Effect of cobalt supported on the hierarchical Ni/HZSM-5 catalyst in hydrocracking of Sunan candlenut oil (*Reutealis trisperma* (Blanco) airy shaw)

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**Abstract.** The effect of cobalt supported on the hierarchical Ni/HZSM-5 on conversion, n-paraffin/aromatic selectivity, the degree of hydrocracking and polymerization in hydrocracking of Sunan candlenut oil was investigated. The hierarchical HZSM-5 was obtained through desilication with 0.2 M NaOH solution. The cobalt (Co), nickel (Ni) and Co-Ni supported on hierarchical HZSM-5 catalysts were prepared by incipient wetness impregnation. Desilication and metal impregnation did not change the crystalline structure of HZSM-5 catalyst. Hydrocracking of Sunan candlenut oil into gasoil-range hydrocarbon was tested with the catalysts at a temperature of 400 °C, and a reactor pressure of 15 bar for 2 h under initial hydrogen pressure in a pressured batch reactor. All catalysts reached conversion almost 100%. Non-catalytic hydrocracking contained large amounts of undesired compounds (50%), N-containing compounds around 1 area% and a small amount of compound containing oxygen including ketone (2-heptadecanone) and alcohol (<1%). The addition of cobalt supported on the hierarchical Ni/HZSM-5 improved C15/C16 ratio up to 11, the n-paraffin selectivity up to 78% and decreased polycyclic aromatic hydrocarbons (2-3.7%). Then, N-containing compounds were not detected. The degree of hydrocracking decreased from 0.28 to 0.23. These results indicated that cobalt could control hydrogenation ability of nickel. The presence of cobalt in the hierarchical Co-Ni/HZSM-5 catalyst increased catalytic activity in decarboxylation route to produce the most abundant n-paraffin, i.e. pentadecane (n-C15) and heptadecane (n-C17). Overall, the monocyclic aromatic hydrocarbons selectivity produced for hierarchical pore structure based HZSM-5 catalyst were 15-18%.

**Keywords:** hierarchical ZSM-5, hydrocracking, monocyclic aromatic hydrocarbons, n-paraffin, *Reutealis trisperma* (Blanco) airy shaw.

1. **Introduction**

The transition metals supported on H-ZSM5 showed the increase of catalytic activity due to specific reactions for the production of gasoil range hydrocarbon. According to Stockwell and Lerner [1], the combined cobalt and nickel have potency as hydrocracking catalyst because it has good hydrogenation activity. The addition of Ni metal to the Co/HZSM-5 system can improve the dispersity and reduction of Co particles so that the increase of activity and catalyst stability in the gasoline-range hydrocarbon synthesis process can be reached [2].

It has been proved that the bimetallic supported on HZSM-5 catalysts (microporous structure) significantly increase gasoil-range hydrocarbon yield, i.e. n-paraffin, cycloparaffin, aromatic and
olefin [3–5]. However, different results were obtained on liquid products produced from the hydrocracking of Sunan candlenut oil. According to previous study [6,7], the presence of nickel and cobalt metals distributed on HZSM-5 support in microporous structures produced aromatic compounds in the range of 10-12 area% and n-paraffin around 6.8 % at temperature of 350 °C.

According to the result in previous work [6,8], the effect of cobalt supported on the hierarchical Ni/HZSM-5 on conversion, n-paraffin/aromatic selectivity, the degree of hydrocracking and polymerization and also forming of gasoil-range hydrocarbon (C14-C18) in liquid product produced from hydrocracking of Sunan candlenut oil were studied. In this work, to observe this effect, Co/HZSM-5meso, Ni/HZSM-5meso and HZSM-5meso catalysts were used in hydrocracking of Sunan candlenut oil at 400 °C. Hydrocracking without catalyst was also studied to support this work. Hierarchical pore structure on HZSM-5 was applied in this work because this structure was proved to increase gasoil-range paraffins, as reported in a previous studies [8,9].

2. Materials and methods

2.1. Materials
Sunan candlenut oil was extracted from seeds from fruits collected from Bogor, West Java, Indonesia and afterwards the seeds were pressed with screw press machine to obtain oil. The oil content obtained was about 50 wt.% of dried seeds [8]. As reported in previous studies [6,7], a high content of polyunsaturated fatty acids was found in Sunan candlenut oil and linoleic acid was the main compound.

