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Triglyceride of Kapok seed Oil to biofuel over a synthesised Cu-Mo supported HZSM-5 catalyst

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Abstract. In this study, triglyceride of kapok seed (Ceiba pentandra) oil was catalytic hydrocracking (T = 350°C, P = 10-20 bar) to biofuel production using Cu-Mo supported HZSM-5 (Cu-Mo/HZSM-5_51) as the catalyst. The catalyst was synthesized using incipient wetness impregnation. The obtained catalysts were characterized by X-ray diffraction (XRD), and Brunauer-Emmett-Teller (BET) method. The catalytic performance on catalytic hydrocracking of kapok seed oil using CuMo/HZSM-5 with ratio molar for Cu:Mo is 1:1 and loading 5%wt. The catalytic evaluation results indicate that for the employed conditions gasoil was the major product. The biofuel fraction formed consisted of 0.98 area% of gasoline, kerosene range of alkanes as much as 1.55 area% and gas-oil range of alkane as much as 1.14 area% at 350°C over Cu-Mo/HZSM-5_51. Triglycerides of kapok seed oil can be cracked by catalytic hydrocracking process to carboxylic acid as much as 78.78 area% by hydrogenation reaction using Cu-Mo/HZSM-5_51 catalyst. The catalyst is proved to be effective for the conversion triglyceride of kapok seed oil to corresponding biofuel gasoil range.

Key words: catalytic hydrocracking, kapok seed oil, biofuel, Cu-Mo metal transition, HZSM-5 catalyst

Introduction
Energy consumption continues to increase along with increasing population growth. The dominated energy consumption area is the transportation sector that demands the amount of fuel and it is unavoidable in the future. The fossil fuels are the vital source for the transportation sector, but it had caused global issues such as increasing CO₂ emission in the air and that is responsible for the greenhouse effect and global warming. The use of vegetable oil as an alternative source of transportation energy can be promoted by national or international legislation, sustainability, and economic growth. Fuels derived from the biomass lipid fraction are an alternative that is very suitable to replace carbon from fossil fuels for the industrial and transportation sectors [1-3]. The first generation developed from renewable fats from edible oil such as coconut oil, palm oil, soybean,
sunflower etc. But, edible oil has the disadvantage which is a food commodity so that currently renewable fuels from non-edible oil are developed. They are cannot be have as a food. In general, transesterification is used to produce fatty acid methylester (FAME), but from this process also produced as the by-product, glycerol [4].

Vegetable oil that can be used as biofuel one of them is kapok seed oil (KSO). KSO can be used for biofuel production by trans-esterification and, it has high free fatty acid content for the general trans-esterification process using basic homogeneous catalysis. Catalytic hydrocracking of triglyceride of kapok seed oil is an alternative route to makes biofuel. The catalytic hydrocracking process consumes a significant amount of hydrogen. Hydrogen consumption can be reduced by the use of catalysts during the process of catalytic hydrocracking [5].

Most researches work had reported on the production of biofuel from the catalytic hydrocracking of vegetable oils using zeolites [6]. The type of zeolite that is widely used is HZSM-5. HZSM-5 zeolite has a crystalline porous structure, high cracking activity, large surface area and strong acid [6,7]. Zeolite also has hydrophobic properties, namely the ability to crack vegetable oil containing triglycerides [8]. The main product using zeolite HZSM-5 as a catalyst is the dominant aromatic compounds and some poly-aromatic [9]. The acidic site can support the hydrogen transfer reaction. Transition metal (Ni, Cu, Co, Mo etc) on zeolite can support modify the acid and textural properties of the support [6, 10].

The combination of metal site and acid site of HZSM-5 gives a bi-functional characteristic of the catalyst. Cu metal catalyst can provide active hydrogen and is in over of promoting hydrogenation [11,12]. Mo metal catalyst is excellent hydrotreating catalyst [13]. Combination of Cu and Mo transition metals loaded into zeolite can form the bi-functional acidic c’atalyst for catalytic hydrocracking of triglyceride of kapok seed oil to biofuel.

Most research in single promoted using Cu or Mo metals [12]. In the previous study, Cu-HZSM-5 is used for continuous processes for hydrogenation of aromatic aldehydes in fixed-bed reactors. Cu can be relied upon as the main active species for the hydrogenation process to biofuel produce [12]. In this study, a dual promoter focused on the use of Cu-Mo/HZSM-5 catalysts was chose to study triglycerides of kapok seed oil for biofuel with gasoil-range alkanes.

