

Biodiesel Production via Transesterification of Palm Oil Using NaOH/Al₂O₃ Catalysts

(Pengeluaran Biodiesel Melalui Pengtransesteran Minyak Sawit
dengan Menggunakan Mangkin NaOH/Al₂O₃)

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ABSTRACT

Due to the increase in price of petroleum and environmental concerns, the search for alternative fuels has gained importance. In this work, biodiesel production by transesterification of palm oil with methanol has been studied in a heterogeneous system using sodium hydroxide loaded on alumina (NaOH/Al₂O₃). NaOH/Al₂O₃ catalyst was prepared by impregnation of alumina with different amount of an aqueous solution of sodium hydroxide followed by calcination in air for 3 h. The prepared catalysts were then characterized by using x-ray diffraction (XRD), Fourier transform infrared spectrometer (FT-IR), Brunner-Emmett-Teller surface area measurement (BET), scanning electron microscopy (SEM) and temperature-programmed desorption of CO₂ (CO₂-TPD). Moreover, the dependence of the conversion of palm oil on the reactions variables such as the molar ratio of methanol/oil, the amount of catalysts used, reaction temperatures and reaction times were performed. The conversion of 99% was achieved under the optimum reaction conditions. The biodiesel obtained was characterized by FT-IR and the pour point was measured.

Keywords: Biodiesel; heterogeneous catalyst; palm oil; transesterification

ABSTRAK

Disebabkan oleh kenaikan harga minyak mentah dan keperihatinan terhadap alam sekitar, penyelidikan terhadap bahan bakar alternatif telah menjadi lebih penting. Dalam kajian ini, pengeluaran biodiesel melalui pengtransesteran minyak sawit dengan metanol telah dikaji dalam sistem heterogen menggunakan natrium hidroksida yang dimuatkan atas alumina (NaOH/Al₂O₃). Mangkin NaOH/Al₂O₃ telah disediakan dengan proses impregnasi alumina dengan larutan sodium hidroksida dengan jumlah yang berbeza diikuti dengan pengkalsinan dalam udara selama 3 jam. Mangkin yang telah disediakan kemudiannya dicirikan dengan menggunakan pembelauan sinar-X (XRD), spektrometer Fourier Transform infra merah (FT-IR), pengukuran luas permukaan Brunner-Emmett-Teller (BET), imbasan mikroskop elektron (SEM) dan Penyahjerapan CO₂ Suhu Berprogram (CO₂-TPD). Selain itu, kebergantungan penukaran minyak sawit kepada hasil pada pembolehkan tindak balas seperti nisbah molar metanol/minyak, jumlah mangkin yang digunakan, suhu tindak balas dan masa tindak balas turut dikaji. 99% hasil diperolehi di bawah keadaan tindak balas optimum. Biodiesel yang diperolehi dicirikan dengan FT-IR dan takat tuang diukur.

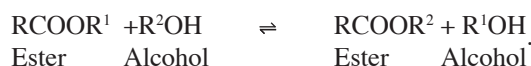
Kata kunci: Biodiesel; mangkin heterogen; minyak sawit; pengtransesteran

INTRODUCTION

Biodiesel is a renewable fuel consists of fatty acid methyl esters (FAME) derived through transesterification of vegetable oils, animal fat and also recycles oil from the food industry with methanol. Biodiesel is recognized as “green fuel” with several advantages; safe, non-toxic and biodegradable compared to petroleum diesel. It is oxygenated and essentially free of sulfur and aromatics making it a cleaner burning fuel with reduced emission of SO_x, CO, unburnt hydrocarbons and particulate matter (Chai et al. 2007). Moreover, using biodiesel as a fuel in a car can give many advantages such as it is not harmful to the environment, reduces the environmental effect of a waste product, and energy efficient. But, when compared with the cost of diesel obtained from petroleum, the

high cost is the main drawback in biodiesel production. However, the cost of biodiesel could certainly be lowered by improving the production process. The first step in this direction could be represented by the use of heterogeneous catalysts instead of homogeneous ones (Di Serio et al. 2007).

