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Co-Ni/HZSM-5 Catalyst for Hydrocracking of Sunan Candlenut Oil (*Reutealis trisperma* (Blanco) Airy Shaw) for Production of Biofuel

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ABSTRACT

The production of biofuel by hydrocracking of Sunan candlenut oil as renewable energy can substitute fossil energy. The purpose of this work is to produce biofuel by hydrocracking of Sunan candlenut oil with Co-Ni/HZSM-5 catalyst. The catalyst was prepared by incipient wetness impregnation method. The characterization of catalyst was determined by X-Ray Diffraction (XRD) and nitrogen adsorption-desorption isotherms. The functional groups of the hydrocarbon was determined by Fourier Transform Infrared (FT-IR). The hydrocarbon composition was determined by Gas Chromatography Mass Spectrometry (GC-MS). The results showed that biofuel composition consist of 0.14 area% isoparaffins, 12.29 area% cycloparaffins, 6.87 area% normal paraffins, 4.18 area% olefin, and 10.52 area% aromatics, and oxygenated compounds including 35.03 area% carboxylic acids. It was necessary to be done that the oxygenated compounds in biofuel were eliminated to produce the abundant paraffin hydrocarbons at reaction temperature above 350 °C.

Keywords: hydrocracking, Sunan candlenut oil, Co-Ni/HZSM-5 catalyst, aromatic, biofuel

INTRODUCTION

Nowadays, the production and consumption of fossil fuel has led to the increasing of carbon dioxide (CO_2) emissions and the environment issue. This is the main factor causing the greenhouse effect. Therefore, it needs a way to develop the alternative energy sources as useful fossil fuel substitutes and reduce greenhouse gas. In this scope, biofuel has been proposed as an alternative energy to substitute the fossil fuels. The renewable energy sources as fuel can be derived from biomass and vegetable oils such as soybean oil, palm oil, waste cooking oil, sunflower oil, Jatropha oil, cotton seed oil which have been intensively studied in recent years. The vegetable oils are very promising to utilize the renewable raw materials for producing biofuel [1].

Sunan candlenut oil included in the non-edible vegetable oil is one of the most potential feedstock for biofuel production because its seed contains high oil yield of 50%, which can be converted to good quality biofuel. Previous study investigated that transesterification of vegetable oils with methanol has applied as the method to produce fatty acid methyl esters (FAMEs) known as biodiesel. Although the transesterification process occurs at a temperature of 65°C, the FAMEs still contain an excess of oxygen atoms in the form of carbonyl group so that they have unfavorable properties as a fuel such as poor energy density and oxidation stability compared to petroleum fuel [2]. FAMEs damage seals and cause plugging on the fuel system. When FAMEs are stored, they tend to form sludge and deposite [3]. FAMEs is also known as the oxygenated biofuel. Hydrocracking with bifunctional heterogenous catalyst, the one of the alternative methods for produce oxygenate-free biofuel is expected to convert vegetable oils into hydrocarbons (C_{15}-C_{18}). Hydrocracking reaction needs a higher temperature (300-400^oC) to crack vegetable oils into hydrocarbons, comparing with transesterification to produce FAMEs [2,4].

Several previous studies have applied hydrocracking of the various types of non-edible vegetable oil at a temperature and pressure with the different types of catalysts. The HZSM-5, γ-Al_2O_3, and Mg-Al hydrotalcite based catalyst have been applied. The HZSM-5 zeolite has high efficiency to reduce the oxygenated compounds and increase aromatic hydrocarbons yields because of acid site, high surface area, shape selectivity and appropriate pore diameter. Transition metal-modified HZSM-5 were applied to enhance catalyst activity. Nickel was favored and distributed on various support to be applied in hydrocracking of vegetable oil. Nickel contributed in hydrogenation of a double bond at triglycerides to a single bond. The addition of the two metals as a promoter is also prefered to increase the catalyst activity in the hydrocracking of triglycerides.