**Experimental methods**

1.1. Material and chemicals
Kapok seed oil content unsaturated fatty acids in the form of linoleic acid and palmitic acid were 78.85% and 21.12% as a majority composition in the previous study [14]. The HZSM-5 zeolite synthesis is made from NH₄-ZSM-5, which was purchased from Zeolyst International. Cu from 98% copper nitrate and Mo from 98% ammonium heptamolybdate tetrahydrate purchased by Merck were used as a metal precursor.

1.2. Catalyst preparation and characterization
NH₄-ZSM5 zeolite (SiO₂/Al₂O₃ = 80), in powder form, was calcined under air at 550°C for 5 hours to obtained HZSM-5, as reported in the previous study [14,15]. The ratio of Cu to Mo used is 1:1 by loading 5% by total weight on the HZSM-5 catalyst. Before impregnation, the incipient wetness volume of support was determined by slowly adding water to 0.5 g of copper nitrate to a solution. A solution of copper nitrate was prepared as the copper precursor. The molybdenum precursor was prepared as same as a copper precursor. The copper precursor solution was slowly adding to HZSM-5 zeolite by the incipient wetness impregnation method while stirring using a magnetic stirrer at 30°C for 3 hours. The catalyst was dried in the oven at 120°C for 12 hours. The catalyst called by Cu/HZSM-5. After that, the molybdenum precursor solution was added to the Cu/HZSM-5 catalyst while stirring using a magnetic stirrer at 30°C for 3 hours too. The catalyst sample was dried in the oven at 120°C for 12 hours. After impregnation, the catalyst was calcinated at 500°C for 5 hours in the air and reduction with hydrogen at 550°C for 3 hours. It is designated as CuMo/HZSM-5_51 catalyst.

The catalyst was characterized by X-ray diffraction (XRD) using XPERT-Pro system apparatus operated at 40 kV, 30 mA, and Cu Kα radiation. The diffraction angle was varied from 10° to 90° at a
scan rate of 10.16 s. The Brunauer-Emmett-Teller (BET) surface area, average pore diameter, and total pore volume were determined from nitrogen adsorption or desorption.

1.3. Catalytic hydrocracking of triglyceride of kapok seed oil

Triglyceride of kapok seed oil via catalytic hydrocracking was carried out in a slurry pressure batch reactor system with a stirrer (PARR 4563) as reported by the previous study \[14-16\]. As much as 200 ml of kapok seed oil is put into the reactor with a Cu-Mo/HZSM-5 catalyst of 1 g. The next step is flowed \(N_2\) gas into the reactor for 5 minutes and stopped the flow to replace hydrogen gas for 1 hour with 10-20 bar. The reaction was carried out at a temperature of 350°C for 2 hours. Liquid products from conversion of kapok seed oil triglycerides were analyzed using Gas Chromatography-Mass Spectrometry (GC-MS) as reported by previous studies. \[14,15\].

Results and discussion

1.1. Characterization of catalyst

The characterization of catalyst was done by X-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET) method. Figure 1 shows the X-ray diffraction pattern of Cu-Mo/HZSM-5 catalyst. The main peak of HZSM-5 zeolite observed at 20 of 22° – 25° with framework type MFI \[16,17\]. After the impregnation process of Cu and Mo metal becomes HZSM-5, the structure of HZSM-5 on the catalyst does not experience significant changes. Cu metal detected a peak at 20 of 43.18° while for Mo metal was detected at peaks at 20 of 37.19° and 41.25°. The XRD pattern also found Cu in CuO detected a peak at 20 of 35.65° and 35.97° while Mo metal in MoO\(_2\) form was detected a peak at 20 of 36.63°, 36.87°, 37.19°, 53.00°, 53.39° and 53.83°.

