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Production of Biofuel by Hydrocracking of *Cerbera Manghas* Oil Using Co-Ni/HZSM-5 Catalyst : Effect of Reaction Temperature

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ABSTRACT

This research aims to investigate the effect of various reaction temperatures on the hydrocracking of *Cerbera manghas* oil to produce biofuel as a paraffin-rich mixture of hydrocarbons with Co-Ni/HZSM-5 catalyst. Co-Ni/HZSM-5 catalyst was prepared by incipient wetness impregnation. The catalyst was characterized by X-ray diffraction (XRD), N_2 physisorption according to the Brunauer-Emmet-Teller (BET) method, and atomic absorption spectrometry (AAS). The hydrocracking reaction was carried out in a pressure batch reactor, reaction temperatures of 300-375 ^oC for 2 hours, reactor pressure of 15 bar after flowing H_2 for at least 1 hour, and a catalyst/oil ratio of 1 g/200 ml. The hydrocarbon composition was determined by gas chromatography-mass spectrometry (GC-MS). With the Co(0.88%)-Ni(3.92%)/HZSM-5 catalyst, the highest yield for gasoil was 46.45% at temperature of 350 ^oC. At this reaction temperature condition, the main abundant hydrocarbon compounds in gasoil-like hydrocarbon were n-paraffin, i.e. pentadecane of 20.06 area% and heptadecane of 14.13 area%. Biofuels produced showed that abundant hydrocarbon compounds were different at different reaction temperatures. Iso-paraffin with low freezing point and good flow property were not found in gasoil-like hydrocarbon. Isomerization depends on reaction condition and type of catalyst.

Keywords: hydrocracking, *Cerbera manghas* Oil, Co-Ni/HZSM-5 catalyst, biofuel, n-paraffin

INTRODUCTION

Renewable energy of 17 % in mix targets of the national primary energy 2025 was national energy policy according to Presidential Regulation of Indonesia No. 5/2006. Biofuel has contribution about 5 % of renewable energy. Biofuel can be obtained from vegetable oil, lignocellulosic biomass, algae, and sewage sludge. Furthermore, it can also be obtained from gas to liquid conversion of biomass via Fischer - Tropsch Synthesis (FTS) [1]. Production of biofuel has problems due to the issue of competition between the use of edible vegetable oil as the source of food and that of the fuel. Therefore, the exploration of non-edible vegetable oil as biofeed can be interesting choice as feedstock for conversion into biofuel [2].

Cerbera manghas oil is non-edible vegetable oil because it contains toxic components, namely cerberin. This oil is extracted from seeds of *Cerbera manghas* plant which is part of the ecosystem of mangrove forests. Atabani *et al.* reported that the seed oil content is 54 wt.% and kernel oil content is 6.4 wt.%. Oleic acid of 48.1% is mainly fatty acid of Cerbera manghas oil [2]. Oilcake, the result of pressing process on seed can be made briquettes and compost for fertilizer. This plant is very potential to contribution and development of renewable raw materials. However, it can not be used directly as biofuel because it still contains high oxygen atoms, high viscosity, high freezing point, low heating value, and thermal instability [3].

HZSM-5 has high efficiency to reduce the oxygenated compounds and increase aromatic hydrocarbons yields because HZSM-5 has the acid site, high surface area, shape selectivity and appropiate pore diameter. The addition of the metals including Co and Ni on HZSM-5 catalysts was prepared by incipient wetness impregnation method. Shimura *et al.* reported that nickel with high hydrogenation ability was very effective as the reduction promoter on supported Co catalysts, such as Co/HZSM-5, Co/SiO_2, dan Co/Al_2O_3 [4]. It was very interesting to add double promoter of Co and Ni metals into HZSM-5 support for hydrocracking of non-edible vegetable oil [5,6]. This prepared catalyst is expected to improve the degree of triglycerides hydrocracking and hydrocarbon components when compared to use only one active metal. In this study, Co-Ni/HZSM-5 catalyst was prepared well so that the properties of catalyst obtained can be used to investigate the influence of the reaction temperature in the hydrocracking process of *Cerbera manghas* oil into biofuel. The dominant reactions occurred during hydrocracking are also studied by determining the hydrocarbon compounds by GC-MS analysis. Liquid product is expected to be grouped based on the fraction of gasoline, kerosene and gasoil.

