Catalytic hydrocracking of Kapuk seed oil (*Ceiba pentandra*)
to produce biofuel using Zn-Mo supported HZSM-5 catalyst

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Abstract. In the present paper Kap uk seed oil (KSO) was considered as a potential biofuel for alternative fuel from inedible oil. Catalytic hydrocracking of Kap uk seed oil using Zn-Mo supported on the HZSM-5 catalyst in a slurry pressure batch reactor at various temperature with reactor pressure in range 10-15 bar. The Zn-Mo/HZSM-5 catalyst was prepared by incipient wetness impregnation. The physicochemical properties of the catalyst were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Brunauer-Emmett-Teller (BET) method. The best catalyst performance on catalytic hydrocracking of KSO using Zn-Mo/HZSM-5 (Si/Al = 25) with loading 2.92%wt for Zn and 7.55%wt for Mo. It displayed the highest hydrocarbon content decarboxylation and/or decarbonylation were 35.51 area% of n-paraffins and the highest content for gasoil-range alkanes was 17.24 area% at 400°C. The liquid product predominant is n-C₁₅, and the second component is n-C₁₇. The catalyst Zn-Mo/HZSM-5 was helpful for the catalytic hydrocracking of KSO for hydrocarbon biofuel production.

1. Introduction

As a results of the rapid economic development, the energy consumption is also growing rapidly. Increasing of energy demands causes declining of fossil oil production for the world and negative environmental issues, such as emission of nitrogen oxides, sulphur oxides, unburned hydrocarbons, and particulate matters [1]. Moreover, global demands for renewable fuel and regulation to reduce consumption of fossil fuel are also increasing. Biofuel, which is composed of various triglycerides, is a type of renewable fuels and an alternative carbon reduction strategy.

Kapuk seed oil (*Ceiba pentandra*) is inedible vegetable oil. This oil is extracted from seeds of *Ceiba pentandra* plant. It grows naturally humid and sub-humid tropical regions. Kapuk seeds make up about 25-28 wt% of each pod with an average potential oil yield of 1280 kg/ha annually. Air dried seeds have typically 58.0% kernel, 3.4% moisture, 28.7% oil and 23.0% protein. *Ceiba pentandra* is one of the most effective CO₂ absorbers [2]. This plant is potential to development of renewable raw materials of biofuel. Nevertheless, it could not be used directly as biofuel because it still contains high oxygen atoms, elevated viscosity, high freezing point, low heating value, and thermal instability [1], [2]. There are several common methods to convert vegetable oil to biofuel, such as transesterification, catalytic cracking and hydroprocessing (catalytic hydrocracking). Catalytic hydrocracking is an effective method to convert vegetable oil to biofuel even though the introduction of hydrogen contributes a portion of the processing cost [3]. The selection of catalyst in the catalytic hydrocracking process is very important. The catalyst type is a bimetal catalyst with supported by HZSM-5. Zeolite HZSM-5 of MFI (Mobile five) structure has hydrophobic site to cracking triglyceride [4]. HZSM-5
has strong acid site, high surface area, appropriate pore diameter and shape selectivity. Metals used as a promote are zinc and molybdenum. The zinc (Zn) metal might promote the hydrogen transfer during the catalytic upgrading of biofuel process and molybdenum (Mo) metal was selectivity a deoxygenation process through the path hydrodeoxygenation process [5]. Further, the use of bimetallic catalyst for catalytic hydrocracking of vegetables oils were investigated.

The main aim of this research is to study catalytic hydrocracking of KSO as potential biofuel for alternative fuel from inedible oil in a slurry pressure batch reactor at various temperatures (300, 325, 350, 375, 400 °C). The effect of Zn-Mo/HZSM-5 catalyst on the product of biofuel, including n-paraffin, the main abundant with hydrocarbon was discussed in this paper. The Zn-Mo/HZSM-5 catalyst was prepared by incipient wetness impregnation. That catalyst was characterized using a variety of techniques, such as Brunauer-Emmett-Teller (BET) method, X-ray diffraction (XRD) and scanning electron microscopy-energy dispersive X-ray (SEM-EDX) for morphology catalyst.

