Hydrocracking of Coconut Oil over Ni-Fe/HZSM-5 Catalyst to Produce Hydrocarbon Biofuel

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Received: February 28, 2018
Accepted: November 29, 2018

DOI: 10.22146/ijc.33590

Abstract: *This present study was aimed to investigate the hydrocracking of coconut oil using Ni-Fe/HZSM-5 catalyst in a batch reactor at three reaction temperatures (350, 375, and 400 °C). The Ni-Fe/HZSM-5 catalyst was prepared by using incipient wetness impregnation. The Ni-Fe/HZSM-5 catalyst was characterized using XRD, BET, and SEM-EDX. From XRD results, the loading of Ni and Fe did not change the crystalline structure of HZSM-5 catalyst. The surface area of HZSM-5 was 425 m^2/g and decreased after the addition of metals (Ni and Fe) into HZSM-5 support. These changes implied that Ni and Fe particles were successfully dispersed on the HZSM-5 surface and incorporated into HZSM-5 pore. The product of hydrocarbon biofuel was analyzed using GC-MS. The GC-MS results of hydrocarbon biofuel showed the highest compounds for n-paraffin and yield for gasoil was 39.24 and 18.4% at a temperature of 400 °C, respectively. The reaction temperature affected the yield and the composition of hydrocarbon biofuel. At this reaction temperature condition, decarboxylation and decarbonylation were favored; lead to the formation of n-alkanes with an odd number of carbon atoms chain length.*

Keywords: *hydrocracking; coconut oil; Ni-Fe/HZSM-5 catalyst; n-paraffin; gasoil*

■ INTRODUCTION

The use of fossil fuel sources and an increase of environmental problems led to a search for an alternative source. Biomass, the most abundant of renewable sources, has a great potential solution to overcome this problem and it can be converted into hydrocarbon fuel or biofuel [1]. The development of new generation of hydrocarbon biofuels from renewable biomass such as vegetable oils has made significant potential benefits for promising future fuel source due to the concerns on environment and traffic fuels [2-3].

Coconut oil is proposed as one of the most potential renewable sources for the production of hydrocarbon biofuel. The coconut seed contains about 63-65% of oil by weight [4]. There are several methods to convert vegetable oils to produce hydrocarbon biofuels such as transesterification, thermal cracking, catalytic cracking, and hydrocracking. Transesterification is a process with the organic solvent such as methanol and ethanol in the presence of a catalyst that is used to chemically break the molecules of vegetable oil into glycerol and esters. However, it is usually used to produce biodiesel [5]. Thermal cracking is usually used to convert vegetable oil to biofuel at a high temperature and high pressure. However, it has a relatively high cost, and the yield of biofuel is relatively low due to over cracking [6]. Catalytic cracking is one method to convert vegetable oil to biofuel without the addition of hydrogen, and it could be operated at atmospheric pressure [7]. Hydrocracking is a promising technology for the conversion of vegetable oils into biofuel with high yields. The presence of hydrogen is helpful to remove oxygen atoms in the fatty acids and form of H_2O, CO, and CO_2. Hydrocracking is usually accomplished with transition metals under a high hydrogen pressure [8]. Hydrocracking reaction of the vegetable oil can consist of two main reactions routes of transforming triglycerides into liquid hydrocarbon fuel such as hydrodecarbonylation/decarboxylation (HDC) and hydrodeoxygenation (HDO) [9-10].

Zeolite catalyst has been used for converting of vegetable oil into hydrocarbon biofuel. HZSM-5 is the most effective catalyst for hydrocracking process because of its shape selectivity, containing active sites, high surface area, and appropriate pore diameter. It is important to improve the hydrocracking process condition to obtain a high yield of hydrocarbon and reduce the formation of coke in zeolite [11]. Weisz et al. [12] used corn, castor, and jojoba oil to produce hydrocarbons over the HZSM-5 catalyst. The results showed that the products contain paraffin, olefins, and aromatics. Buzetski et al. [13] also studied the cracking of rapeseed and sunflower oil over HZSM-5 catalyst. They used a stirred batch reactor and temperature between 350 and 440 °C. The results showed that the most saturated oil (rapeseed oil) produced more cracking residue and the most unsaturated (sunflower oil) produced more gaseous products. Chung et al. [14] reported cracking of soybean oil with HZSM-5 catalyst at 60 °C and 1 h reaction times produces 80% biodiesel yield.

Iliopoulou et al. [15] reported that the different transition metal in HZSM-5 such as Co and Ni for the catalytic cracking of biomass pyrolysis vapors and found that the transition metal- modified HZSM-5 improved the production of aromatics. Doronin et al. [16] reported that catalytic cracking of vegetable oil for producing gasoline. They found the presence of HZSM-5 catalyst promoted the formation of light olefin (C2-C4). Vichaphund et al. [17] reported that pyrolysis over Ni/HZSM-5 catalyst showed the highest hydrocarbon yield, 97%.

