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Catalytic Cracking of Used Cooking Oil Using Cobalt-impregnated Carbon Catalysts

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Abstract

This study investigated the cracking of used cooking oil using cobalt-impregnated carbon catalysts (Co-carbon) to produce biofuel. Carbon was impregnated with cobalt at concentrations of 1%, 2%, and 3% to produce Co-carbon catalysts. X-ray diffraction and scanning electron microscopy (SEM) demonstrated the amorphous nature of the catalysts. SEM-energy-dispersive X-ray analysis confirmed the successful impregnation of cobalt into carbon at levels of 4.46%, 6.74%, and 0.86% and further revealed that the Co-carbon catalysts contained pores and that each of them was slightly unique. The cracking procedure was conducted at 450 °C, 500 °C, and 550 °C. Analysis of the catalytic cracking products revealed that the highest liquid oil fraction was obtained by catalytic cracking at 500°C using 1% Co-carbon catalyst, which also provided the lowest activation energy ($E_a$). Catalytic cracking using 3% Co-carbon provided the highest yield of diesel oil (C12–C18) in the product.

Keywords: catalyst, cracking, cracked liquid, renewable energy, used cooking oil

Introduction

Within the next few years, it is predicted that Indonesia will face a fuel crisis due to diminishing petroleum stocks. Crude oil is a primary fossil energy source that cannot be renewed. Nevertheless, the global energy consumption is ever increasing, resulting in dwindling fuel resources. The global transport sector has considerably increased its fuel consumption, especially in the past decade, and currently accounts for 61.5% of the total fuel consumption. In fact, recent studies have indicated that the supply of fossil-based fuels will last only for the next 46 years[1, 2].

As a potential solution to these problems, it is necessary to develop the use of alternative energy based on renewable sources. One such alternative energy strategy is the use of biodiesel. Biodiesel is defined as the alkyl monoesters of fatty acids derived from vegetable or animal fats. It can be used as an alternative to petrodiesel as it is a renewable, nontoxic, and biodegradable fuel[3-7]. Biodiesel can be obtained from oils such as cassava oil, palm oil, and corn oil, but the use of these sources for the production of biodiesel would have a negative impact on food supplies[8].

Waste cooking oil is defined as the vegetable oil obtained after cooking food. The repeated use of vegetable oils for frying food makes the oil no longer suitable for consumption due to the increase in its free fatty acid content [1, 4, 9]. Almost all types of cuisine in Indonesia involve the use of palm oil, which consequently increases the demand for cooking oil every year. For example, in 2011, the consumption of cooking oil in Indonesia was 7.1 million tons, but by 2013, this had reached 8.5 million tons [10]. Therefore, the amount of used cooking oil has also increased. This used cooking oil can be utilized as a raw material for the production of biofuel [11-13]. Used cooking oil is derived from crude palm oil, which primarily consists of triglycerides with long-chain hydrocarbon compounds. Used cooking oil is a household waste and a by-product of the canning industry. Hence, it is nonedible; thus, exploiting used cooking oil will not affect food supplies [14-16]. Heating oil for a long time and at high temperatures leads to the formation of solid polymer compounds and increases its free fatty acid content. Consequently, used cooking oil is typically dark in color and has a specific odor.

Long-chain hydrocarbons can be converted into shorter chains through cracking processes. Therefore, cracking
is a potential solution for recycling used cooking oil into fuel. Compared with transesterification, a process that converts triglycerides into biodiesel (i.e., the methyl or ethyl esters of fatty acids), cracking has the following advantages: (a) lower processing cost, (b) production of standard engine fuels, (c) flexibility in the use of raw materials (triglycerides from biomass sources can be used), and (d) compatibility with existing infrastructures [14, 17-19].