Recently, biodiesel is mostly produced by a transesterification reaction of oil with an alcohol in the presence of a catalyst, to yield mono-alkyl esters and glycerol, which are then separated, and purified (Akgün & İşcan 2007). Transesterification or alcoholysis is the displacement of alcohol from an ester by another in a process similar to hydrolysis, except than alcohol is used instead of water (Meher et al. 2004). The reaction is represented by the general equation below:



Transesterification is one of the reversible reactions and proceeds essentially by mixing the reactants. However, the presence of a catalyst accelerates the conversion of triglycerides to biodiesel (Meher et al. 2004).

Current technology processes for biodiesel manufacturing employ transesterification of triglycerides with methanol using homogeneous acid or base catalysts. The homogeneous acid-catalyzed process often uses hydrochloric acid and sulfonic acid as a catalyst. The problem with this process is the costly separation of the catalyst, corrosive to equipment and toxic (Chai et al. 2007; Kiss et al. 2006). Moreover, the reaction time is very long and a high molar ratio of methanol to oil is needed (30-150:1 mol %) (Xie et al. 2006). Potassium hydroxide and sodium hydroxide are usually used as a homogeneous base-catalyst. These base catalysts show higher performance for obtaining biodiesel but, they also react with free fatty acids (FFA) to form unwanted soap by-products in which an expensive separation is required (Chai et al. 2007; Kiss et al. 2006). Since the homogeneous catalysts can cause many problems and increased the production cost, they can be replaced by environmentally friendly heterogeneous catalysts because of environmental constraints and simplifications in the existing processes. Moreover, heterogeneous catalysts can be more easily separated and give place to higher quality of ester products and glycerol by product. In this case, pure high grade glycerol can be obtained without expensive refining operations (Di Serio et al. 2007).

Most heterogeneous catalysts employed for transesterification are solid bases. Solid base catalysts have a higher activity and faster reaction rate as compared to solid acid catalysts. If the oil has a high free fatty acid and water content, solid acid catalysts is generally used (Boz & Kara 2009). However, solid acid catalysts need high reaction temperature to complete the reaction. Nevertheless, one of the major problems associated with heterogeneous catalysts is the formation of three phases with alcohol and oil which leads to diffusions limitations thus lowering the rate of reaction (Mbaraka & Shanks 2006). One way of overcoming mass transfer problem in heterogeneous catalysts is using structure promoters or catalysts supports which can provide more specific surface area and pores for active species where they can anchor and react with large triglycerides molecules (Zabeti et al. 2009). Alumina has been widely used as a support in catalysis processes owing to its extremely thermal and mechanical stability, high specific surface area, large pore size and pore volume.

Kim et al. (2004) reported on Na/NaOH/ γ -Al₂O₃ for the production of biodiesel from soybean oil. The biodiesel yields reached 83% when methanol to oil loading ratio 9:1 was used with the presence of *n*-hexane as the co-solvent. Arzamendi et al. (2007) have studied the performance of NaOH/Al₂O₃ as a solid base catalyst for transesterification

of sunflower oil to biodiesel. They found that, the as prepared catalyst is better than that of the calcined catalysts. For calcined catalysts, the oil conversion achieved about 86% after 24 hours of reaction at 12:1 molar methanol/oil ratio. However, for the non calcined catalysts with the reaction parameters same as the calcined catalysts, the conversion increased up to 99%. In another work, Xie and Li (2006) developed KI/Al₂O₃ to catalyze the transesterification of soybean oil to biodiesel. The catalyst with 35 wt.% KI loaded on Al₂O₃ and calcined at 773 K for 3 h was found to be the optimum catalyst. The highest conversion 96% reached when the reaction was carried out for 8 hours, 2.5% catalyst amount and 15:1 methanol to soybean oil molar ratio. Boz and Kara (2009) found that KF/Al₂O₃ are the active catalyst in the transesterification of canola oil with methanol and give highest yield of 99.6% at the end of 8 hours at 60°C with methanol/oil molar ratio of 15:1 and catalyst amount of 3 wt.%.