Nickel was successfully distributed on hydrotalcite, as reported by Hafshah et al. When the Ni(7.56)/Hydrotalcite catalyst was used in hydrocracking of *Calophyllum inophyllum* oil at temperature of 350 ^oC and pressure of 15 bar for 2 h, the obtained hydrocarbon compounds were gas oil of 54.88 area% in the range of C_{15}-C_{18}. The oxygenated compounds containing carboxylic acid of 4.16 area% were found [5]. Marlinda et al. reported that n-C_{15} and n-C_{17} were the main abundant hydrocarbon compounds in biofuel produced through hydrocracking on *Cerbera manghas* oil at temperature of 350 ^oC and pressure of 15 bar for 2 h with Co(0.88)-Ni(3.92)/HZSM-5 catalyst. Decarboxylation/decarbonylation was proceed well because carboxylic acids of 2.33 area% were found [6]. As reported by Savitri et al., hydrocracking on *Calophyllum inophyllum* oil with NiMo/H-Zeolite catalyst, at temperature of 350 ^oC and pressure of 60 bar for 2 h produced n-paraffin of 90.89 area% in the range of C_{10}-C_{19}. Carboxylic acids of 5.21 area% were found. Hydrocracking still applied high pressure with zeolite as natural minerals [7]. When Ni/HZSM-5 catalyst was used in the catalytic hydroprocessing on FAMEs, the increasing temperature of 260-280^oC will increased n-paraffin (C_{17}-C_{18}) and isoparaffin (C_5-C_{16}) [2]. Iliopoulou et al. reported that when the different transition metal-modified ZSM-5 zeolite was used in biomass pyrolysis, all metal-modified catalyst enhanced the aromatics and phenols production[8].

Vichapund et al. reported the catalytic fast pyrolysis of Jatropha waste with HZSM-5 and metal (Co, Ni)-HZSM-5. From the result, the effect of metals on the HZSM-5 increased aromatic hydrocarbons as well as the decrease in the oxygenated and nitrogen-containing compounds. Both of Co/HZSM-5 and Ni/HZSM-5 catalyst promoted the production of aliphatics. The Ni/HZSM5 catalyst showed the highest hydrocarbon yield of 97%. The yields of aromatic hydrocarbon increased rapidly up to 87.85%, 85.19% and 85.97% for HZSM-5, Co/HZSM-5, and Ni/HZSM-5 [9]. The purpose of metal impregnation into the zeolite framework is to improve the catalyst activity in terms of eliminating the oxygenated compounds, increasing aromatic hydrocarbons yields and reduce the formation of coke during hydrocracking [10].

The aim of this work is the hydrocracking of Sunan candlenut oil with Co-Ni/HZSM-5 catalyst in pressured batch reactor to produce biofuel containing hydrocarbons which are similar to petroleum diesel. Through this work, the potential non-edible vegetable oil for producing second-generation biofuel can be explored.

EXPERIMENT

Chemicals

Cobalt(II) nitrate hexahydrate ($Co(NO_3)_2.6H_2O$) and nickel(II) nitrate hexahydrate $Ni((NO_3)_2.6H_2O$ with 98% purity were purchased from Merck. NH_4-ZSM-5 catalyst was purchased from Zeolyst International, USA (SiO_2/Al_2O_3, Mole Ratio: 40).