There are two types of cracking processes, i.e., (1) thermal degradation and (2) catalytic degradation. Thermal degradation is a simple process because the only requirement is heat. However, it is not economically effective due to the requirement of high temperatures, and the products are hydrocarbons with a wide range of boiling points, thereby necessitating further treatment [20-23]. On the other hand, catalytic cracking is the process of breaking hydrocarbon chains using a catalyst [24-27]. The catalysts used in the cracking process must be stable at high temperatures and easily separated from the product, such as heterogeneous catalysts consisting of metals with active materials and metal-supported catalysts.

Activated charcoal has been widely used as a catalyst support due to its high adsorption capacity and stability in acidic and alkaline environments. Activated carbon prepared from coconut shells is the best material to produce activated carbon because it has large micropores and a low ash content and provides high reactivity [28].

Cobalt is one of the transition metals that can be used as a catalyst. It has an incomplete electron configuration and hence performs better when used as a catalyst, especially in hydrogenation reactions; however, the application of cobalt-imregnated carbon as a catalyst in the catalytic cracking process is still rare. Dispersing the active component onto the carrier provides a large surface area for the active component and makes it easy to use. The process of preparing supported catalysts involves several important parameters, such as the precursors used, the composition, and the mixing process, all of which affect the activity of the resultant catalyst. Moreover, these parameters have a large impact on the economic value of the catalyst, which also influences its industrial and environmental applications [29].

The most common methods used for catalyst preparation are precipitation or coprecipitation, impregnation, ion exchange, adsorption, and deposition–precipitation methods [29]. Impregnation involves total substance saturation by adsorbing precursor salts containing the active metal onto the catalyst carrier from the solution. This system is formed by filling the catalyst carrier pores with active metal solutions and immersing it in a solution containing active metals. The use of activated carbon as a catalyst carrier using an active metal can increase the selectivity of the catalyst [30]. In this case, the function of the catalyst carrier is to provide a large surface area, so that the process of impregnation would be efficient. Impregnation can be performed when there is no anion or cation that can be exchanged with the active phase [30]. The impregnation steps include (1) contacting the support catalyst with the active phase precursors for a certain period of time, (2) a drying process, and (3) catalyst activation by calcination, reduction, or any other appropriate process.

The objective of this study was to prepare a cobalt-imregnated carbon catalyst for the cracking of used vegetable oil. The effects of the concentration of the active metal solution, the characteristics of the catalysts formed, and the cracking temperature were investigated.

**Materials and Methods**

**Materials.** The materials used in this study were used cooking oil acquired from household waste after three times of cooking and containing 65.02% peak area of long-chain hydrocarbons (C18–C24), 34.48% peak area of hydrocarbons with C12–C18, and the remaining was hydrocarbons with C6–C12; charcoal derived from palm shells; sodium carbonate; acetic acid; cobalt II nitrate hexahydrate; and distilled water.

**Instrumentation.** The instrumentation used in this study included an X-ray diffraction apparatus, a cracking reactor, and other typical laboratory analysis tools such as an analytic balance, a hot plate, a magnetic stirrer, and measurement cylinders.

**Preparation of samples.** Used household cooking oil utilized for frying was filtered using a device assembled from a 2-inch pipe with a mesh and a filter paper. First, 350 g palm shell charcoal was fed into the adsorption column. Then, it was filtered until 660 mL of used cooking oil was obtained. These processes were similar to those developed by Nazarudin et al. [31].

**Catalyst production process.** This process involved the following two steps: (1) charcoal activation and (2) preparation of the active Co-carbon catalyst using an impregnation process.

For charcoal activation, sodium carbonate was mixed with distilled water and then added to the charcoal at a 1:1:1 ratio. The mixture was stirred for 2 h at room temperature, and the solid was filtered and washed with distilled water. Then, the solid was soaked in 25% acetic acid solution for 30 min. Filtration and washing were performed until the pH of the washed solutions was 7 (neutral). The charcoal was then heated in an oven at 105 °C for 4 h.
The active Co-carbon catalyst was then prepared using the impregnation method developed by Nazarudin et al. [7]. Briefly, cobalt nitrate solutions at different concentrations (1%, 2%, and 3%) were prepared in 100 mL of distilled water. The activated charcoal and the nitrate solution were mixed at a ratio of 1:10 and then stirred for 24 h. The solid was then filtered and dried in an oven at 105 °C for 12 h. Calcination was performed at 450 °C for 5 h. The prepared catalysts were analyzed using scanning electron microscopy-energy-dispersive X-ray (SEM-EDX) analysis.

