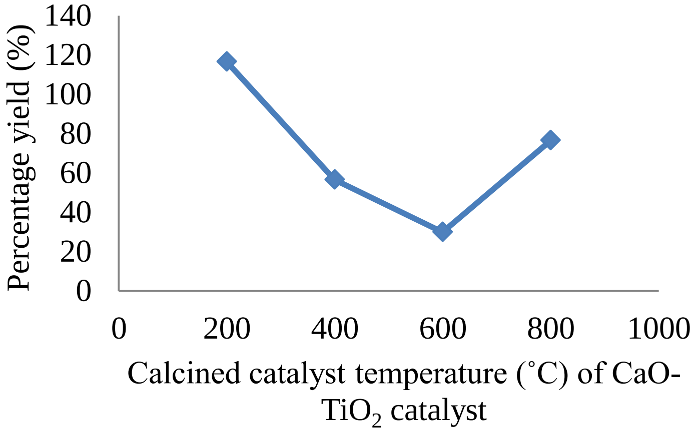

Fig. 2: Calcined catalyst temperature on percentage yield. (Conditions: oil to methanol ratio 3:5, catalyst dosage 0.5 wt%, reaction temperature 65 °C, reaction time 1 hour, stirring speed 250 rpm).

Figure 2 indicates the effect of calcined catalyst ($CaO-TiO_2$) temperature on percentage yield of biodiesel. From Figure 2, biodiesel conversion was gradually decreased when the calcined temperature was increased from 200 to 600˚C. However, a slightly increased conversion was observed from further increased calcined temperature 600 to 800˚C. As shown in Figure 2, 200 ˚C of calcined temperature gave excess biodiesel yield which is over 100%. This trend is due to the samples were not completely activated from temperature 200 to 600˚C, while sample was completely activated at 800˚C temperature of furnace. Samples were also analyzed by Brunauer, Emmett and Teller (BET) test method and the results are as tabulated in Table 1.

Table 1: Surface area of calcined temperature.

Calcined temperature (˚C)	BET multipoint area (m^2/g)
200	14.3675
400	10.5597
600	22.9605
800	15.4284

From Table 1, surface areas of the samples are found ununiformed and further analysis on catalyst bonding and morphology should be done. Hence, 800 ˚C of calcined temperature is selected as the best condition dues to the maximum yield which is 76.67%.

Conclusion

From this study, it showed that methanol to oil molar ratio, temperature of calcined catalyst and catalyst dosage give significant effect on the percentage conversion of oil to biodiesel. Based on this study, about 76.67 % of Seri Murni cooking oil was successfully converted to biodiesel using 800˚C calcined CaO catalyst with molar ratio oil to methanol 3:5, stirring speed of 250 rpm, reaction temperature of 65˚C, and 1 hour reaction time.

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