Procedure and Instrumentation

NH_4-ZSM-5 zeolite was converted into HZSM-5 through calcination process at 550 °C for 5 hours [6,11]. Then, Co-Ni/HZSM-5 catalyst was prepared by a procedure based on the incipient wetness impregnation step previously [6] with the designed concentration of aqueous metal solution. Before impregnation, HZSM-5 as support was dried overnight at 120 ^oC. The HZSM-5 zeolite was impregnated with an aqueous solution of $Co(NO_3)_2.6H_2O$ and $Ni(NO_3)_2.6H_2O$ at room temperature and kept in a desiccator for 12 h. After impregnation, the catalyst was dried at 120 ^oC for 12 h. The catalyst was calcinated at 400 ^oC for 2 h with air. In the reduction process, metal oxide was reduced at 450 ^oC for 3 h with hydrogen. The metal oxide should be reduced to obtain an active metallic phase, i.e. Co and Ni, as reported in previous study [12,13]. The metals content measured by atomic absorption spectrometry (AAS) was 3.55 wt.% Co and 3.30 wt.% Ni of the total catalyst weight. X-ray Diffraction (XRD) was used to determine the crystalline structure and phase analysis of the catalyst. Catalyst was measured in the 2θ range from 5^o to 90^o. Measurement was performed using a PANalytical X'Pert PRO X-ray diffractometer with a Cu Ka radiation source operating at 40 kV and 30 mA. Nitrogen adsorption-desorption isoterms were conducted in 77 K on a Quantachrome instrument to obtain the BET surface area and pore volume of the catalyst. Before measurement, the catalyst was outgassed at 300^{o}C for 3 h. The BET surface areas were calculated using the BET method and Horvath-Kawazoe (HK) method was used to calculate pore size distribution.

By using a batch reactor as reported by previous study [6], hydrocracking of Sunan candlenut oil was conducted under initial hydrogen pressure at a temperature of 350 ^oC for 2 h with reactor pressure of 10 bars. After Sunan candlenut oil of 200 mL and catalyst of 1 g were placed in the reactor, nitrogen was flowed into reactor about twice to remove oxygen. With procedure in literature [6], the estimation of relative percentages and distribution of products to their carbon numbers were determined by gas chromatography-mass spectrometry with standard GC : Agilent HP 6890 models 19091S-433, HP–5MS capillary column 30 m x 250 µm x 0.25 µm. Chemical bond and functional groups of liquid product were determined by Fourier Transform Infrared (FT-IR) spectra recorded in the wavenumber range 500–4000 cm^{-1} with Thermo Scientific Nicolet iS10. The liquid product was identified based on hydrocarbon fraction from GC-MS analysis. The result from GC-MS compared to the GC-MS result of commercial fuel from the refueling public [14]. It was divided into three fraction such as gasoline-like hydrocarbon (C_5-C_9), kerosene-like hydrocarbon (C_{10}-C_{13}), and gasoil-like hydrocarbon (C_{14}-C_{22}) [6,13]. By using the Wiley275 and NIST02 mass spectral library of data, all hydrocarbon compounds were identified. With a probability match equal to or higher than 80% were considered to determine the hydrocarbon compounds.

RESULT AND DISCUSSION

Catalyst Characterization

The XRD patterns of the HZSM-5 and Co-Ni/HZSM-5 catalysts were shown in Figure 1. The main peaks of HZSM-5 zeolite were observed at 2θ of 7.87^o, 8.7^o, 23.03^o, 23.64^o, 23.9^o, and 24.3^o which were in the range of specific peaks of HZSM-5 at 2θ of $7\text{-}9^o$ and 23-

25° as shown in Figure 1(a). It suggested that HZSM-5 have a framework type MFI. This result was similar to previous study [6,15]. After impregnation metals into the HZSM-5, structure of Co-Ni/HZSM-5 catalyst was still similar to HZMS-5 as reported also by Vichaphund et al. [10] with different metals. From the angle range ($2\theta = 5 - 90°$), the small metals peaks were detected. The diffraction peaks of cobalt oxide phase were observed at 2θ of 19.19°, 31.34°, and 36.16°. The nickel oxide phase and metallic phase of nickel were observed at 2θ of 37.56° and at 2θ of 52.01°, respectively. However, in Figure 1(a) and (b) the peak intensities of Co-Ni/HZSM-5 catalyst were lower than HZSM-5. According to Vichaphund et al. [10], the metals impregnated into HZSM-5 decreased the degree of crystallinity (%). By atomic absorption spectrometry, the actual metals content on HZSM-5 was found, i.e cobalt of 3.55 wt.% and nickel of 3.30 wt.%. This values were in the range of initial total metal content of 5 wt.%. This indicated that Co and Ni were detected on the HZSM-5 support.