**Catalytic cracking process.** The cracking reactor was charged with the appropriate catalyst, and then the used cooking oil was added into the reactor. The cracking process was performed at 450 °C, 500 °C, or 550 °C for 60 min. The product obtained from the cracking process was sampled every 5 min.

**Results and Discussion**

**Characteristics of activated charcoal.** Surface morphology of the activated palm shell charcoal was analyzed using SEM-EDX. The analysis results are shown in Figure 2.

As shown in the SEM image, the activated charcoal has pores of ca. 1 µm diameter. The morphology of the activated charcoal after modification with Co at concentrations of 1%, 2%, and 3% is depicted Figure 3.

As shown in the images, the diameters of the pores in the Co-modified activated charcoal samples are in the range 2–10 µm. Results of the SEM-EDX analysis showed that the elemental content of each activated charcoal sample was different.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Before Modification</th>
<th>After modification with Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>62.32</td>
<td>84.33</td>
</tr>
<tr>
<td>Co</td>
<td>0.00</td>
<td>6.47</td>
</tr>
<tr>
<td>Si</td>
<td>35.35</td>
<td>8.22</td>
</tr>
<tr>
<td>P</td>
<td>2.14</td>
<td>0.85</td>
</tr>
<tr>
<td>Ca</td>
<td>0.00</td>
<td>0.15</td>
</tr>
<tr>
<td>Mg</td>
<td>0.00</td>
<td>0.18</td>
</tr>
<tr>
<td>Al</td>
<td>0.00</td>
<td>0.13</td>
</tr>
<tr>
<td>K</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

As shown in Table 1, Co was successfully impregnated into the activated charcoal. Due to the unequal pore size of the activated charcoal, the impregnation process did
not show the same trend with the concentration of Co. This implies that the amount of Co impregnated into the activated charcoal was not affected by the concentration of Co.

**Effect of cracking process temperature and Co concentration.** The cracking process was conducted both thermally and catalytically. Thermal cracking was performed at 450 °C, 500 °C, and 550 °C for 60 min, whereas catalytic cracking was performed at the same temperatures with different Co-carbon catalysts. Table 2 summarizes the results of the thermal cracking process.

Table 2. Results of the Thermal Cracking Process

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Used Cooking Oil (g)</th>
<th>Liquid yield (%)</th>
<th>Residue (%)</th>
<th>Gas yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>52.72</td>
<td>35.60</td>
<td>6.64</td>
<td>57.76</td>
</tr>
<tr>
<td>500</td>
<td>52.09</td>
<td>47.14</td>
<td>11.31</td>
<td>41.54</td>
</tr>
<tr>
<td>550</td>
<td>53.13</td>
<td>52.34</td>
<td>2.90</td>
<td>44.76</td>
</tr>
</tbody>
</table>

The results demonstrated that temperature influenced the yield of cracking liquid. The higher the temperature was, the more was the liquid produced. The yield of the cracking liquid was 52.34% at 550 °C, which was greater than those at produced at 450 °C and 500 °C.

In the catalytic cracking process, 1%, 2%, or 3% Co-carbon was used as the catalyst. The results are presented in Table 3.

The results demonstrated that the highest yield of 32.65% was obtained using 1% Co-carbon catalyst at a temperature of 500 °C, whereas the yield was lower at 550 °C. With the 2% Co-carbon catalyst, the yield increased with an increase in temperature. At 550 °C, the yield was 32.21%. Therefore, the concentration of 1% Co-carbon and a temperature of 500 °C were chosen as the optimum cracking process conditions.