EXPERIMENT

Chemicals

NH_4-ZSM-5 zeolite were taken from Zeolyst International (CBV 8014, a surface area of 400 m^2/g, Na_2O 0.05 wt.%), whilest $Ni(NO_3)_2.6H_2O$ and $Co(NO_3)_2.6H_2O$ was purchased from Merck with 98 % purity.

Procedure and Instrumentation

NH_4-ZSM-5 zeolite was first converted into HZSM-5 through calcination process at 550 °C for 5 hours [7]. Co-Ni/HZSM-5 catalyst was prepared by incipient wetness impregnation method based on literature [7,8]. From BET analysis, it was obtained total pore volume of HZSM-5 was 0.245 cm^3/g. The amount of aqueous metal solution was calculated by using the total pore volume of the support. HZSM-5 as support was dried overnight at 120 ^oC before impregnation. By successive impregnation [8], the amount of an aqueous $Ni(NO_3)_2.6H_2O$ solution of 2.89 M and $Co(NO_3)_2.6H_2O$ solution of 0.72 M were slowly added to the support. After impregnation, the catalyst was kept overnight in a desiccator and dried at 120 ^oC for 12 h. Subsequently, the catalyst was calcined at 400 ^oC for 2 h with air. As reported in a previous study [9,10], the active metal usually exist as a form of metal oxide. Therefore, the metal oxide should be reduced to metallic phase, i.e. Co and Ni using hydrogen at 450 ^oC for 3 h. By atomic absorption spectrometry (AAS), the metals content was 0.88 wt.% of Co dan 3.92 wt.% of Ni of the total catalyst weight. The sample of the catalyst is denoted as Co(0.88%)-Ni(3.92%)/HZSM-5 catalyst. X-ray diffraction (XRD) was used to measure phase analysis and the crystallinity of Co-Ni/HZSM-5 catalyst. XRD diffraction patterns of the catalyst were recorded on $2\theta = 5\text{-}90^o$ using a PANalytical X'Pert PRO X-ray diffractometer with a Cu Ka radiation source operating at 40 kV and 30 mA. The surface area of the catalyst was measured by Brunauer-Emmett-Teller (BET) method on Quantachrome NovaWin Version 10.0 based on the adsorption data with partial pressure (P/Po), range 0095-0297 through recording process of isotherm BET on 5 points. The pore volume was calculated using adsorption model of Barrett-Joyner-Halenda (BJH).

Hydrocracking reaction was conducted under hydrogen initial pressure in a 600 ml batch reactor (Parr Instrument Company 4563) equipped with a mechanical stirrer. According to experimental condition, reaction pressure changed between 10 bar and 15 bar after flowing H_2 for at least 1 hour. The reaction was carried out at a temperature from 300 to 375 °C for 2 hours. *Cerbera manghas* oil of 200 ml and catalysts of 1 g were placed in the reactor. Liquid products were analyzed by gas chromatography-mass spectrometry (GC-MS) with standard GC : Agilent HP 6890 models 19091S-433, HP–5MS capillary column 30 m x 250 µm x 0.25 µm to estimate the relative percentages and distribution of products to their carbon numbers. Biofuel was defined as gasoline-like hydrocarbon (C_5-C_9), kerosene-like hydrocarbon (C_{10}-C_{13}), and gasoil-like hydrocarbon (C_{14}-C_{22}), as reported by Barron *et al.* [11].

