Preparing Activated Carbon from Palm Shell for Biodiesel Fuel Production

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ABSTRACT

Palm shell is a cheap and abundant agricultural by-product in many tropical countries, particularly Malaysia, Indonesia and Thailand. Several techniques including thermal activation (physical activation) and chemical activation have been successfully developed to convert palm shell into an activated carbon (AC). One technique is to use an activating agent such as Ca(NO₃)₂·4H₂O. The objective of this work was to optimize the process for biodiesel fuel production from palm stearin using activated carbon supported calcium oxide. Transesterification of palm stearin with methanol was investigated under a heterogeneous catalysis system. The reaction was studied by various amount of metal loading in activated carbon. The supported alkali earth metal catalysts, Ca(NO₃)₂/AC showed almost the same activity under the optimized reaction conditions compared to calcium oxide catalyst (CaO). The catalysts were characterized, using thermogravimetric analysis (TGA), scanning electron microscope (SEM), X-ray diffraction (XRD) and surface area analyzer. The results indicated that the Ca(NO₃)₂/AC had relatively low surface area, compared to CaO. The suitable conditions for heterogeneously catalyzed transesterification of Ca(NO₃)₂/AC and CaO were the methanol/oil molar ratio of 20, temperature of 60°C and reaction time of 4 h, with 10.5 and 6 % (w/w) catalyst to oil ratio for Ca(NO₃)₂/AC and CaO, respectively.

Keywords: activated carbon, palm shell, heterogeneous catalyst, biodiesel.

1. INTRODUCTION

Biodiesel, a mixture of alkyl esters, is an alternative diesel fuel because the physicochemical and fuel properties are similar to those of petroleum-based diesel oil. The advantage of biodiesel is that the exhaust gas from combustion contains no SOx and a relatively small amount of CO₂, compared to the combustion of diesel fuel [1]. Biodiesel could be synthesized by transesterification using homogeneous catalysts. Although the reaction itself is easily performed, subsequent neutralization, separation, and purification steps are time-consuming and non-environmentally friendly due to a large amount
of water requirement during washing steps. Replacement of the homogeneous catalysis with a heterogeneous route has received much attention since the process can be simplified by facilitating the catalyst separation and purification steps [2].

Activated carbon can be produced from a variety of raw materials. However, palm shells are mainly used as a raw material because it can be sought in the country. The global production of palm oil is reported to be around 48 million tons, which corresponds to a palm shell generation of 1,500 million tons. The availability of palm shells far exceed the total demand for activated carbon, which is estimated to be only around 1.2 million tons [3]. The palm shell has no specific technical use and only a small portion is used as fuel to generate process steam in the palm-processing mill [4]. However, its high density, relatively high carbon content and low ash content are desirable properties of a suitable precursor for the preparation of high-grade activated carbon. These renewable agricultural wastes are cost-effective alternatives to more expensive and polluting precursors like coal for the production of activated carbon [5].

In this study, activated carbon was used in the preparation of a solid base catalyst for the transesterification. In addition, the results were compared to the catalytic activity of calcium oxide. The reaction conditions were optimized by separately changing the experimental condition.

2. MATERIALS AND METHODS
2.1 Preparation Catalyst Preparation

Supported metal oxide catalysts were prepared according to the conventional incipient-wetness impregnation of aqueous solutions of the corresponding Ca(NO₃)₂·4H₂O (AR grade, Ajax Finechem) precursors on an activated carbon support (100 mesh particle size, Darco). Calcium nitrate salt was completely dissolved in deionized water at room temperature. Various amount of metal loading was maintained at 10, 15 and 20 mmol metal/g support. The support was then added into the solution followed by vigorous mixing. After mixture for 4 h, the paste was dried in an oven at 120°C overnight. The dried solid was calcined at 450°C for 4 h.

Calcium oxide (CaO) used in the transesterification process was obtained from the calcination of precipitated calcium carbonate (puriss, Sigma-Aldrich) at 800-900°C for 1.5 to 4.5 h in muffle furnace.