2. Material and Methods

2.1. Raw Material
Kapuk seed oil (KSO) used as raw material in this research was obtained from Pandaan district, East Java Province, Indonesia. Linoleic acid (C18:2) and palmitic acid (C16:0) found in KSO were 78.85% and 21.12%, respectively. It suggested that the composition of KSO was dominated by polyunsaturated fatty acids.

2.2. Catalyst preparation and characterization
A commercial ammonium-ZSM-5 zeolite (a surface area of 425 m²/g, Na₂O of 0.05 wt.% and mole ratio of SiO₂/Al₂O₃ = 80) purchased from Zeolyst International was used as a catalyst support and calcined at 550°C for 5 hours under an air atmosphere to obtain HZSM-5. A double promoted Zn-Mo/HZSM-5 catalyst was prepared by incipient wetness impregnation methods. A zinc nitrate salt is of Zn(NO₃)₂·6H₂O and ammonium heptamolybdatetetrhydrate of (NH₄)₆Mo₇O₂₄·4H₂O purchased from Merck was used as metallic precursors. To obtain Zn-Mo/HZSM-5, in this experiment 0.015 M of zinc nitrate and 1.0318 M of ammonium heptamolybdatetetrhydrate was dissolved in the volume of solution corresponding to the total pore volume of the HZSM-5 support. With the successive impregnation, the solution was poured over 4.75 g of HZSM-5 and stirred for 3 hours to ensure that the attachment to the mouth of HZSM-5 pores to occur. After that, the catalyst was dried at 120°C for 12 hours and calcined at 400°C in a flowing air for 5 hours. Finally, the metal impregnated catalyst was reduced at 450°C for 2 hours in hydrogen atmosphere to obtain an active metal phase.

The phase analysis of Zn-Mo/HZSM-5 catalyst was characterized by X-ray diffraction (XRD). Morphology catalyst, actual metal content and dispersion on zeolite were performed by scanning electron microscopy-energy dispersive X-ray (SEM-EDX). In addition, the total surface area, pore volume and pore size were determined by N₂ adsorption-desorption isotherms at 77K. Prior to measurement, the samples were out gas at 300°C for 3 hours. Brunauer-Emmett-Teller (BET) method was applied to calculate the total surface area. Pore size distribution of catalyst was determined by Horvath-Kawazoe (H-K) method.

2.3. Catalytic hydrocracking of KSO
The catalytic hydrocracking of kapuk seed oil was carried out in a slurry pressure batch reactor (Parr USA 4563) with a mechanical stirrer. The reaction conditions were applied in catalytic test, i.e. reaction temperatures of 300, 325, 350, 375 and 400°C, reaction time of 2 hours, and reactor pressure at the range of 10-15 bar after flowing hydrogen for about one hour. Approximately 0.56 wt.% of the catalyst to KSO (200 ml) were loaded into the reactor. After that, nitrogen was purged into a reactor to remove air that might have been dissolved in oil for twice. After processing for 2 hours, liquid product was collected and analyzed by gas chromatography-mass spectrometry (GC-MS). The liquid product
was considered as hydrocarbon biofuel such as gasoline (C_5-C_{12}), kerosene (C_{10}-C_{13}), and gas oil (C_{14}-C_{22}) [6], [7].

3. Result and Discussion

3.1. Characterization of catalyst

The characterization of catalyst was done by XRD, SEM-EDX and BET methods. The X-ray diffraction patterns of the HZSM-5 catalyst used for catalytic hydrocracking of KSO. The characteristic’s peaks of HZSM-5 at 2θ of 7.87°, 8.74°, 23.04°, 23.24°, 23.91° and 24.31° indicate that HZSM-5 have a framework type MFI. The XRD patterns of catalyst showed small peak intensity at 2θ of 36.0899° for ZnO, while for MoO_2 detected on three main diffraction peak at 2θ i.e. 26.0182°, 36.9332° and 53.3027° as reported by previous study [8]. Molybdenum catalyst can facilitate the hydrodeoxygenation reaction at catalytic hydrocracking triglyceride of KSO [9].