In this work, a series of solid base catalyst consisting of NaOH supported on commercial alumina were prepared for the transesterification of palm oil with methanol in order to find a proper support which can work better compared to homogeneous catalyst. During catalyst preparation, different amount of sodium compounds were impregnated into alumina. A screening of the reaction condition has been carried out by examining the effect of methanol/oil molar ratio, catalyst amount, reaction temperatures and reaction times.

EXPERIMENTAL DETAILS

PREPARATION OF THE CATALYST

All the catalysts were prepared by impregnation of alumina with an aqueous solution of sodium hydroxide. Alumina was impregnated with 15 ml of different amounts sodium hydroxide (45 and 50 wt.%) solutions. This impregnate was dried overnight in oven. The catalysts were then calcined in air for 3 hours. The obtained catalysts were denoted as 45 Na and 50 Na (before calcine) 45 NaC, and 50 NaC (after calcined). Finally, the prepared catalysts were characterized by XRD, FT-IR, BET, SEM, and CO₂-TPD.

CATALYSTS CHARACTERIZATIONS

X-ray diffraction (XRD) analysis of all the synthesized catalysts was carried out using a Shidmadzu diffractometer model XRD 6000 employing CuK_α radiation to generated diffraction patterns at ambient temperature. The Universal Attenuated Total Reflection method was applied for determining IR spectra of the samples. Spectra were recorded on Perkin Elmer model 100 Series instrument with scanning range from 280 to 4000 cm⁻¹. The BET surface area of the catalysts was measured by performing nitrogen absorption at 77 K. The experiment was done by using Thermo Finnigan Sorptomatic Instrument model 1990. Surface structure and morphology of the catalysts was observed under a scanning electron microscope

(SEM) using LEO 1455 VP electron microscope operated at accelerating voltages of 30 kV. Micrographs were recorded at various magnifications. Finally, the basic strength of the catalysts was evaluated by temperature-programmed desorption of CO₂ (CO₂-TPD) was performed by using the Thermo Finnigan TPD/R/O 1100 series instrument.

TRANSESTERIFICATION REACTION

The typical reaction was carried out in a 250 mL round-bottom flask, with a thermometer, mechanical stirring, and coil condenser. The system was preheated to 60°C, and then the desired amount of palm oil was added. Molar ratio of methanol to palm oil used was 15:1. When the system reached the desired temperature again, methanol and 3 wt.% catalyst were added while stirring at 1200 rpm in order to keep the system uniform in temperature and suspension. The reaction was performing for 3 h. Samples were taken out and catalyst were separated from the reaction product by centrifugation. The reaction product was then poured into a separation funnel and was left overnight for settlement. In this process, the two layers were formed, whereby the upper layer was the biodiesel and glycerin would settle down at the bottom of the separation funnel. The synthesized biodiesel was characterized by FT-IR and the pour point was measured according to ASTM D97 standard methods.

RESULTS AND DISCUSSION

CATALYST CHARACTERIZATIONS

XRD analyses have been performed to obtain more information about the catalyst structure. Figure 1 shows the XRD patterns of NaOH/Al₂O₃ catalyst (before and

after calcination) with different loading amounts of NaOH. XRD patterns shows that 45Na catalyst had form as semi amorphous and almost identical to the support, Al₂O₃ unless that the intensity of the peak was decreased indicating the good dispersion of NaOH on alumina. For the other catalysts, several diffractions peaks clearly visible showing the presence of NaOH and sodium aluminate (NaAlO₂). These indicate that NaOH has reacted with the support, Al₂O₃ giving rise to the formation of aluminates that originated the stronger basic sites of the catalysts (Arzamendi et al. 2007; Kim et al. 2004).

To further understand the correlation between the catalysts composition and calcination temperature, characterization by FT-IR was carried out. From the FT-IR spectra shown in Figure 2, all the catalysts showed a very intense broad band at 3300 to 3700 cm⁻¹ that corresponding to O-H stretching vibration of the hydroxyl groups attached to Al₂O₃. However, the bands become weaker after calcination. Additionally, there was another band at 1450 cm⁻¹ which were probably attributed to carbonate (Wan et al. 2009). But when the catalysts were calcined, the intensity of this band was gradually decreased.