In comparison with noble metals, nickel and iron are inexpensive catalysts for hydrocarbon biofuel production. Nickel, a cheap transition metal can be used to modify HZMS-5 and commonly studied for deoxygenation process. Iron is the most abundant, stable, environmentally friendly, its economic convenience, and known as quite a favorable one in catalytic fields based upon its good activities on C-O bonds hydrogenation and inhibited the C-C breaking [18-20].

Metals such as Pd and Ni were also added with Fe to improve their activity in the deoxygenation process. Shafaghat et al. [21] reported that the doping of Fe (4.98 wt.%) to 4.94 wt.% Ni/HBeta was able to increase the aromatic selectivity from 7.12 wt.% to 29.48 wt.% during the deoxygenation of phenolic bio-oil. However, there is little information which reported Fe supported on HZSM-5 zeolites as a catalyst for hydrocracking process of vegetable oils to produce hydrocarbon biofuel. Leng et al. [22] reported that NiFe/Al_2O_3 improved the heating value of biofuel and the main involved reaction pathway was C-O cleavage rather than C-C cleavage during the hydrodeoxygenation process.

In this experiment, the Ni-Fe/HZSM-5 catalyst designed as a bifunctional catalyst. The purpose of loading metal into an HZSM-5 framework was to improve the activity of catalyst both of metal active sites and zeolite acid sites. The objective of this research is to study the effect of Ni-Fe/HZSM-5 catalyst on the hydrocracking performance of coconut oil to produce hydrocarbon biofuel in a batch reactor. The effect of the reaction temperature on the product of hydrocarbon biofuel was discussed. The chemical composition of biofuel was analyzed by using Gas Chromatography-Mass Spectrometry (GC-MS). The ultimate goal is to produce high n-paraffin compounds from coconut oil via hydrocracking process.

■ EXPERIMENTAL SECTION

Materials

The Ammonium ZSM-5 (NH_4-ZSM-5) zeolite powders were purchased from Zeolyst International, USA (CBV 8014, Na_2O weight content of 0.05%, Si/Al mole ratio: 40). Nickel(II) nitrate hexahydrate and iron(III) nitrate nonahydrate with 98% purity were purchased from Merck. The coconut oil was commercially purchased from local market in East Java Province, Indonesia. It was used as a raw material to produce biofuel.

Instrumentation

X-Ray Diffractometer series PANalytical X'Pert PRO), Scanning Electron Microscope with Energy-Dispersive X-ray (SEM-EDX) series model: EVO MA10, Brunauer- Emmett-Teller (BET) series Quantachrome

NovaWinVersion 11.03, Gas Chromatography-Mass Spectrometry (GC-MS) series Agilent HP 6890 models 19091S- 433.

Procedure

Preparation of catalyst

The HZSM-5 catalyst was obtained from the calcination process of a commercial NH4-ZSM-5 at a 550 °C for 5 h. The Ni-Fe/HZSM-5 catalyst was prepared by using incipient wetness impregnation. The zeolite HZSM-5 was impregnated with aqueous solution of Nickel(II) nitrate hexahydrate and iron(III) nitrate nonahydrate. After impregnation, 5wt.% metal loading of nickel and iron salts, the catalyst was kept overnight in a desiccator and dried at 120 °C for 12 h in an oven. Then after being dried, the powder catalyst calcined at 550 °C in the air for 3 h and catalyst was reduced by hydrogen at 550 °C in the H_2 for 2 h to become active metal phase. The Ni-Fe/HZSM-5 catalyst was analyzed by X-Ray Diffractometer series PANalytical X'Pert PRO) to determine crystallinity of catalyst. Surface morphology and the amount of metal impregnated on HZSM-5 of catalyst was analyzed using Scanning Electron Microscope with Energy-Dispersive X-ray (SEM-EDX) series model: EVO MA10. Surface area and pore volume of the catalyst was characterized by Brunauer-Emmett-Teller (BET) series Quantachrome NovaWinVersion 11.03.

Hydrocracking Process

Fig. 1 shows the equipment used to make the hydrocarbon biofuel from coconut oil by hydrocracking process. The hydrocracking of coconut oil was carried out in a batch reactor type Parr Instrument Company 4563 with a maximum volume of 600 mL. This reactor equipped with a mechanical stirrer. As much as 2 g of catalyst and 200 mL of coconut oil were placed in the reactor. The reaction temperature of experiments was carried out at 350, 375, and 400 °C for 2 h. After 2 h, the liquid product was produced and collected into a vial. The 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 × 250 µm × 0.25 µm to determine the hydrocarbon components in the liquid products. It was held at nominal initial pressure 13.3 psi, and the temperature for the oven was at 150 °C for 2 min, then it increased to 240 °C at a rate of 10 °C/min for 11 min.