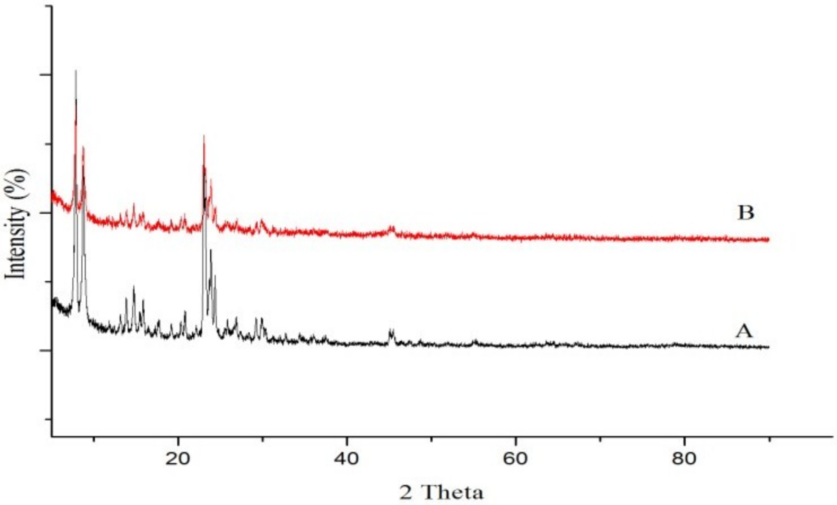


Figure 1. XRD patterns of (A) HZSM-5, (B) Co-Ni/HZSM-5

Table 1 lists the surface area, average pore size, and pore volume of HZSM-5 and Co-Ni/HZSM-5 catalysts. After impregnation by Co and Ni into HZSM-5, the surface area and pore volume of HZSM-5 decreased from 355.967 to 223.140 m^2/g and from 0.22 to 0.15 cm^3/g, respectively. According to Chen et al. [2], the internal Ni particles can block a portion of micropores of HZSM-5. It also indicated that the metal particles were well dispersed into pore and surface of HZSM-5, as reported by previous study [6,10].

Table 1. Physical properties of HZSM-5 and Co-Ni/HZSM-5 catalysts

Sample	**BET surface area (m^2/g)**	**Average pore size (nm)**	**Pore volume (cm^3/g)**	**Element (wt.%)**	
				Co	**Ni**
HZSM-5	355.967	2.4904	0.2216	-	-
Co-Ni/HZSM-5	223.140	2.7136	0.1514	3.55	3.30

Analysis of Biofuel

Figure 2 show the analysis of the oxygen atoms in liquid product by FT-IR. The band in 1680-1750 cm^{-1} region of –C=O stretching is attributed to compounds containing carbonyl group, i.e esters and acids. As shown in Figure 2(b), the bands in 1707.60 cm^{-1} and 1743.74 cm^{-1} were detected with the lower intensity, compared to the same band region in Figure 2(a).

It implied that the oxygen removal occured during hydrocracking. The bands in 3000-2800 cm^{-1} region of C-H streching are attributed to hydrocarbon located at 2921 cm^{-1} and 2852 cm^{-1}, as presented in Figure 2(b). The presence of oxygen in alcohols and ethers was still found in the 1200 – 1100 cm^{-1} region of C-O streching located at 1160.46 cm^{-1} with lower intensity. However, the reaction temperature above 350 °C was required to decrease the oxygenated compounds such as carboxylic acids, esters, ketones, alcohols, and ethers from liquid product, as reported in a previous study [4,10,16].