From the results shown in Table 1, the BET surface area of the synthesized catalysts was found to be lower than the pure alumina. From a qualitative point of view, this was an expected result since in heterogeneous catalysis; the reduction of the specific surface area of the support is a well documented consequence when a catalyst was promoted with alkali metals (Mross 1983; Perrichan & Durrupty 1988; Szczepańska & Malinowski 1969). These results are not surprising since surface and pores of alumina were covered by sodium compounds during the impregnation step (Arzamendi et al. 2007; Boz & Kara 2009). However, after calcination, there is a slightly increased in the BET surface area of the catalysts. From

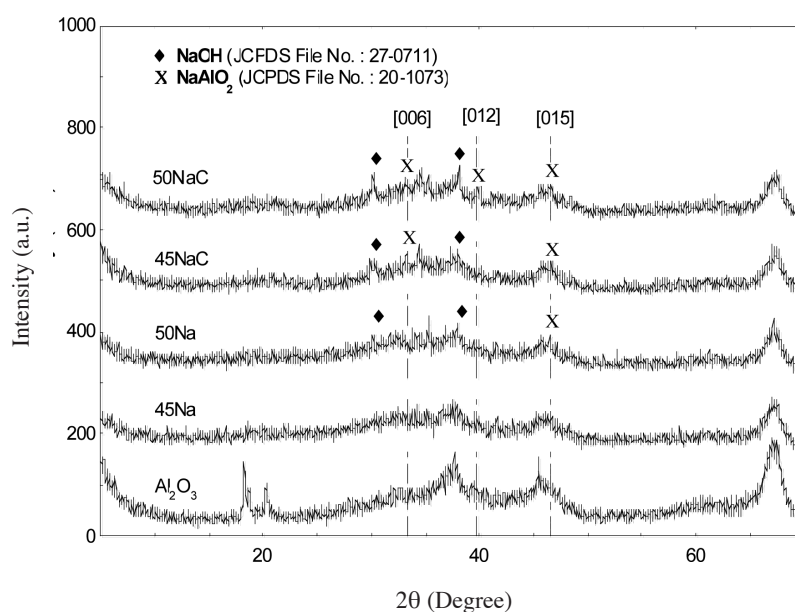


FIGURE 1. XRD patterns for support, Al₂O₃ and the prepared catalysts before (45 Na, 50 Na) and after calcined (45 NaC, 50 NaC)

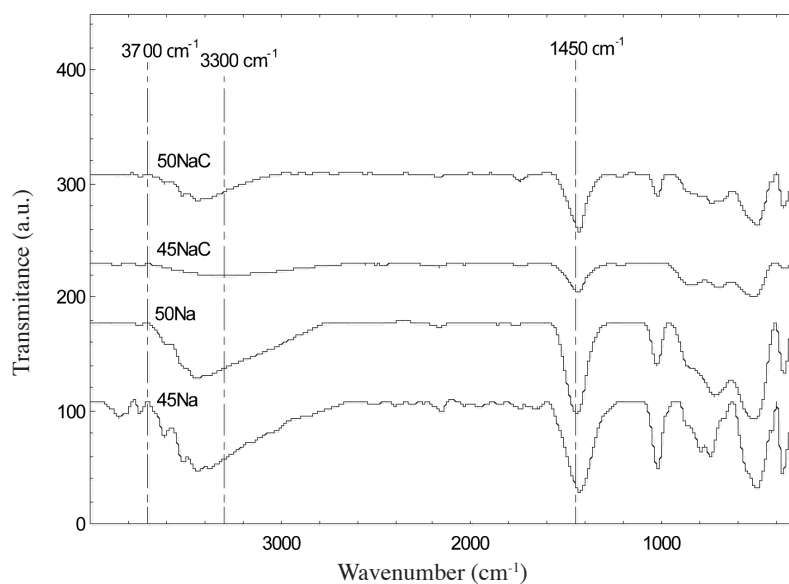


FIGURE 2. FT-IR spectra for all synthesized catalysts

TABLE 1. BET surface areas of both non-calcined and calcined catalysts

Catalyst	BET Surface Area (m ² /g)
Al ₂ O ₃	136
45 Na	37
50 Na	45
45 NaC	44
50 NaC	51

here, it can be concluded that calcination has a positive effect on the prepared catalysts.