Table 3. Results of Catalyst Cracking with Different Co-Carbon Catalyst

<table>
<thead>
<tr>
<th>Co-charcoal concentration</th>
<th>Temperature (°C)</th>
<th>Used cooking oil (g)</th>
<th>Liquid product (%)</th>
<th>Residue (%)</th>
<th>Gas yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3%</td>
<td>450</td>
<td>17,43</td>
<td>17,15</td>
<td>29,89</td>
<td>52,95</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>21,39</td>
<td>27,54</td>
<td>10,66</td>
<td>61,80</td>
</tr>
<tr>
<td></td>
<td>550</td>
<td>27,07</td>
<td>31,14</td>
<td>4,36</td>
<td>64,50</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>24,10</td>
<td>13,94</td>
<td>8,22</td>
<td>77,84</td>
</tr>
<tr>
<td>2%</td>
<td>500</td>
<td>23,69</td>
<td>19,12</td>
<td>16,55</td>
<td>64,33</td>
</tr>
<tr>
<td></td>
<td>550</td>
<td>18,63</td>
<td>32,21</td>
<td>12,88</td>
<td>54,91</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>17,69</td>
<td>12,95</td>
<td>10,01</td>
<td>77,05</td>
</tr>
<tr>
<td>1%</td>
<td>500</td>
<td>20,61</td>
<td>32,65</td>
<td>8,49</td>
<td>58,85</td>
</tr>
<tr>
<td></td>
<td>550</td>
<td>23,17</td>
<td>30,25</td>
<td>4,36</td>
<td>65,39</td>
</tr>
</tbody>
</table>

![Figure 4. Liquid Yield vs. Temperature for Catalytic Cracking](image)
Kinetics study. Figure 5 displays the plots of ln k vs. 1/T for each catalyst. According to the regression analysis, the slope for 1% Co-carbon is 6290.096 and the r value is 0.825. The gas constant is 8.314 J K⁻¹ mol⁻¹, and hence the activation energy (Eₐ) is approximately 52.29 kJ or 16.66 kJ. The slope for 2% Co-carbon is 0.597 and the r value is 0.758, and thus the Eₐ is approximately 16.66 kJ. The slope for 3% Co-carbon is 0.962, and the r value is 0.962, so that the Eₐ is approximately 16.66 kJ. Negative values of Eₐ indicate that the reaction rate decreases with increasing temperature. The Eₐ indicates the minimum energy required for a chemical reaction to occur, and a lower Eₐ indicates a higher reaction rate. From the regression analysis, the lowest Eₐ was provided by the 2% Co-carbon catalyst, implying that this was the best catalyst among the three prepared catalysts for this process. This could be because 2% Co was the maximum Co concentration impregnated into the charcoal; the amount of impregnated Co determined the effectiveness of the catalyst.

Gas chromatography-mass spectrometry (GC-MS) analysis. The GC-MS analysis results (Table 4) showed that the cooking oil used in this study contained longer cha hydrocarbons (C₁₈–C₂₄) than those produced using thermal and catalytic cracking processes.

The highest product yield with the thermal cracking process was that of diesel oil (C₁₂–C₁₈) with 73.76% peak area. The highest product yield with the catalytic cracking process using 1% Co-carbon was that of diesel oil (C₁₂–C₁₈) with 82.59% peak area. In the catalytic cracking process using 2% Co-carbon, the highest product yield was that of diesel oil (C₁₂–C₁₈) with 73.76% peak area. Finally, catalytic cracking using 3% Co-carbon resulted in the highest diesel oil (C₁₂–C₁₈) product yield with a peak area of 84.74%.

Conclusion

In the thermal cracking process, the highest conversion (53.34%) was achieved at 550 °C.

In the catalytic cracking process, the temperature and the Co concentration used in catalyst preparation had a significant influence on the process results. The highest
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liquid oil fraction was obtained by catalytic cracking at 500 °C using 1% Co-carbon, which also provided the lowest $E_a$.

The catalytic cracking process performed using 3% Co-carbon provided the highest diesel oil (C12–C18) product yield.

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