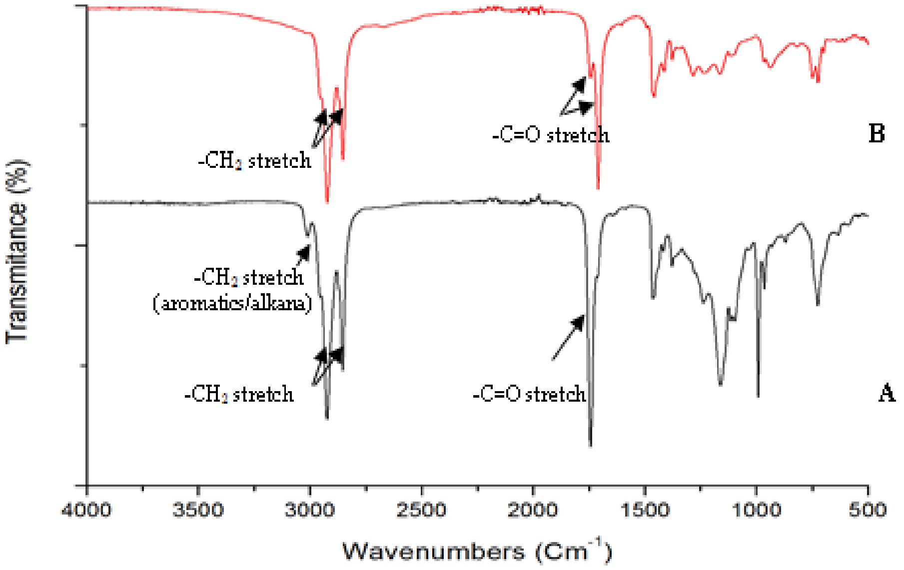
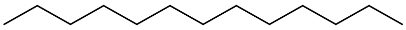
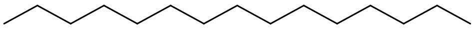
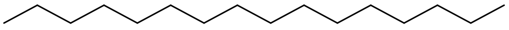
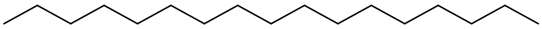
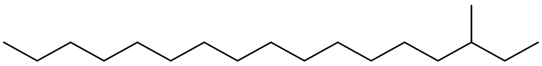
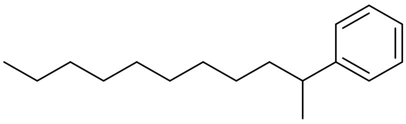
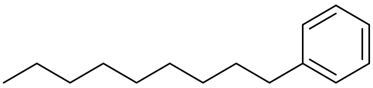
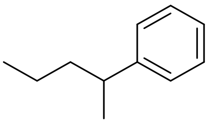
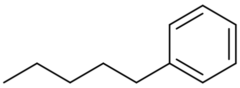
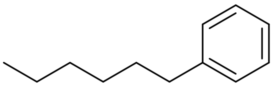
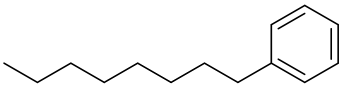
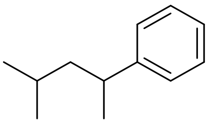
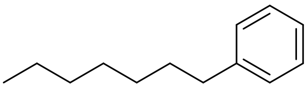
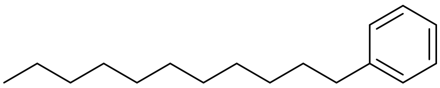
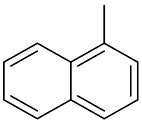
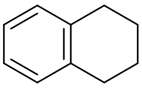
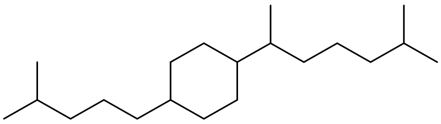
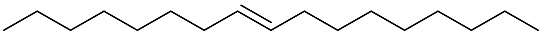