The results from BET surface area were further confirmed by SEM images. From the SEM images in Figure 3, it clearly showed that before calcined, the catalysts (45 Na and 50 Na) were still in bulky form. However, a plate-like form of catalysts was observed after calcination (45 NaC and 50 NaC). The result suggested that the shape of a catalyst can affect the surface area.

The CO₂-TPD profiles for all the tested catalysts are displayed in Figure 4. From the CO₂-TPD analysis, a very broad desorption band can be observed extending from 450 to 630°C that could be assigned to stronger basic sites (Albuquerque et al. 2008; Di Serio et al. 2006). However, among the four catalysts that have been presented in

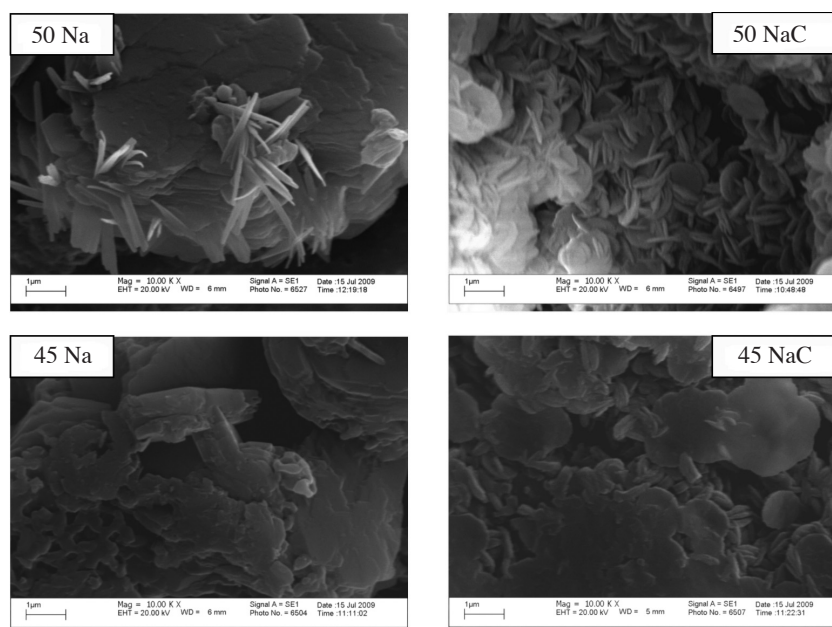


FIGURE 3. SEM images of before and after calcined catalysts

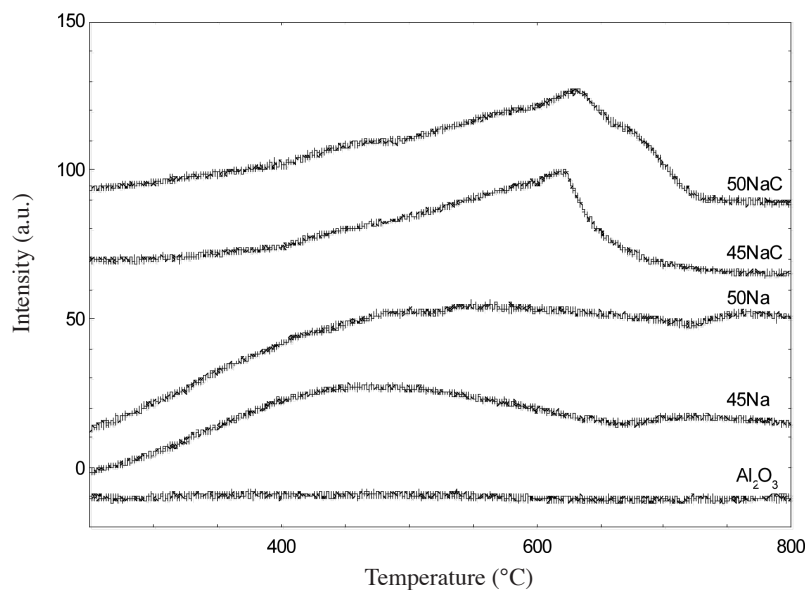


FIGURE 4. Temperature-Programmed Desorption of Carbon Dioxide (CO_2 -TPD) profiles of all synthesized catalysts and support

this Figure, 50 NaC gave the strongest basic sites. This conclusion has been made due to the CO_2 desorption peak occurred at higher temperature and large area of CO_2 desorption peak which suggested that 50 NaC has the highest basic concentration from the other catalysts.

TRANSESTERIFICATION REACTION

