Catalytic cracking of used cooking oil using Chromium impregnated charcoal (Cr-charcoal) catalyst

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Abstract. One of the solutions for fossil fuel crisis is to find alternative energy based on renewable materials. In this research, catalytic cracking of used cooking oil has been investigated to produce biofuel using Cr-charcoal catalyst. The charcoal was produced from solid waste (shell) of palm oil industry. Chromium solutions with various concentrations (1%, 2%, and 3%) were impregnated into charcoal to produce Cr-charcoal catalyst. The catalysts were used for catalytic cracking of used cooking oil at three levels of temperature: 450°C, 500°C and 550°C. The XRD patterns and SEM images of the catalyst showed that the catalyst was in amorphous form. SEM-EDX analysis showed that the Chromium was impregnated into charcoal successfully with amount of Chromium absorbed into charcoal was 0.51%; 1.07% and 14.38% respectively. The SEM images also showed that charcoal as supported catalyst and Cr-charcoal catalyst have unique pores. The highest liquid oil fraction was obtained by catalytic cracking at 500°C using 3% Cr-Charcoal catalyst. The liquid product of this process was mainly diesel oil with 8-24 carbon atoms (86.35%) and the rest was liquid product with 6-7 carbon atoms.

1. Introduction

Waste cooking oil is defined as used vegetable oil obtained after cooking food. Repeated frying food makes the vegetable oil is no longer suitable for human consumption due to high free fatty acid (FFA) content [1-3]. In 2011 the consumption of cooking oil in Indonesia was 7.1 million tons and by 2013 this reached 8.5 million tons [4]. This in turn makes the amount of used-cooking oil also increased. This used-cooking oil can be used as raw material for biofuel production [5-7]. Used cooking oil is derived from crude palm oil (CPO) which consists mainly of triglycerides with long chain hydrocarbon compounds. Used cooking oil is a waste from the food industry and household with non-edible properties, therefore using used cooking oil will not interferes food needs. Heating oil for a long time and at high temperatures causes the formation of solid polymer compounds and the increase in amount of free fatty acids. The characteristics of used cooking oil are dark color and have a specific odor [8-10].
Compared to trans esterification, which converts triglycerides to biodiesel (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 raw materials, triglyceride from biomass sources can be used; and (d) compatibility with existing infrastructure [8, 11-13]. Catalytic cracking is a process to cut the long hydrocarbon chain with the help of a catalyst as a substance to accelerate chemical reactions and improve product quality and quantity [14]. The catalyst that is stable at high temperatures and easily separated from the product is more preferred for catalytic cracking such as heterogeneous catalysts consist of metal with active materials and metal-supported catalysts. For catalyst carrier, activated charcoal is widely used because it is stable in acidic and alkaline environments. Charcoal made from coconut shell is a good material to be processed for activated charcoal due to its large micro pore, low ash content, and high reactivity.

Chromium is a metal that can be used as a catalyst. To obtain a catalyst with wide surface of an active component and easy to use is by dispersing the active component into the carrier [15]. The process of making a catalyst has some important parameters which basically can control various catalyst properties such as precursors, compositions, mixing processes, etc. These parameters have a large economic impact on the economic value of the catalyst, which also affects industrial and environmental applications [16]. The most common methods for catalyst preparation are precipitation or co-precipitation, impregnation, ion exchange, adsorption, and deposition-precipitation methods [16]. Impregnation is the process of total substance saturation by adsorbing precursor salts containing active metal into the catalyst carrier using solution. This system is carried out by filling the catalyst carrier pores with active metal solution through metal adsorption process by immersing catalyst carrier in a solution containing active metals. Fulfillment of activated carbon as catalyst carrier using active metal can increase the selectivity of the catalyst [17].

The objective of this study was to determine the effect of Cr-solution concentration on the characteristic of catalyst and to determine the effect of both cracking temperature and type of Cr-charcoal on liquid yield from catalytic cracking of used cooking oil.

2. Experimental Section

2.1. Materials and Instruments
The materials used in this study were charcoal from palm oil shell, used cooking oil, sodium carbonate, acetic acid, and chromium trinitrate nanohydrate. Analytical instruments used in this study were XRD, cracking reactor, and other laboratory analysis such as analytic balance, hot plate, magnetic stirrer, and measurement glass.