2.2 Characterization

The BET surface area, total pore volume and average pore diameter of the prepared catalysts were measured with surface area analyzer (Quintchrome, Autosorb-IMP). The structural of metal oxide catalysts was confirmed by X-ray diffractometer (JEOL, JDX-3530, 2kW). Morphological study was carried out with a scanning electron microscope (JSM-5800LV). A Perkin-Elmer Pyris Diamond thermogravimetry (TG/DTA) was used for TGA. Composition of the methyl ester was analyzed with a gas chromatograph (GC) equipped with a FID detector and a capillary column 30 m × 0.32 mm × 0.25 μm (DB-WAX, Carbowax 20M).

2.3 Transesterification Procedure

Palm stearin used in this study was obtained from Weerasuwan Co., Ltd. Methanol was commercial grade with 95% purity. Transesterification was carried out in a 250 mL 3-neck round bottom flask equipped with a reflux condenser and a magnetic stirrer. Ca(NO₃)₂/AC and CaO were used as catalysts with the amount varied from 3 to 15 wt.% and the methanol/oil molar ratio was kept constant at 20:1. Catalysts were first suspended in a methanol at 60°C. Palm stearin was then heated at 60°C and added into the mixture.
under vigorous stirring. After four hours of reaction time, the catalyst was separated by centrifuge, and the reaction mixture was loaded into a rotary evaporator to remove excess methanol. Methyl ester phase was then obtained in a separating funnel. The obtained methyl ester product was then washed with hot water and dried in the oven. Products in the biodiesel consist of methyl esters, monoglycerides, diglycerides and triglycerides. Composition of the methyl esters was analyzed using GC method.

3. RESULTS AND DISCUSSION

3.1 Catalysts Characterization

The measured multipoint BET, total pore volume, and average pore diameter are shown in Table 1. The BET surface areas and the total pore volumes of activated carbon decreased with loading calcium nitrate, and less than in the case of calcium oxide [6]. The surface area of activated carbon increases with increasing impregnation ratio from 0.5 to 1.0 and decreased slightly for ratios larger than 1. However, mesoporous surface area increased continually. There was a pronounced decrease in micropore surface area when the ratio was higher than 1 due to enlargement of micropores to mesopores. These results suggested that to obtain the optimal value of surface area, the impregnation ratio should be around 1.0 [7].

Figure 1 shows TGA patterns of activated carbon, calcium carbonate, non-calcined Ca(NO₃)₂/AC and calcined Ca(NO₃)₂/AC. It was found that Ca(NO₃)₂ in non-calcined Ca(NO₃)₂/AC was completely decomposed to CaO at about 450°C. On the other hand, calcined Ca(NO₃)₂/AC exhibited one-step decomposition of activated carbon (38% weight loss) at 650°C, while pure activated carbon showed weight loss of around 87% from decomposition at 600°C. The results indicated that the catalysts contained metal more than 50 wt.% and the calcium carbonate was completely decomposed to CaO at temperature about 800°C.

Figure 2 compares XRD patterns of Ca(NO₃)₂/AC catalysts with various amounts of metal loading in activated carbon after the calcination at 450°C. The several diffraction patterns corresponding to CaO phase remained concomitantly with the presence of weak peaks related to nitrate salts when amount of metal loading was maintained at 10 mmol metal/g support (Figure 2a). At 20 mmol

![Figure 1. TGA patterns of activated carbon, calcium carbonate, non-calcined Ca(NO₃)₂/AC and calcined Ca(NO₃)₂/AC.](image)
metal/g support, the amount of nitrate salts was greatly increased with an increase in the CaO peaks [8, 9].

Since the calcinations time and temperature largely affect the structural and catalytic properties of the resultant catalysts, we treated the impregnated catalyst samples at various times and temperatures to attempt to optimize this. Figure 3 compares XRD patterns of CaCO₃ catalysts calcined at 800-900°C for 1.5 to 4.5 h. The diffraction patterns correspond to CaO phase with the presence of CaCO₃ phase when the calcination was performed at 800°C for 1.5 h (Figure 3b). At 800°C for 4.5 h, the amount of CaCO₃ was greatly reduced with an increase in the CaO peaks (Figure 3c) due to calcium carbonate decomposition at temperatures above 800°C, as observed in the TGA results (Figure 1). As a result, no peaks of CaCO₃ were found when the calcination temperature above 800°C for 4.5 h (Figure 3c, d and e).