2.2. Catalyst preparation and characterization
The ammonium-ZSM-5 zeolite was obtained from Zeolyst International (CBV 8014, a surface area of 400 m²/g, Na₂O content less than 0.05 wt.%). The zeolite was calcined at a temperature of 550 °C for 5 h to obtain HZSM-5. Other materials were Ni(NO₃)₂.H₂O and Co(NO₃)₂.H₂O from Merck with ≥98% purity. The hierarchical Co-Ni/HZSM-5 catalyst used in this work had been obtained with a procedure as reported by previous works [8,9]. Furthermore, the detailed characterizations of the hierarchical Co-Ni/HZSM-5 catalyst have been listed in previous report [8,9]. Then, the hierarchical HZSM-5 catalyst obtained was denoted with HZSM-5meso catalyst as support.

2.3. Hydrocracking process
Hydrocracking of candlenut oil was conducted with equipment and procedure described in previous works [3,8]. The reaction temperature was carried out at a temperature of 400 °C for 2 h. In practically, the reaction pressure changed between 10 bar and 15 bar. Liquid products produced were analyzed by gas chromatography-mass spectrometry with procedure reported in a previous study [8]. Equation (1) to equation (4) were used to calculate the catalytic performance. All value was in percentage of an area (area%).

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\text{Conversion, XTg} = \frac{\text{carboxylic acid in feed} - \text{carboxylic acid in product}}{\text{carboxylic acid in feed}} \times 100 \quad (1)
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\text{Paraffin selectivity} = \frac{\text{paraffins yield}}{\text{total hydrocarbon yield}} \quad (2)
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\frac{\text{C}_{15}}{\text{C}_{16}} \text{ ratio} = \frac{\text{yield of C}_{15}}{\text{yield of C}_{16}} \quad (3)
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\text{Degree of hydrocracking} = \frac{\text{yield of C<15}}{\text{total hydrocarbon yield}} \quad (4)
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\text{Degree of polymerization} = \frac{\text{yield of C>18}}{\text{total hydrocarbon yield}} \quad (5)
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3. Results and discussion

3.1. Analysis of biofuel
Figure 1 shows GC-MS chromatogram of a liquid product without catalyst and liquid products produced at 400 °C using Ni/HZSM-5meso catalyst. According to GC-MS chromatogram of Sunan candlenut oil and liquid product produced at a temperature of 400 °C with Co-Ni/HZSM-5meso...
Figure 1. GC-MS chromatogram of (a) liquid product without a catalyst, (b) liquid products produced at 400°C using Ni/HZSM-5meso catalyst, under 15 bar in the batch reactor.

catalyst [8], peaks at retention time of 0–12 min also appeared and indicated the increasing many of hydrocarbon compounds. Nevertheless, the peaks in figure 1a also show the presence of other undesired compounds in the liquid hydrocarbon product (biofuel). This suggested that thermal cracking without catalysts was not capable of directing the deoxygenation of Sunan candlenut oil triglyceride into hydrocarbon compounds as the main compounds in gasoil. It was slightly different. Figure 1b indicates that the presence of nickel metal distributed on the pore/surface of HZSM-5 catalyst was more or less able to direct the reactions that occur during the hydrocracking process so that the number and variation of undesired compounds can be minimized as much as possible. Peaks showing n-paraffin were clearly observed, especially pentadecane and heptadecane, as reported by Marlinda et al. [8].