The FT-IR result shows the quality of the biodiesel (Figure 5). The palm oil and the biodiesel were analyzed using FT-IR. In the transesterification of palm oil, the FT-IR spectra of palm oil and biodiesel are very similar because of high chemical similarities that exist among triglycerides and methyl ester. However, small different are observed in

this three region (C=O ester, CH_3 and C-O ester) because biodiesel had a different compound bonded compared to the palm oil. The strong ester peaks at 1750 cm^{-1} (C=O ester) and at $1170\text{--}1200\text{ cm}^{-1}$ (C-O ester) are clearly present in the spectra. Outside these two regions, another characteristic peak that indicates the presence of CH_3 group in the mixtures of methyl ester can be observed at 1445 cm^{-1} (Siatis et al. 2006).

METHANOL/OIL MOLAR RATIO

The stoichiometric ratio for transesterification requires 3 moles of methanol for each mole of to yield 3 moles of fatty acid methyl ester and 1 mole of glycerol. Since the

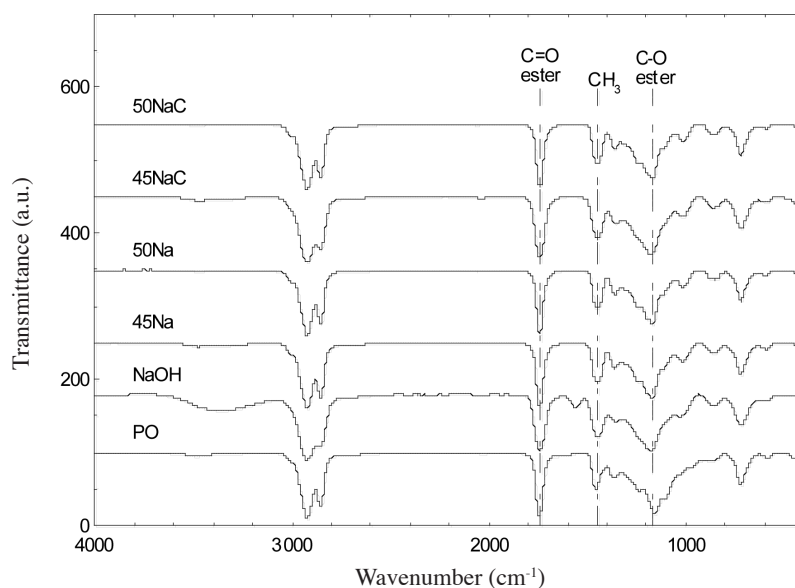


FIGURE 5. FT-IR spectra for palm oil and synthesized biodiesel from various prepared catalysts

transesterification reaction is reversible reaction, excess methanol is required to drive the reaction towards product. As represented by Figure 6, when methanol/oil molar ratio was increased, conversion was increased considerably. The maximum conversion was obtained when the methanol/oil ratio reach 15:1. There is evident that to elevate the conversion, an excess methanol feed was effective only to a certain extent (Kim et al. 2004; Wan et al. 2009; Xie et al. 2006; Xie & Li 2006).