Table 1 shows the properties of Cu-Mo/HZSM-5 catalyst with 5% metal loading and 1:1 metal ratio to the total weight of HZSM-5 catalyst (Cu-Mo/HZSM-5_51). On the HZSM-5 catalyst, a surface area of 375.121 m\(^2\).g\(^{-1}\) was obtained as reported in a previous study \[15\]. Then, after the impregnation Cu and Mo, the wet impregnation method into HZSM-5 has reduced the surface area to 281.140 m\(^2\).g\(^{-1}\). This is due to the presence of Cu and Mo metal which cover the pores on the catalyst surface.

| Catalyst         | surface area, m\(^2\).g\(^{-1}\) | Total pore volume, cm\(^3\).g\(^{-1}\) | Average pore diameter, nm |
|------------------|----------------------------------|---------------------------------------|--------------------------|
| HZSM-5*          | 375.121                          | 0.2712                                | 2.89                     |
| Cu-Mo/HZSM-5_51  | 281.140                          | 0.1618                                | 1.15                     |

*\[15\]
1.2. Catalytic hydrocracking of triglyceride of kapok seed oil

Figure 2 shows the GC-MS spectrum of catalytic hydrocracking of triglyceride products from kapok seed oil using CuMo/HZSM-5_51 catalyst at 350°C. The fatty acid content of kapok seed oil is dominated by linoleic acid then after catalytic hydrocracking occurs, the carbon chain triglyceride linoleic acid is cracked into palmitic acid by 26.67 area%. At 350°C, the formation of carboxylic acids in hydrocarbon liquid products shows that triglycerides found in kapok seed oil are cracked to free fatty acids (etc. palmitic acid, oleic acid). The formation of free fatty acids in the catalytic hydrocracking process is caused by hydrogenation reactions in the crack chain of triglycerides [16–18]. In addition to free fatty acids, 14.56% of the hydrocarbon compounds have been formed. Olefin detection shows that in the hydrogenation reaction there has been a cyclization reaction simultaneously as has been reported in previous studies [15].

Figure 2. GC-MS spectra of liquid hydrocarbon products using Cu-Mo/HZSM-5_51 catalyst at 350°C

Figure 3 showed that the compounds of liquid hydrocarbon products using Cu-Mo/HZSM-5_51 catalyst at 350°C. The liquid hydrocarbon products are dominated by carboxylic acid as much as 78.78 area%. This shows that unsaturated fatty acids have broken the chain into saturated fatty acids. Cu metal is more selective for hydrogenation reactions when combined with HZSM-5 and has the role of adding acidic side so it is more effective for hydrogenation reactions [12]. And Mo metal leads to the hydrodeoxygenation reaction. Hydrocarbon compounds formed consist of 1.5 area% of n-paraffin, 2.4 area% of the cycloparaffin, 9.79 area% of olefins and 0.76 area% of the aromatic area. This shows that at 350°C it has succeeded in breaking the double chains on the long chain of fatty acids. The presence of 9.79 area% olefins in hydrocarbon liquid products shows that there has been a dehydrogenation reaction from n-paraffin.
Figure 3. The compounds of liquid hydrocarbon products using Cu-Mo/HZSM-5_51 catalyst at 350°C

Table 2 shows the number of variations of biofuel in liquid products in the catalytic hydrocracking process of triglycerides of kapok seed oil using Cu-Mo/HZSM-5_51 catalyst at 350°C. The biofuel fraction formed consisted of 0.98 area% gasoline, the kerosene alkane range was 1.55 area% and the gas-oil alkane range was 1.14 area%. Whereas for the other products formed were classified into cycloparaffin, olefin and aromatic as much as 11.07 area%.

Table 2. Contents of various biofuel in liquid product over Cu-Mo/HZSM-5_51 catalyst at 350°C

| Contents of various hydrocarbon in liquid product (area%) | nC_{5}-nC_{9} | nC_{10}-nC_{14} | nC_{15}-nC_{18} | nC_{>18} | Cycloparaffin, olefin, and aromatic |
|----------------------------------------------------------|----------------|----------------|-----------------|--------|----------------------------------|
| 0.98                                                     | 1.55           | 1.14           | 0.00            | 11.07  |                                  |

\textsuperscript{a}kerosene range alkanes  
\textsuperscript{b}gas-oil range alkanes

Conclusion

A catalytic hydrocracking process for the produced biofuel from triglyceride of kapok seed oil over Cu-Mo/HZSM-5_51 in the slurry pressure batch reactor was established. Cu-Mo/HZSM-5_51 can support hydrogenation reactions. Where HZSM-5 is a catalyst that has strong acidic properties and the acidic side participates in hydrogenation reactions. From the analysis of the liquid product content of biofuel alkane gas-oil range is formed as much as 1.14 area%. Whereas the hydrocarbon content of liquid products is dominated by carboxylic acid as much as 78.78 area%.

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