■ RESULTS AND DISCUSSION

Catalyst Characterization

The XRD patterns of HZSM-5 and Ni-Fe/HZSM-5 catalyst are shown in Fig. 2. The main peaks of HZSM-5 were presented at the 2θ° of 7.9°, 8.8°, 23.1°, 23.4°, 24°, 24.4° which are in the range typical peaks of MFI type

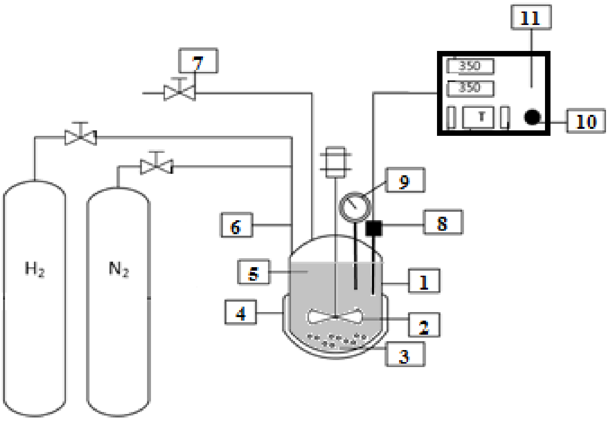

Fig 1. The equipment of hydrocracking process, consist of (1) Reactor, (2) stirrer, (3) catalyst, (4) heater, (5) coconut oil, (6) valve tube reactor of N_2/H_2, (7) liquid sampling tube, (8) thermocouple, (9) reactor pressure indicator, (10) stirrer speed control, (11) the control panel of heater reactor

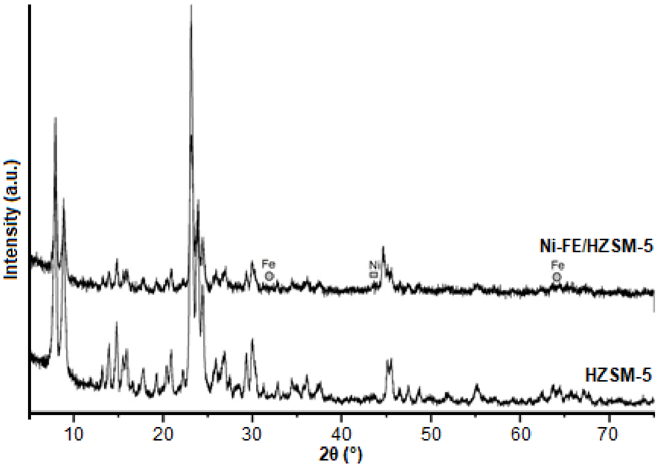

Fig 2. XRD spectra of catalyst: (a) HZSM-5, and (b) Ni-Fe/HZSM-5

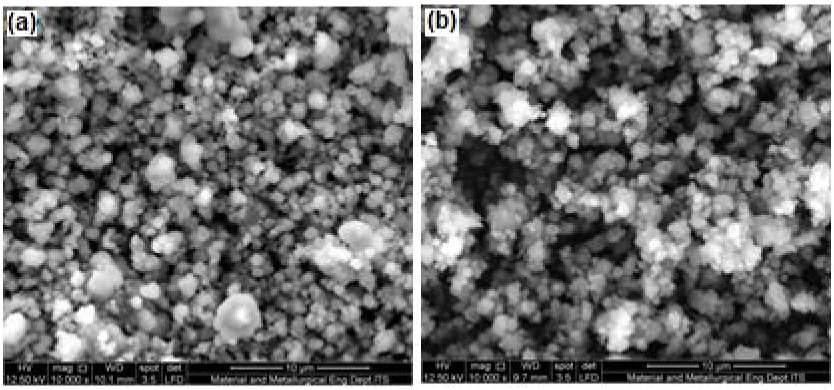

Fig 3. SEM of catalyst: (a) HZSM-5, and (b) Ni-Fe/HZSM-5

Table 1. Properties of Ni-Fe/HZSM-5 catalyst

Catalyst	Surface area (m^2/g)	Pore Size (nm)	Total Pore Volume (cm^3/g)	Element (wt.%)	
				Ni	Fe
HZSM-5	425	3.12	0.32	-	-
Ni-Fe/HZSM-5	325.013	3.00	0.09	2.19	4.30

zeolite at 7-8° and 23-24° [23,9-10]. In addition, the diffraction peaks were located at 2θ° of 32.71° and 63.64° which was attributed to the existence of Fe. Nickel was detected at 2θ° of 44.63°. As can be seen in Fig. 2, Ni-Fe/HZSM-5 catalyst shows a similar characteristic to HZSM-5 catalyst. It indicates that the addition of nickel and iron on/into the HZSM-5 did not change their structures but reduce the intensity of diffraction peak. However, the Ni-Fe/HZSM-5 catalyst was shown to have lower crystallinity than HZSM-5 catalyst because of the metal dispersion on/into the surface of HZSM-5 catalyst [10,17].