2.2. Procedure

2.2.1. Sample preparation
Used-cooking oil was obtained from 3 times used household frying oil. Used-cooking oil is filtered using an adsorption device assembled from a 2 inches pipe with stainless filter with 200 mesh and filter paper with 100 mesh. The adsorption column was filled with 350 gr palm shell charcoal. Filtering was carried out until 660 ml of clean used-cooking oil was obtained. Experimental filter set up refereed to previous research [18-21].

2.2.2. Catalyst preparation
There are two steps involve in the preparation (1) charcoal activation and (2) impregnation of Cr metal into active-charcoal [22]. Charcoal activation: sodium carbonate, distilled water and charcoal were mixed using 1:1:1 ratio. The mixture was stirred for 2 hours in the room temperature and washed with distilled water. The mixture was then soaked with 25% acetic acid solution for 30 minutes. The filtration and washing process was repeated until pH of rinse solution reached 7. The catalyst was dried in the oven at 105°C for 4 hours. Impregnation of Cr metal into active-charcoal: Chromium Trinitrate Nano-
hydrate solution with various concentrations (1%, 2% and 3%) was produced using distilled water. Activated charcoal and this Cr solution were mixed at a ratio 1:10, stirred for 24 hours, filtered, dried and calcined. The catalyst was characterized using SEM-EDX.

2.2.3. Catalytic cracking
Used-cooking oil cracking using Cr-charcoal catalyst was carried out using ratio catalyst to raw material 1:10. The cracking reactor was filled with a chosen catalyst and used-cooking oil. The cracking processes were carried out at various temperatures: 450°C, 500°C and 550°C for 60 minutes. Product from the cracking process taken every 5 minutes. Experimental semi-batch reactor set-up refereed to previous research [19].

3. Result and Discussion

3.1. Preparation of used cooking oil
High temperature during frying process causes damage in the used-cooking oil chemical structure. The damage can be seen by physical characteristic such as changing colors from yellow to black brownish, increasing viscosity, and increasing the content of free fatty acids. Filtering procedure produced used-cooking oil with clearer appearance than initial used-cooking oil.

3.2. Catalyst characteristics
The activated palm shell charcoal and Cr-charcoal surface morphology were analyzed using Scanning Electron Microscopy and Energy Dispersive X-ray (SEM-EDX). The results are shown in Fig. 1 and Fig. 2. Fig. 1 shows that the activated charcoal has cavities or pores with 1 µm size. The area of pores at activated charcoal with 1% Cr-metal concentration was 17.27 µm², the same with 2% Cr-metal concentration, but at 3% Cr-metal concentration, the area of pores was 95.36 µm². All figures show that the pores sizes in modified activated charcoal using Cr-solution are between 2 – 10 µm. From SEM-EDX analysis, it can be seen that the activated charcoal contain different amount of element (Table 1). This also indicates that Cr-metal was successfully impregnated into the activated charcoal. The highest Cr content is in 3% Cr-solution.

![Figure 1](image1.png)

**Figure 1.** SEM image of activated palm shell charcoal (10,000 times magnification)

![Figure 2](image2.png)

**Figure 2.** SEM image of activated palm shell charcoal after modification using Cr-solution (10,000 times magnification), (a) 1% Cr-solution, (b) 2% Cr-solution, (c) 3% Cr-solution

X-ray Diffraction (XRD) analysis is a method used to identify the crystalline phase in material and to obtain the size of the particles. This analysis can provide qualitative and semi-quantitative data on solids or samples. Based on the the diffraction pattern shown in Fig.3, it can be seen that all catalyst
has the similar pattern with a high enough intensity at 2θ = 21.8°, 21.9° and 26.5°; 21.9°, 26.5° and 36°; 21.0°, 26.5° and 20.8°; 20.83°, 26.62°, 26.51° for charcoal without Cr-metal, 1% Cr-solution, 2% Cr-solution and 3% metal-solution, respectively.