CATALYST AMOUNT

The influence of catalyst amount on the conversion of biodiesel was investigated. The catalyst amount was varied in the range of 1-5 wt.%. As shown in Figure 7, the conversion was increased with the increased of catalyst amount from 1 to 3 wt.%. However, with further increased in the catalyst amount the conversion was slightly decreased. This was probably because the slurry (mixture of catalyst and reactants) become too viscous giving rise to a problem of mixing and demand of higher power

consumption for adequate stirring (Kim et al. 2004; Wan et al. 2009; Xie et al. 2006; Xie & Li 2006).

REACTION TIME

The influences of reaction time on palm oil conversion are illustrated in Figure 8. The reaction time was varied in the range 1-7 hours. As can be seen, the conversion was increased steadily in the first 3 hours and reached 99% conversion. The conversion thereafter remained nearly constant after 3 hours of reaction time.

REACTION TEMPERATURE

Transesterification can occur at different temperatures depending on the types of catalyst and alcohol used. The influenced of reaction temperature on conversion of palm oil to biodiesel was investigated with four different temperature. From the result shown in Figure 9, the conversion increased as the reaction temperature increased and give the highest conversion of 99% at 60°C. However,

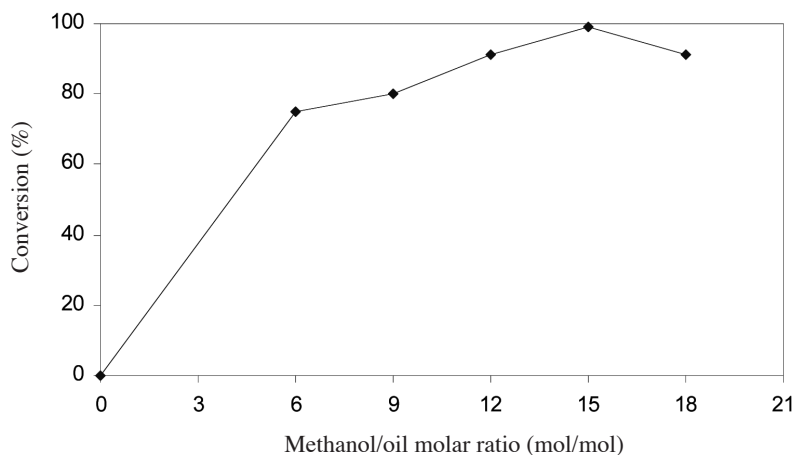


FIGURE 6. Influence of methanol/oil molar ratio on the conversion. Reaction condition: catalyst amount 3 wt.%, reaction time 3 hours, reaction temperature 60°C

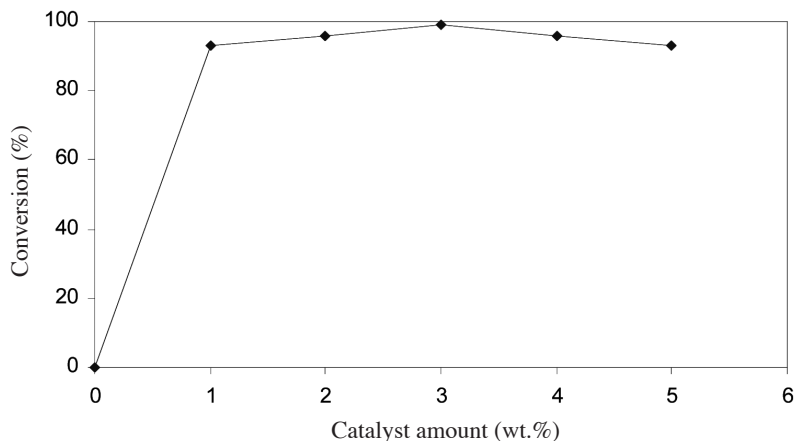


FIGURE 7. Influence of catalyst amount on the conversion. Reaction condition: methanol/oil molar ratio 15:1, reaction time 3 hours, reaction temperature 60°C