RESULT AND DISCUSSION

Cerbera Manghas Oil

Cerbera manghas seeds (Figure 1c) were obtained from *Cerbera manghas* fruits (Figure 1a) that grow in Surabaya, Indonesia. Before they are pressed with a manual hydraulic machine, the seeds were dried in the sun. If *Cerbera manghas* seed was exposed to air, it would change the seed color from white to dark gray and finally brown or black. This observation is consistent with the literature [2]. *Cerbera manghas* oil yellowish-colored liquid (Figure 1d), was analyzed by gas chromatography-mass spectrometry (GC-MS).

GC-MS analysis results indicated that the largest component in *Cerbera manghas* oil contains oleic acid of 76.21 %. The *Cerbera manghas* oil used in this research has a high content of unsaturated carboxylic acids, such as oleic, pentadecylic and linoleic, which is an indication that cerbera manghas oil contains mostly trioleic.

a b c d

Figure 1. *Cerbera manghas* (a) fruit, (b) seeds before skin removed, (c) seeds after skin removed, (d) oil.

Catalyst Characterization

Figure 2 showed the X-ray diffraction patterns of catalyst used for hydrocracking process of Cerbera manghas oil. The X-ray diffraction pattern of HZSM-5 was presented in Figure 2a. The characteristics peaks at the 2θ of 7.9°, 8.8°, 23.09°, 23.31°, 23.69° , 23.9° and 24.4° indicate that HZSM-5 have a framework type MFI. Figure 2b showed that the XRD patterns of Co(0.88%)-Ni(3.92%)/HZSM-5 catalyst were similar to the characteristic structure of the commercial HZSM-5 in Figure 2a. It showed that metals impregnation do not change the crystal structure of the zeolite but reduce the intensity of each diffraction peak, as reported a previous study [12]. The XRD patterns of catalyst showed small peak intensity at 2θ of 31.27°, and 43.29° for the diffraction of Co_3O_4 and NiO respectively as shown in Figure 2b. Shimura *et al.* stated that nickel supported on Co/HZSM-5 can reduce Co_3O_4 and CoO particle into metallic phase of Co [4]. This indicated that Co and Ni were obtained on the support HZSM-5. The result of AAS measurement also proved the existence of cobalt and nickel in HZSM-5.

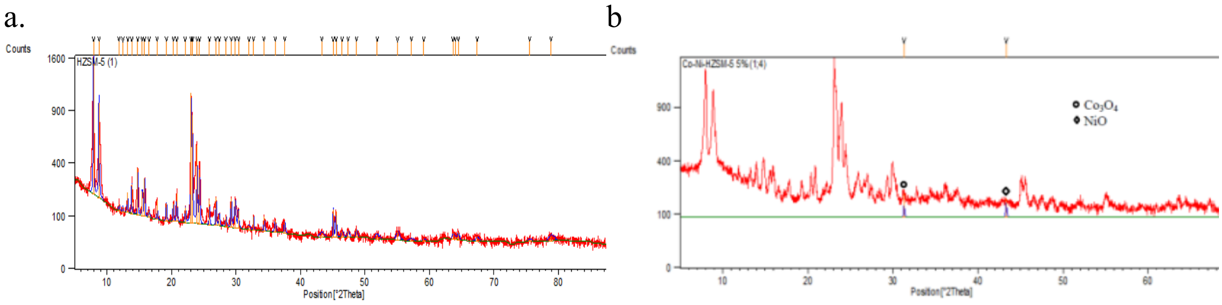


Figure 2. XRD pattern of (a) HZSM-5, (b) Co(0.88%)-Ni(3.92%)/HZSM-5 catal

The surface area, average pore size, and pore volumes of the HZSM-5 support and Co-Ni/HZSM-5 catalyst are listed in Table 1. The HZSM-5 has high surface area of 362.776 m^2/g, while the impregnation of Co and Ni into the HZSM-5 support causes the decrease of surface area and pore volume of Co-Ni/HZSM-5 catalyst. As reported by Vitale *et al.*, these changes indicated that these metals are blocking some micropores and clogging the external mesopores [13].