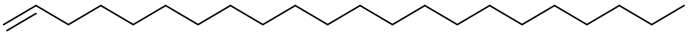
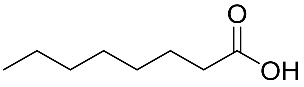
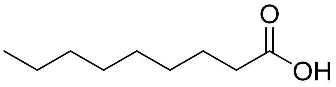
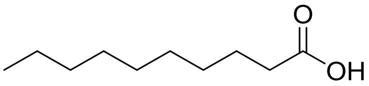
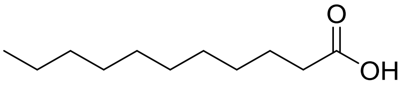
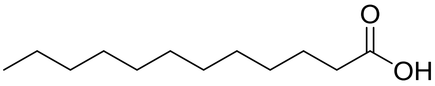
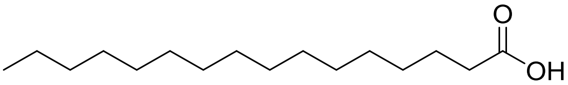
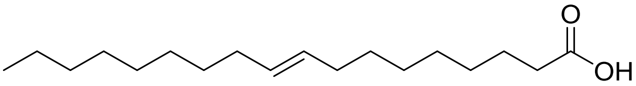
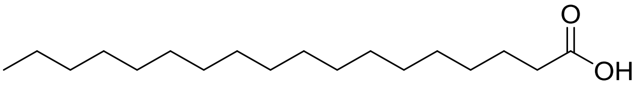
Figure 2. FT-IR spectra of (A) Sunan candlenut oil and (B) liquid product produced at 350 °C under 10 bar

The GC-MS analysis of hydrocarbon compounds was shown in Table 2. The results showed that the liquid product composition consisted of 34 area% hydrocarbons (i.e. 0.14 area% isoparaffins, 12.29 area% cycloparaffins, 6.87 area% n- paraffins, 4.18 area% olefins, and 10.52 area% aromatics), and oxygenated compounds including 35.03 area% carboxylic acids. The presence of oxygenated compounds including carboxylic acids showed that the cracking occured at temperature above 350 °C to produce hydrocarbon compounds such as n- and iso-paraffin, cycloparaffin and aromatic. The increasing temperature will improve the catalytic activity in hydrocracking reaction and contributed to cleavage a long chain of hydrocarbon molecules in liquid product into a short chain hydrocarbon molecules, as reported in previous study [6,17]. According to Chen et al., high temperature was favored by decarboxylation/decarbonylation because these reaction routes are endothermic reactions and isomerizations. The conversion of the branched long paraffins into light paraffins easily occurred at high temperature [2].

Table 2 The compounds product of liquid produced using Co-Ni/HZSM-5 catalyst at a temperature of 350 °C, pressure of 10 bar in a batch reactor

Components/Formula	Area%	Retention time (RT)	Structure
Normal Paraffin			
Tridecane/$C_{13}H_{28}$	0.3	3.05	
Tetradecane/$C_{14}H_{30}$	0.2	3.86	
Pentadecane/$C_{15}H_{32}$	3.74	4.82	
Hexadecane/$C_{16}H_{34}$	0.18	5.85	

Heptadecane/$C_{17}H_{36}$	2.45	6.92	
Isoparaffin			
3-Methylheptadecane	0.14	9	
Aromatic			
(1-methyldecyl) benzene/ $C_{17}H_{28}$	4.9	7.05, 7.13, 7.25	
Nonylbenzene/$C_{15}H_{24}$	0.48	5.66	
(1-methylbutyl)benzene	0.81	2.4	
Pentylbenzene/ $C_{11}H_{16}$	0.64	2.34	
n-hexylbenzene/$C_{12}H_{18}$	0.52	2.9	
1-methyl-2-n-hexylbenzene/$C_{13}H_{20}$	0.25	3.73	
n-octylbenzene/ $C_{14}H_{22}$	0.4	4.61	
1,3-dimethylbutylbenzene/ $C_{12}H_{18}$	0.31	2.96	
n-heptylbenzene/$C_{13}H_{20}$	0.62	3.67	
n-undecylbenzene/ $C_{17}H_{28}$	0.65	7.86	
2-phenyl-3-propyl hexane	0.64	5.72	
1-methylnaphthalene	0.1	3.44	
1,2,3,4-tetrahydronaphthalene	0.2	2.45	
Cycloparaffin			
1-(1,5-dimethylhexyl)-4-(4-methyl pentyl) cyclohexane	12.29	6.54, 11.72	
Olefin			
8-heptadecene	3.73	6.71, 6.77	