3.2. Effect of cobalt supported on the hierarchical Ni/HZSM-5 catalyst on performance catalyst

Figure 2 shows hydrocarbon product distribution produced from hydrocracking at 400 °C. The effect of Co supported on Ni/HZSM-5meso was clearly observed. Although hydrocracking of Sunan candlenut oil without catalyst produced n-paraffin of 30 area%, a liquid product still contained the heavy oxygenated compound, i.e. 2-heptadecanone, which is the resultant compound of ketone cracking process obtained from the ketonization of fatty acids. A non-catalytic hydrocracking also contained large amounts of undesired compounds (50 %), N-containing compounds around 1 area% and small amount of compound containing oxygen including ketone (2-heptadecanone) and alcohol (<1 %). The 4-ethylcyclohexene (<0.5) was also found. It shows during hydrocracking of Sunan candlenut oil without catalyst occurred some various reactions, i.e. cyclization and dehydration, as reported by a previous study [7]. It was interesting to be observed. When Ni/HZSM-5meso catalyst was used, carboxylic acid was not detected. It was proved that nickel distributed in HZSM-5meso has enough strong hydrogenation ability if it is compared with cobalt. In addition, when the Co supported on Ni/HZSM-5meso catalyst was used, polycyclic aromatic hydrocarbons (PAHs) decreased from 5.9 to 2.4 area%. Meanwhile, n-paraffin and cycloparaffin increased from 32.5 to 38 area% and from 0 to 2.8 area%, respectively. Undecyl benzene content was corresponding to heptadecane which was appeared, as reported by literature [10]. However, olefin content reached a maximum value for Ni/HZSM-5meso catalyst. The presence of cobalt in the Ni/HZSM-5meso improved cycloparaffin content produced from cyclization of olefin. Based on the GC-MS results, nickel has an important role in hydrogenation reactions to produce olefins. It is known that cobalt has lower hydrogenation ability than nickel. Thus, this large hydrogenation ability of nickel is controlled by cobalt through the cyclization reaction on olefins to form cycloparaffin. It was implied that the presence of cobalt supported on Ni/HZSM-5 can control hydrogenation ability of nickel.
Table 1. Performance of catalysts in hydrocracking of Sunan candlenut oil at 400 °C.

| Catalyst         | Ni/Co weight ratio | Conversion | Paraffin selectivity (%) | Aromatic selectivity (%) | Palmitic acid selectivity (%) | C15/C16 ratio b | Degree of hydrocracking | Degree of polymerisation |
|------------------|---------------------|------------|--------------------------|--------------------------|-------------------------------|------------------|--------------------------|--------------------------|
| Without          | -                   | 98.9       | 78                       | 14                       | -                             | 9.6              | 0.23                     | 0.141                    |
| HZSM-5mesoa      | -                   | 84.7       | 76.6                     | 18                       | 8.8                           | 8.9              | 0.17                     | 0.052                    |
| Co-              | -                   | 96.6       | 84                       | 12                       | 1.99                          | 6.37             | 0.26                     | 0.053                    |
| Ni-              | -                   | 100        | 77                       | 17                       | 0                             | 8.28             | 0.28                     | 0.015                    |
| Co-Ni-a          | 1.65                | 96.5       | 78.3                     | 15                       | 0                             | 11               | 0.23                     | 0.013                    |

a The detailed characteristic of catalyst had been presented [9]
b C15/C16 ratio was used to observe decarboxylation pathway

Figure 2. Hydrocarbon product distribution for various catalyst at 400 °C.

Conversion and n-paraffin selectivity from hydrocracking without catalyst were high enough as shown in table 1. Nevertheless, many contain a variety of undesirable compounds were found in a liquid product produced; correspond with figure 1a. When HZSM-5meso catalyst was used, conversion and n-paraffin selectivity were lower than the others. It indicated that transition metal was needed to hydrogenate triglyceride or carboxylic acid. The presence of cobalt in Ni/HZSM-5meso catalyst improved n-paraffin and C15/C16 ratio up to 78 % and 11 %, respectively. In addition, the degree of hydrocracking and degree of polymerization decreased from 0.28 to 0.23 and from 0.015 to 0.013. The decreasing of hydrocracking degree indicated that hydrocracking activity due to hydrogenation ability of nickel could be controlled by the presence of cobalt. It was the same reason for the degree of polymerization. Overall, the monocyclic aromatic hydrocarbons selectivity produced for hierarchical pore structure based HZSM-5 catalyst were 15–18%.
4. Conclusions
According to the result, the presence of cobalt supported on Ni/HZSM-5 meso catalyst improved n-paraffin content, C15/C16 ratio, the degree of hydrocracking and degree of polymerization. Overall, all catalyst can reach conversion almost 100%. The decreasing of hydrocracking degree indicated that hydrocracking activity due to hydrogenation ability of nickel could be controlled by the presence of cobalt.

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