Table 1. The elemental content of activated charcoal before and after modification with 1%, 2% and 3% Cr-solution

| Elements | Before modification | After modified with Cr-solution |
|----------|---------------------|---------------------------------|
|          |                     | 1% | 2% | 3% |
| C        | 63.32               | 97.85 | 79.93 | 70.57 |
| Cr       | -                   | 0.51 | 1.07 | 14.38 |
| Si       | 35.35               | 0.33 | 1.69 | 8.22 |
| P        | 2.14                | 1.06 | - | 3.01 |
| Mg       | -                   | 0.24 | - | - |
| Ca       | 0.2                 | 0.12 | - | 3.83 |
| O        | -                   | - | 17.30 | - |

Figure 3. Diffraction XRD Pattern: Charcoal catalyst (a) without Cr-metal; (b) impregnated by 1% Cr-solution; (c) Impregnated by 2% Cr-solution; (d) Impregnated by 3% Cr-solution

3.3. The Effect of Cracking Temperature and Cr-Charcoal Concentration

Thermal and catalytic cracking were carried out at 450°C, 500°C, and 550°C for 60 minutes. The results of thermal and catalytic cracking process are shown in Table 2. The higher of the temperature in the thermal cracking, the more liquid yield produced. In the catalytic cracking process, Cr-charcoal modified with 1%, 2% and 3% Cr-solution were used as catalyst. There was different effect on the temperature on the amount of liquid yield using these catalysts. Increasing temperature decreased liquid yield when Cr-charcoal modified using 1% Cr-solution was used as catalyst. The opposite occurred when Cr-charcoal catalysts modified using 2% and 3% Cr-solution were used as catalyst and temperature was increased from 450 to 500°C (Table 2), followed with a decreasing liquid yield when temperature increased to 550°C.
Table 2. The result of thermal and catalytic cracking of used cooking oil

| Thermal/Catalyst          | Temperature (°C) | Liquid product (%) | Residue (%) | Gas yield (%) |
|---------------------------|------------------|--------------------|-------------|--------------|
| Thermal Cracking          |                  |                    |             |              |
| 450                       | 35.60            |                    |             |              |
| 500                       | 47.14            |                    |             |              |
| 550                       | 52.34            |                    |             |              |
| Cr-charcoal modified using|                  |                    |             |              |
| 1% Cr-solution            |                  |                    |             |              |
| 450                       | 32.06            | 9.21               | 58.73       |
| 500                       | 22.08            | 4.69               | 73.23       |
| 550                       | 12.94            | 8.46               | 78.60       |
| 2% Cr-solution            |                  |                    |             |              |
| 450                       | 10.19            | 27.52              | 62.29       |
| 500                       | 29.99            | 17.10              | 52.91       |
| 550                       | 24.13            | 3.45               | 72.43       |
| 3% Cr-solution            |                  |                    |             |              |
| 450                       | 17.03            | 18.78              | 64.20       |
| 500                       | 34.59            | 13.89              | 51.51       |
| 550                       | 21.33            | 14.39              | 64.28       |

3.4. Gas chromatography-mass spectrometry (GC-MS) analysis

GCMS analysis result shows that used cooking oil contained 2 to 25 carbon atom with range of molecular weight from 58 to 354g/mol. The detailed result is shown in Table 3. Based on the number of carbon atom, the main product of used cooking oil catalytic cracking was diesel oil (C8 – C24) with 86.35% area.

Table 3. GCMS analysis result for used cooking oil

| No | Number of Carbon | % Area | Molecular Weight |
|----|------------------|--------|------------------|
| 1  | C2               | 1.12   | 60               |
| 2  | C3               | 7.08   | 58               |
| 3  | C4               | 2.14   | 89               |
| 4  | C6               | 2.34   | 86 – 164         |
| 5  | C8               | 1.90   | 110              |
| 6  | C10              | 2.96   | 172              |
| 7  | C11              | 38.26  | 154              |
| 8  | C12              | 5.86   | 168 – 198        |
| 9  | C13              | 6.25   | 180 – 198        |
| 10 | C14              | 3.38   | 196 – 212        |
| 11 | C17              | 6.28   | 270 – 320        |
| 12 | C18              | 8.90   | 250 – 280        |
| 13 | C20              | 9.28   | 310              |
| 14 | C24              | 0.97   | 354              |

4. Conclusion

Cr-metal has successfully impregnated to charcoal catalyst and can be used as an alternative catalyst for catalytic cracking of used cooking oil. The highest Cr-metal impregnated to the charcoal was by using 3% Cr-solution. Both cracking temperature and type of Cr-charcoal influences the catalytic cracking process. The highest liquid oil fraction was obtained by catalytic cracking at 500°C using 3% Cr-Charcoal. The liquid product of this process was mainly diesel oil.
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