1-docosene	0.45	14.28	
Carboxylic acid			
Octanoic acid	1.8	2.26	
Nonanoic acid	1.47	2.79	
n-Decanoic acid	1.87	3.54	
Undecanoic acid	0.61	4.44	
Dodecanoic acid	0.5	5.45	
n-hexadecanoic acid	13.88	9.59,9.76, 10.01, 10.82,11.03	
9-octadecenoic acid	14.8	11.11,11.56, 11.90	
9,12-octadecadienoic acid	0.1	7.37	

As reported by previous study [6], with the different metal loading of Co-Ni/HZSM-5 catalyst hydrocracking of *Cerbera manghas* oil produced n-paraffin of 59.1 area% and aromatic of 2.9 area% at the same temperature and pressure in this work. Oleic acid were predominant in the composition of *Cerbera manghas* oil. In this work, hydrocracking of Sunan candlenut oil had linoleic acid as the most abundant fatty acids produced aromatics of 10.52 area% in liquid product. As also stated by Rabaev et al., when Pt/Al_2O_3/SAPO-11 catalyst was used, the formation of aromatics were affected by the presence of the polyunsaturated fatty acid in vegetable oil. The aromatics content in liquid product produced by hydroprocessing of sunflower oil and palm oil was 15.5 wt.% and 1.7 wt.%, respectively [18]. From the result, the type of catalyst and metal loading on support catalyst also affected the formation of hydrocarbon. A certain amount of nickel and hydrogen are also considered to hydrogenate the double bond in triglycerides to obtain the abundant paraffin compounds. However, the catalytic hydroprocessing can be inhibited by a higher hydrogen pressure.

In this work, in liquid product short-branched isomeric paraffins, i.e 3-methylheptadecane, was found in small amount. However, it indicated that in hydrocracking reaction methyl alkanes can pass through the catalyst because their molecular size is smaller than the micropore diameter, as reported by Chen et al [2]. It is implied that the transportation of hydrocarbon molecules from and to the active site is determined by the pore diameter of catalyst [2]. However, the hierarchical HZSM-5 catalyst was very favorable for the mass transport of triglyceride molecules [19]. After deoxygenation finished, isomerization occurred completely, as reported by Wang et al. [20].

The monocyclic aromatic hydrocarbons, the other substituted benzenes found in liquid product consist of short-branched benzenes, e.g. pentylbenzene, n-hexylbenzene, 1,3-

dimethylbutylbenzene, n-heptylbenzene, 1-methyl-2-n-hexylbenzene, n-octylbenzene, nonylbenzene, 2-phenyl-3-propylhexane, (1-methyldecyl) benzene, and n-undecylbenzene. Furthermore, the polycyclic aromatic hydrocarbons, e.g. 1-methylnaphthalene, was found in small amount about 0.1 area% and tri-aromatics were not found. However, tri-aromatics such as phenantrene and anthracene caused the coke formation leading to the deactivation on HZSM-5 occurred, as reported by previous study [10]. The paraffin (n- and iso-) and aromatic hydrocarbons in biofuel had high heating value properties in small amounts. The metals impregnated into HZSM-5 catalyst had acid and metal sites can promote the formation aliphatics and aromatics from the conversion of oxygenated compounds [10].

CONCLUSION

The production of biofuel by hydrocracking of Sunan candlenut oil with Co-Ni/HZSM-5 catalyst can be applied as an alternative substituted fuel. When Co-Ni/HZSM-5 catalyst was used, biofuel contained 34 area% hydrocarbon compounds and oxygenated compounds including 35.03 area% carboxylic acids. Temperature above 350 °C was required to produce the abundant hydrocarbon compounds such as n- and iso-paraffins, cycloparaffins and aromatics.

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