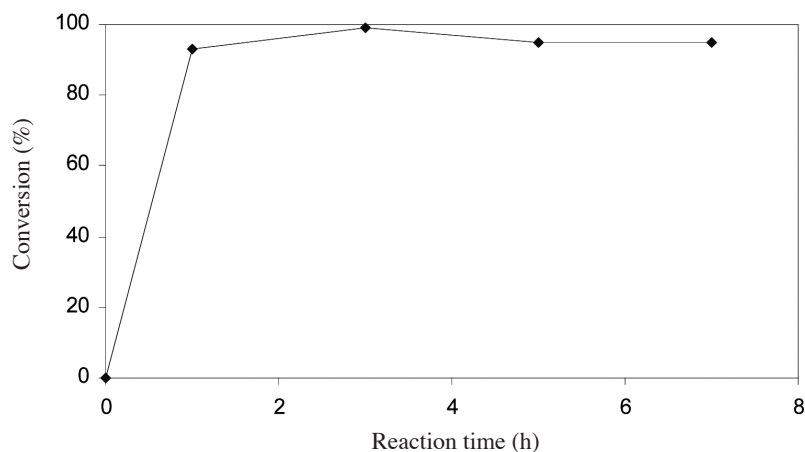


FIGURE 8. Influence of reaction time on conversion. Reaction condition: molar ratio methanol/oil 15:1, catalyst amount 3 wt.%, reaction temperature 60°C

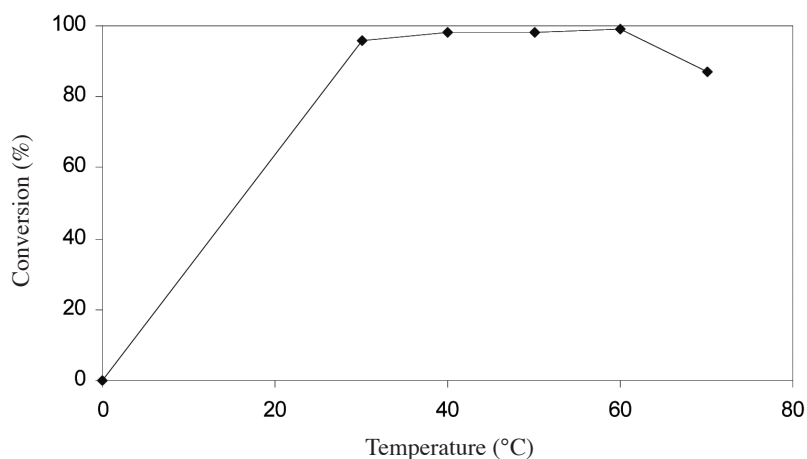


FIGURE 9. Influence of reaction temperature on conversion. Reaction condition: methanol/oil molar ratio 15:1, catalyst amount 3 wt%, reaction time 3 hours

when the temperature reaches to the boiling point of methanol, a lot of methanol's bubbles were formed hence inhibit the mass transfer on the phase interface thus lower the conversion (Zabeti et al. 2009).

POUR POINT

The prepared palm oil methyl ester was evaluated for their potential as diesel fuel based on pour point characteristic. Pour point is defined as the lowest temperature that the product still can be poured by gravity (May et al. 2005). From this study, the pour point of methyl ester of palm oil prepared is 10°C. The pour point of this methyl ester was found to be comparable with Malaysian petroleum diesel and it also was found to be in reasonable agreement with the ASTM biodiesel standard.

CONCLUSION

Among all the synthesized catalysts in this work, the catalyst with 50 wt.% sodium hydroxide loaded on

alumina and calcined in air for 3 h was found to be the optimum catalyst which gave the best catalytic activity. Formation of sodium aluminate by loading sodium hydroxide on alumina originated the active basic sites of the catalysts. The highest conversion 99% reached when the reaction was carried out at 60°C with molar ratio of methanol/oil 15:1, reaction time 3 h and catalyst amount 3 wt.%. Moreover, the biodiesel synthesized also has a pour point that in reasonable agreement with the ASTM biodiesel standard.

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