Figure 1a and Figure 1b shows electron microscopy images of the calcined HZSM-5 and Zn-Mo/HZSM-5. The HZSM-5 (Si/Al=25) crystals assemble to uniform small cuboid particle (Figure 1a). The SEM picture of the Zn-Mo/HZSM-5 to show evidence that crystals of Zn and Mo can be impregnation into HZSM-5 (Figure 1b). The presence of Zn and Mo are evidenced by EDX analysis. Based on EDX, Zn and Mo loading was approximately 2.92%wt for Zn and 7.55%wt for Mo.

![Figure 1. SEM image and the corresponding EDX patterns of (a) HZSM-5 obtained from the calcined NH_4-ZSM-5 zeolite, (b) Zn-Mo/HZSM-5 catalyst.](image)

Table 1 shows properties of catalyst from BET analysis. The surface area and total pore volume about HZSM-5 significantly decrease after calcined from 425 m²/g to 375.121 m²/g. The characterization of Zn-Mo was modified in HZSM-5 through impregnation given by analyzes obtained BET surface area of 250.704 m²/g. The addition of metals led to micropore surfaces are and total pore volumes were reduced through blocking.

| Catalyst        | BET surface area, m²/g | Total pore volume, cm³/g | Average pore diameter, nm | Metal contenta, wt.% |
|-----------------|------------------------|--------------------------|--------------------------|----------------------|
|                 |                        |                          |                          | Zn   | Mo   |
| HZSM-5          | 375.121                | 0.2712                   | 2.89                     |       |      |
| Zn-Mo/HZSM-5    | 250.704                | 0.1613                   | 2.57                     | 2.92  | 7.55 |

3.2. Analysis biofuel

Figure 2 shows the GC-MS spectra of kapuk seed oil (KSO) and liquid product produced at 400°C using Zn-Mo/HZSM-5 catalyst. Figure 2a show that the linoleic and palmitic acid from KSO was predominant, so KSO include as polyunsaturated fatty acid. Figure 2b show that the various compounds in biofuel after hydrocracking reaction using Zn-Mo/HZSM-5 catalyst. The first most abundant n-paraffin is pentadecane (n-C_{15}), and the second most abundant n-paraffin is heptadecane.
(n-C\textsubscript{17}). This shows the reaction of decarboxylation or decarbonylation dominated KSO hydrocracking process. The existence of palmitic acid indicates that the process hydrogenation and cracking linoleic acid successfully performed at 400°C using Zn-Mo/HZSM-5. As shown in Figure 2a, some peaks of linoleic acid disappear at retention time of 11-15. After hydrocracking reaction (Figure 2b), palmitic acid and n-paraffin appeared at retention time of 9.6 and in range of 3-8, respectively. The presence of the n-C\textsubscript{15}-nC\textsubscript{19} showed biofuel contained gasoil-like hydrocarbon. It is interesting to study later, compound14-beta-h-pregna and 1,2-Benzisothiazole, 3-(hexahydro-1H-azepin-1-yl)-1,1-dioxidewere detected on biofuel grouped in gasoil-like hydrocarbon at retention time of 10.8-11.6, which corresponding to GC-MS analysis of petroleum diesel [10].

Figure 2. GC-MS spectra of (a) Kapuk seed oil (KSO), (b) liquid product produced at 400°C, using Zn-Mo/HZSM-5 catalyst. Saturated chain hydrocarbons (n-paraffin): C\textsubscript{12} to C\textsubscript{23}.