Table 1. Physical properties of HZSM-5 support and Co(0.88%)-Ni(3.92%)/HZSM-5 catalyst

Sample	BET surface area (m^2/g)	Average pore size (nm)	Pore volume (cm^3/g)
HZSM-5	362.776	2.709	0.245
Co(0.88%)-Ni(3.92%)/HZSM-5	275.297	6.266	0.431

Analysis of Biofuel

GC-MS spectra of cerbera manghas oil and biofuel produced in the various temperature reactions were shown in Figure 3. Figure 3a shows that the compounds with retention time of 10-18 min in the cerbera manghas oil disappear after reaction. Zheng *et al.* reported that triglycerides were converted into short chain molecules by cracking, isomerization, aromatization and cyclization reaction [14]. Figure 3b showed that the amounts of different compounds with retention time of 0-12 min in biofuel increase after cracking reaction. The presence of Co-Ni impregnated in HZSM-5 can hydrogenate unsaturated substances into paraffin compounds.

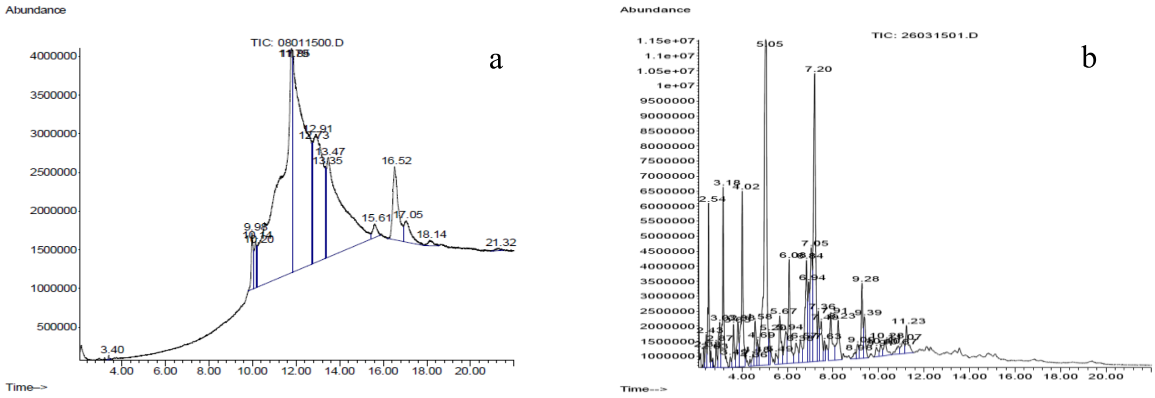
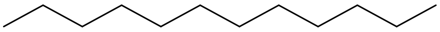
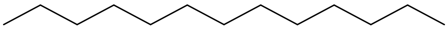
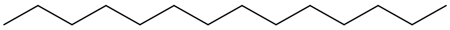
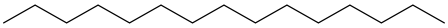
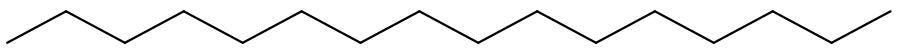
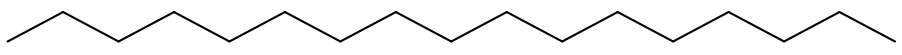
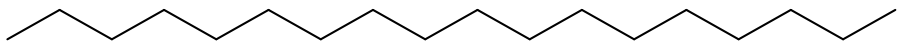
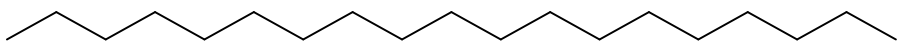
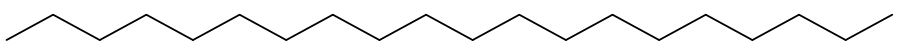
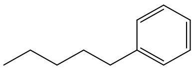
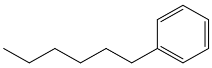
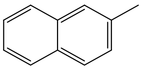
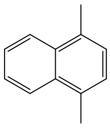
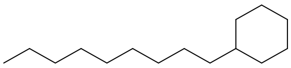
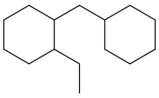
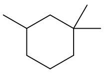
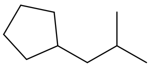
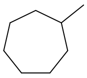
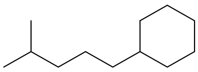
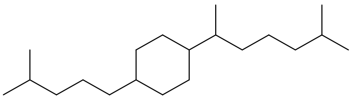
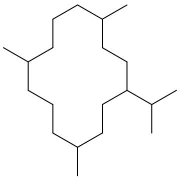
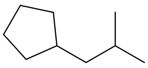
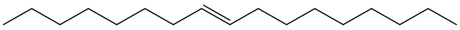
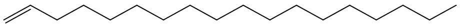
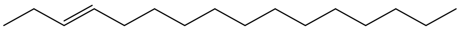
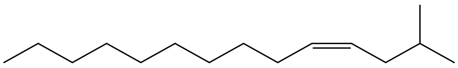


