Selectivity of zinc-molybdenum catalyst to produce gasoil via catalytic hydrocracking of Kapook seed oil (Ceiba pentandra)

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Abstract. Various type of Zinc (3.25 %) Mo (6.34 %) Hz catalysts have been prepared using incipient wetness impregnation method. The catalysts were characterized by X-ray diffraction (XRD), energy dispersive analysis x-ray (EDAX) and Brunauer-Emmet-Teller (BET) method. The performance of the catalysts, Zinc (3.25 %) Mo (6.34 %) Hz was investigated for the catalytic hydrocracking of Kapook seed oil (KSO) to hydrocarbon biofuel in a slurry pressure batch reactor system with a stirrer. The hydrocracking reaction was carried out at reaction temperatures from 300-400 °C and reactor pressure of 15 bar for 2 h under H2 flowing. The effect of reaction temperature on composition of hydrocarbon compounds, n-paraffin, conversion and selectivity in liquid products was studied with a variation of ZincMoHz catalysts. It showed the highest hydrocarbon content decarboxylation and/or decarbonylation were 18.61 area% of n-paraffin and the highest content for gasoil-range alkanes was 10.44 area% obtained at 400 °C. The result show that the Zinc (3.25%) Mo (6.34%) Hz catalyst activity was found that the gasoil fraction which triglycerides where cracked with long carbon double bonds chains over Zinc (3.25%) Mo (6.34%) Hz catalyst.

Keywords: catalytic hydrocracking, gasoil, Kapook seed oil, Zinc-molybdenum.

1. Introduction
One type of vegetable oil that can be utilized to synthesize bio-hydrocarbons is Kapook seed oil (KSO). Kapook (Ceiba pentandra) plant is a tropical plant commonly cultivated in Indonesia. The cottonseeds contain about 20–28 % weight of oil. Under suitable conditions, the kapook plant can produce up to 1.160 kg of seed per hectare per year assuming 25 % oil in the seed. The productivity of kapook oil is about 70 % of the soybean productivity oil. So far, kapook seeds has been treated as wastes. Kapook seed oil is not used as food, mainly due to its low stability [1].

The catalytic hydrocracking process is an alternative process for producing biofuels, because it can convert vegetable oils into hydrocarbons (in particular, C18) using bifunction heterogeneous catalysts. Process of catalytic hydrocracking removes double bonds and carboxyl groups in fatty acids to obtain n-paraffin compounds [2]. The catalytic hydrocracking is the incorporation of catalytic cracking process with the addition of H2 gas. The method is capable of producing biofuels at high temperatures (300–400°C) having high oxidation stability and cetane rates [3]. The catalytic hydrocracking process involves a hydrodeoxygenation reaction as main reaction and decarboxylation as a side reaction [4]. The liquid product generally contains a n-alkane-rich straight chain of C18 through three different reaction stages: decarboxylation, decarbonylation and hydrodeoxygenation [5].

The aim of this study is investigating content of n-paraffin fraction produced by catalytic hydrocracking of Kapook oil at various reaction temperatures i.e. 300, 325, 350, 375 and 400°C using Zinc (3.25 %)-Mo (6.34 %)/HZSM-5 catalyst. The Zinc (3.25 %)-Mo (6.34 %)/HZSM-5 catalyst was prepared by incipient wetness impregnation. That catalyst was characterized in terms of crystallinity,
surface area, composition and morphology, such as Brunauer-Emmett-Teller (BET) method and X-ray diffraction (XRD) for morphology catalyst and energy dispersive X-ray (EDX).

2. Materials and methods

2.1. Raw materials
Kapook oil (KSO) has linoleic acid (C18: 2) and palmitic acid (C16: 0) are the most dominant fatty acids. Linoleic acid (C18:2) and palmitic acid (C16:0) found in Kapook oil were 78.85 % and 21.12 %, respectively [6].

2.2. Catalyst preparation and characterization
HZSM-5 was prepared by calcined ammonium-ZSM-5 zeolite at 550 °C (5 h). For the metal catalyst, a Zn (3.25%)–Mo (6.34%) HZSM-6 catalyst was prepared by incipient wetness impregnation methods. A zinc nitrate salt and ammonium heptamolybdate tetrahydrate by Merck was used as metallic precursors. To obtain Zn (3.25%)–Mo (6.34%) HZSM-5, in this experiment used the different metal loading and different metal ratios were attempted. The volume of the solution of zinc nitrate and ammonium heptamolybdate tetrahydrate is dissolved accord to the total pore volume of the HZSM-5 support. With the successive impregnation, the solution was poured 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 a hydrogen atmosphere to obtain an active metal phase. The method of using the technique has reported in previous studies [6]. Zn (3.25 %)-Mo (6.34 %)/HZSM-5 catalyst was characterized by X-ray diffraction (XRD). 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 and Energy Dispersive X-ray (EDX).

2.3. Catalytic hydrocracking of KSO
The hydrocracking of Kapook oil was carried out in a slurry pressure batch reactor with a mechanical stirrer. The reaction temperature using 300, 325, 350, 375 and 400 °C, the reaction time of 2 hours and flowing hydrogen for about one hour. Nitrogen was purged twice into a reactor to remove air that might have been dissolved in oil for twice. After processing for 2 hours, the liquid product was collected and analysed by gas chromatography-mass spectrometry (GC-MS).