**Figure 2.** XRD patterns of Ca(NO₃)₂/AC catalysts prepared from various amounts of metal loading: 10 (a), 15 (b) and 20 mmol metal/g support (c). (Symbols: □ nitrate salts, ▼ metal oxides).

**Figure 3.** XRD patterns of CaCO₃ (a), CaCO₃ after the calcination at 800°C/1.5 h (b), 800°C/4.5 h (c), 900°C/1.5 h (d) and 900°C/4.5 h (e). (Symbols: ▼ CaO, ○ CaCO₃).
Figure 4 shows the SEM images of the catalyst which illustrate the porous nature of the activated carbon supported catalyst. In general, the high porosity of activated carbon provides a large surface area for attachment of calcium nitrate. Figure 4a shows that the metal loading of 10 mmol metal/g support affected the partial metal coverage on activated carbon surface. When metal loading increased, activated carbon was covered with metal almost all the surface (Figure 4c), increasing the active sites. The photographs of calcium nitrate supported catalyst on activated carbon (Ca(NO₃)₂/AC) showed a good dispersion of calcium nitrate on the surface of activated carbon. Based on these results, after loading of calcium nitrate, activated carbon retained its structure that was important for catalysis and therefore the calcium species was found highly distributed upon the surface of the support [10].

Table 1. BET surface areas, pore volumes and pore diameters of the prepared catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Multipoint BET (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Average pore diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon</td>
<td>829.68</td>
<td>0.9377</td>
<td>45.21</td>
</tr>
<tr>
<td>Ca(NO₃)₂/AC</td>
<td>6.64</td>
<td>0.0921</td>
<td>554.3</td>
</tr>
<tr>
<td>Calcium oxide</td>
<td>13.12</td>
<td>0.1077</td>
<td>328.3</td>
</tr>
</tbody>
</table>

Figure 4. SEM images of Ca(NO₃)₂/AC catalysts prepared from various amount of metal loadings: 10 (a), 15 (b), 20 mmol metal/g support (c), and 20 mmol metal/g support (SET mode, d).
3.2 Effects of Reaction Conditions

The effects of catalyst amount on the methyl ester content in the transesterification are shown in Figure 5. The results showed that the use of 10.5 wt.% Ca(NO$_3$)$_2$/AC catalyst calcined at 450°C gave 95.3% methyl ester yield (Figure 5). However, when reducing the catalyst amount to 7.5 wt.%, the methyl ester content decreased remarkably, and slightly increased with the use of 15 wt.% catalyst. Therefore, a 10.5 wt.% of Ca(NO$_3$)$_2$/AC is the optimal catalyst amount for the transesterification in this work. Compared to the transesterification over CaO catalyst with the same catalyst amount (10.5 wt.%), the methyl ester content about 98.5% was obtained, which was 3% FAME high than in the case of Ca(NO$_3$)$_2$/AC catalyst. As low as 6 wt.% in the amount of CaO catalyst was required to produce the biodiesel with the comparable methyl ester content as in Ca(NO$_3$)$_2$/AC catalyst. This could be due to higher surface area of CaO catalyst (Table 1), which results in an activation of active sites of the catalyst. Using the catalyst amount of 12 wt.% can improve the methyl ester content to 100%. Therefore, the suitable amount of CaO catalyst in the transesterification of palm stearin is in the range of 6–12 wt.%.

4. CONCLUSIONS

Transesterification of palm stearin was studied using various catalyst types to produce the biodiesel with high methyl ester content under different conditions. It was found that Ca(NO$_3$)$_2$/AC yielded high methyl ester contents (>95%) when the calcination was performed at 450°C and amount of metal loading was maintained at 20 mmol metal/g support. In addition, the activity of CaCO$_3$ catalysts was remarkably improved when the calcination was at 800°C for 4.5 h.

The suitable conditions for the transesterification of palm stearin with methanol over Ca(NO$_3$)$_2$/AC and CaO catalyst are the methanol/oil ratio 20, temperature 60°C, reaction time 4 h, and the appropriate catalyst amount 10.5 wt.% and 6 wt.% for Ca(NO$_3$)$_2$/AC and CaO catalyst, respectively.

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