Figure. 3. GC-MS spectra of (a) *Cerbera manghas* oil, (b) biofuel obtained at 350 °C for 120 min using Co(0.88%)-Ni(3.92%)/HZSM-5 catalyst

Table 2. The compounds of biofuel produced using Co-Ni/HZSM-5 catalyst at a temperature of 350 °C, pressure of 15 bar in a batch reactor*)

Compound	Area%	Structure
Saturated chain hydrocarbon		
Dodecane/$C_{12}H_{26}$	3.33	
Tridecane/$C_{13}H_{28}$	5.15	
Tetradecane/$C_{14}H_{30}$	6.03	
Pentadecane/$C_{15}H_{32}$	**20.06**	
Hexadecane/$C_{16}H_{34}$	4.49	
Heptadecane/$C_{17}H_{34}$	**14.13**	
Octadecane/$C_{18}H_{38}$	2.20	
Nonadecane/$C_{19}H_{40}$	2.68	
Eicosane/$C_{20}H_{42}$	0.99	
Aromatic		
n-Pentylbenzen	0.93	
Hexylbenzene	1.55	
2-methylnaphthalen	0.27	
1,4-Dimethylnaphthalene	0.15	
Cycloalkane/Saturated naphthene		
n-Nonylcyclohexane	2.07	
1-(Cyclohexylmethyl)-2-ethylcyclohexane	1.89	
1,1,3-Trimethylcyclohexane	1.44	
Isobutylcyclopentane	1.31	
Methylcycloheptane	0.7	
(4-Methylpentyl)cyclohexane	0.6	
1-(1,5-Dimethylhexyl)-4-(4-methyl pentyl)cyclohexane	0.53	
Cyclotetradecane,1,7,11-trimethyl-4-(1-methylethyl)- / Cembrane	0.34	
Isobutylcyclopentane	0.36	
Olefin/Alkenes		
8-Heptadecene	12.35	
1-Octadecene	1.65	
3-Hexadecene	1.82	
1-Tetradecene	1.59	

2-Methyl-Z-4-tetradecene	1.33	

*Adopted from table format in literature [14]

The GC-MS analysis of the chemical composition of hydrocarbons is shown in Table 2. The results show that biofuel composition consists of 89.98 area% of the hydrocarbons, i.e. 59.1 area% of n-paraffin, 9.24 area% of cycloparaffin, 18.74 area% of olefin, and 2.9 area% of aromatics, and 9.51 area% of oxygenated compounds that includes carboxylic acids of 2.33 area%. The oxygenated compounds including carboxylic acid show that the hydrodeoxygenation takes place at temperatures above 350^{o}C. The increasing temperatures will lead to improve the activity of hydrocracking and help to cleavage a long chain of hydrocarbon molecules of biofuel produced into a short chain hydrocarbon molecules as reported in previous study [3,9,14].