Figure 3 shows that the effect of reaction temperature on hydrocarbon compounds of liquid product. The hydrocarbon, including n-paraffin, cycloparaffin and aromatic increased with the increasing temperature. A decrease in carboxylic acid of 72.25-36.69 area% with increasing temperature was observed. This indicated that the first of triglycerides were converted into free fatty acids, likely through \(\beta\)-elimination mechanism [11]. The carboxylic acids as intermediate compound according to GC-MS analysis at 400°C, the most abundant hydrocarbon in liquid product during decarboxylation and/or decarbonylation was 35.51 area% of n-paraffins. In addition, a small amount of cycloparaffins and aromatics also found were 2.92 area% and 0.80 area%, respectively. It is implied that has occurred the cyclization and dehydration reaction. It was interesting to be observed that olefin was only found in liquid product produced at 375°C. The olefin was produced via dehydrogenation and/or hydrogenolysis of n-paraffin [12]. When temperature of 400°C was applied, the olefin was not observed. It suggested that the cracking of olefins occurred to produce light hydrocarbon compounds. Analysis of biofuel was compared against the results of GC-MS commercial diesel [10]. The biofuel was identified based on carbon number of hydrocarbon compounds obtained from the GC-MS analysis. It was defined as gasoline-range hydrocarbon (C\textsubscript{5}-C\textsubscript{10}), kerosene-range hydrocarbon (C\textsubscript{10}-C\textsubscript{13}), and gasoil-range hydrocarbon (C\textsubscript{14}-C\textsubscript{22}) [6]. The contents of various hydrocarbon in liquid product over Zn-Mo/HZSM-5 catalyst at the reaction temperature ranging from 300 to 400°C are shown in Table 2. Gasoil-range alkanes produced increased with increasing temperature, as reported in previous study [12, 13]. A decrease in the n-C\textsubscript{30} compound with increasing gasoil-range alkanes was observed at temperature in range of 375-400°C. It implied that the cracking of long chain hydrocarbon molecules into short-chain hydrocarbon molecules occur as reported in previous study [9], [13], [14]. With Zn-Mo/HZSM-5 catalyst, the highest content of gasoil is 17.24 area% at a temperature of 400°C. According gasoil range alkanes, reaction decarboxylation and/or decarbonylation conducted at temperatures above 350°C and prefers to take place at temperatures above 400°C for improving the conversion of carboxylic acids to hydrocarbons. This corresponded with the reported that the decarboxylation and/or decarbonylation reaction was endothermic reaction [10].
Figure 3. Effect of reaction temperature on hydrocarbon compounds of liquid product produced using Zn-Mo/HZSM-5 catalyst. Others were 14-BETA, 1,2-Benzothiazole, 3-(hexahydro-1H-azepin-1-yl)-1,1-dioxide.

Table 2. Contents of various hydrocarbon in liquid product over Zn-Mo/HZSM-5 catalyst

| Temperature (°C) | nC5-nC9 | nC10-nC14 | nC15-nC18 | nC18 | Cycloparaffin, olefin, and aromatic |
|------------------|---------|-----------|------------|------|-----------------------------------|
| 300              | 0       | 0.12      | 0.07       | 0    | 0.36                              |
| 325              | 0       | 0.96      | 1.15       | 0    | 15.33                             |
| 350              | 0       | 0.96      | 1.34       | 0    | 6.71                              |
| 375              | 0       | 7.4       | 15.02      | 2.88 | 11.11                             |
| 400              | 0       | 9.24      | 17.24      | 1.09 | 18.24                             |

*a* kerosene range alkanes  
*b* gasoil range alkanes

4. Conclusion

Inedible kapuk seed oil can be hydroprocessed to produce hydrocarbon biofuel by catalytic hydrocracking using the Zn-Mo/HZSM-5 catalyst in a slurry pressure batch reactor. With the Zn-Mo/HZSM-5 catalyst, the most abundant hydrocarbon in liquid product through decarboxylation and/or decarbonylation was 35.51 area% of n-paraffins, and the highest content for gasoil-range alkanes was 17.24 area% at a temperature of 400°C. The first most abundant compound is n-C15, and the second most abundant component is n-C17. The decarboxylation and decarbonylation are the dominant reaction pathways. The Zn-Mo/HZSM-5 catalyst is an effective catalyst to produce biofuel by hydrocracking of kapuk seed oil, including n-paraffin, the main abundant with hydrocarbon.

5. References

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6. Acknowledgments
The authors would like greatfully acknowledge to the head of chemical reaction engineering laboratory, Department of Chemical Engineering, Faculty of Industrial Technology, Sepuluh Nopember Institute of Technology for the facilities and also thanks for the crews of laboratory, i.e. Varantika Eka Pramesti and Muhammad Faishal Razin.