3. Results and discussion

3.1. Characterization of catalyst
The XRD patterns of the HZSM-5 support showed by figure 1. The characteristic’s peaks of HZSM-5 at 2θ of 7.93°, 8.86°, 23.09°, 23.40°, and 24.0° indicate that HZSM-5 have a framework type MFI. The XRD patterns of Zn (3.25 %)-Mo (6.34 %)HZSM-5 catalyst showed small peak intensity at 2θ of 26.94°, 36.97°, 41.32° and 53.55° for MoO, while for Zn detected on 2θ = 38.85° and for ZnO detected at 2θ = 47.38°. That is showed that metals impregnation not change the crystal structure of the zeolite but reduce the intensity of each diffraction peak.

The properties of Zn (3.25 %)-Mo (6.34 %) catalyst showed by BET analysis in table 1. The surface area and total pore volume about HZSM-5 significantly decrease after calcination to 375.121 m²/g. The characterization of Zinc-Mo was modified in HZSM-5 through impregnation given by analyses obtained BET surface area of 251.607 m²/g for Zn (3.25 %)-Mo (6.34 %) Hz. Table 1 shows that the surface area of the Zn (3.25 %)-Mo (6.34 %) HZSM-5 has decreased from the HZSM-5 surface area, but the decrease does not affect the metal side activity of the catalyst. The presence of Mo metal can facilitate the hydrodeoxygenation reaction to protonize n-paraffin.

3.2. Analysis biofuel
GC-MS spectra for liquid hydrocarbon products at 400 °C using Zn (3.25 %) Mo (6.34 %)/HZSM-5 catalyst has been shown in figure 2. GC-MS spectrum of Kapook seed oil has been reported in previous studies [6]. The resulting spectra showed that some linoleic acid disappear at retention time of 11–15 as has been reported in previous studies [6]. Figure 2 shows the formation of variations of compounds contained in hydrocarbon biofuel after catalytic hydrocracking reaction using Zn (3.25 %)
Table 1. The properties of catalyst.

| Catalysts                | BET Surface area, m/g | BET Total pore volume, cm/g | BET Average pore diameter (nm) | Metal content* (wt.%) |
|--------------------------|------------------------|-----------------------------|--------------------------------|----------------------|
| HZSM-5 (Hz)              | 375.121                | 0.2712                      | 2.89                           | -                    |
| Zn-Mo/HZSM-5             | 251.607                | 0.1788                      | 2.84                           | 3.25                 |

* EDX analysis

Figure 1. XRD pattern of (a) HZSM-5 and (b) Zinc (3.25%) Mo (6.34%) Hz.

-Mo (6.34 %) HZSM-5 catalyst. Based on the chromatogram of figure 2, decarboxylation requires a temperature above 400 °C (preferably at a range of 400-500 °C) to maximize the formation of n-paraffin. The hydrogenation reaction is more dominant during the catalytic hydrocracking reaction to the double bond on triglyceride oil of the cotton seed oil at 400 °C. The n-paraffin compounds (nC13-nC19) have been detected already formed at 400 °C. This indicates that the decarboxylation reaction has taken place. The cycloparaffin and aromatics compounds are detected in small quantities to indicate that during the catalytic hydrocracking reaction there has been a cyclization and aromatization reaction in the cottonseed oil.

Figure 3 shows effect of reaction temperature on hydrocarbon compounds of liquid product produced using Zinc (3.25 %) Mo (6.34 %) Hz catalyst. Cyclo-paraffin achieved the highest value (25.42% area) at 325 °C. As temperature increases from 350 to 400 °C, cyclo-paraffin in the form of
cyclohexane rings undergoes cracking into cyclohexane, olefin and paraffin. This is evidenced by increased paraffin from 2% at 350 °C to 14.76% at 375 °C and increased olefin from 3% at 350 °C to 5% at 375 °C. The produced paraffin continues to increase along with the reduction of olefin to a temperature of 400 °C. Indicates that the olefin was thermally and catalytically hydrogenated to paraffin. Aromatic compounds are hardly found in biofuel produced at any reaction temperature, except for temperature 375 °C, aromatics are formed because cyclo-paraffin is dehydrogenated to aromatic. Compounds paraffin began to be detected at a temperature of 350 °C to 2.20% and increased quite high at 375 °C as high as 14.76%. At temperature of 400 °C an increase in the amount of paraffin to 18.61% was observed. From the distribution of hydrocarbons resulting from temperature variations from figure 3, the possibility of reaction pathways hydrocracking oil kapok seed begins with the formation of cycloparaffin, namely (1) hydrogenation of tri-linoleic be tri-oleic, (2) trioleic cracked into oleic acid and decarboxylated into heptadecene, (3) This heptadecene finally undergoes a cyclization reaction to cycloparaffin. Overall, the carboxylic acid decreased with increasing temperature. However, it can be said that the higher temperatures required for cyclization reaction as compared to the deoxygenation of fatty acids. That is because at 375°C, carboxylic acid...
content increases with decreasing the formation of oxygenated compounds. The content of the various hydrocarbons in liquid products by using this type Zn (3.25 %) Mo (6.34 %)/HZSM-5 catalyst at the reaction temperature of 300 to 400°C are shown in table 2.

4. Conclusions
The Zn (3.25 %) Mo (6.34 %)/HZSM-5 catalysts have successfully been prepared using the incipient wetness impregnation method based on the pore volume of the zeolite HZSM-5. The performance of Zn (3.25 %) Mo (6.34 %)/HZSM-5 catalyst type through catalytic hydrocracking process on Kapook seed oil to produce liquid hydrocarbon was potential as it facilitated biofuel production with 18.61 % of n-paraffins alkane of 10.44 % at temperature of 400°C.

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