The results of analysis of biofuel compared to the results of GC-MS commercial fuel sold to the public refueling unit [15]. The product was identified based on a hydrocarbon fraction obtained from the GC-MS analysis. It was defined as gasoline-like hydrocarbon (C_5-C_9), kerosene-like hydrocarbon (C_{10}-C_{13}), and gasoil-like hydrocarbon (C_{14}-C_{22}). Gasoline/kerosene/gasoil yields for the liquid hydrocarbon product produced using Co-Ni/HZSM-5, at reaction temperature ranging from 300 to 375 ^{o}C are shown in Figure 4. Yield of gasoil produced increases with increasing temperature, as reported in previous study [9,16]. The increasing reaction temperature causes gasoil increase because of abundant main component, i.e. pentadecane (C_{15}) and heptadecane (C_{17}). With the Co(0.88%)-Ni(3.92%)/HZSM-5 catalyst, the highest yield for gasoil was 46.45% at temperature of 350 ^{o}C. The decarboxylation/decarbonylation reaction conducted at temperatures above 300 °C.

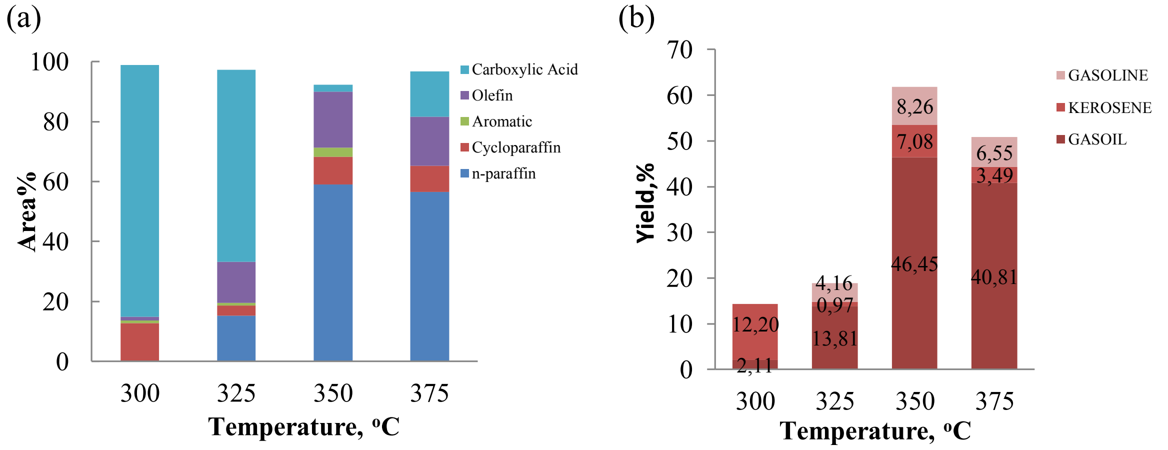


Figure. 4. Effect of reaction temperature on (a) hydrocarbon compounds, (b) gasoline/kerosene/gasoil yields of biofuel profuced using Co(0.88%)-Ni(3.92%)/HZSM-5 catalyst

CONCLUSION

At a temperature of 375 ^{o}C, n-paraffin content in gasoil was more than 40 area% with the Co(0.88%)-Ni(3.92%)/HZSM-5 catalyst. With the Co(0.88%)-Ni(3.92%)/HZSM-5 catalyst, the highest yield for gasoil was 46.45% at temperature of 350 ^{o}C. At this reaction temperature condition, the main abundant hydrocarbon compounds in gasoil were n-paraffin, i.e. pentadecane of 20.06 area% and heptadecane of 14.13 area%. The most abundant component is n-C_{17} and the second most abundant component is n-C_{15} if decarboxylation and/or decarbonylation are the dominant reaction pathways. Co-Ni/HZSM-5 catalyst is an effective catalyst to produce biofuel by hydrocracking of Cerbera *manghas* oil, including n-paraffin, the main abundant of hydrocarbon.

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