SEM micrographs of HZSM-5 and Ni-Fe/HZSM-5 catalyst prepared by incipient impregnation methods are presented in Fig. 3. HZSM-5 and Ni-Fe/HZSM-5 catalyst appeared in agglomeration due to the interconnection of particles with size less than 10μm. In addition, the small particles were interconnected each other. The HZSM-5 catalyst tended to grow into a cubic shape, as the same reported by Vichaphund et al. [17] and Zhao et al. [24].

Fig. 4. shows N2 adsorption and desorption isotherm of Ni-Fe/HZSM-5 catalyst as type IV. This characteristic indicates microporous molecular sieves. It can be seen that the curves of adsorption and desorption between the relative pressures (P/P°) of 0.5-1.0 [25]. BET surfaces area determined by the N_2 adsorption-desorption method of HZSM-5 and Ni-Fe/HZSM-5 catalyst are given in Table 1. The surface area of HZSM-5 was 425 m^2/g, and the surface area, pore diameter, and pore volume of the Ni-Fe/HZSM-5 catalyst decreased after the addition of metal into HZSM-5 support. One possible explanation could be that some of the micropores and mesopores of the support HZSM-5 were filled up with metal particles after the metal-loading. This assumption is in accordance with the result that the total pore volume and pore diameter of metal-loading HZSM-5 catalyst decreased compared to HZSM-5. These changes implied that Ni and Fe particles were

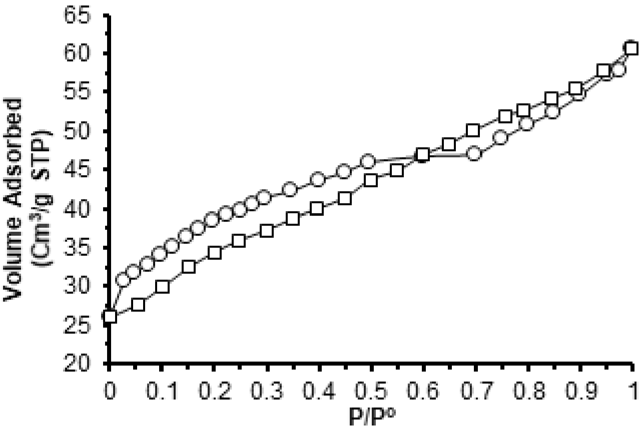

Fig 4. N_2 adsorption and desorption isotherm of Ni-Fe/HZSM-5 catalyst

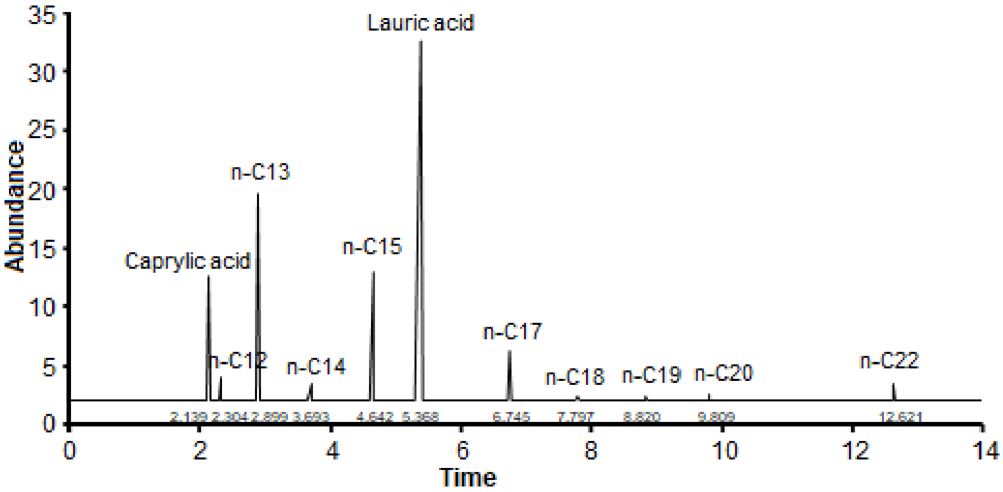

Fig 5. GC-MS chromatogram of liquid products produced at 400 °C using Ni-Fe/HZSM-5 catalyst

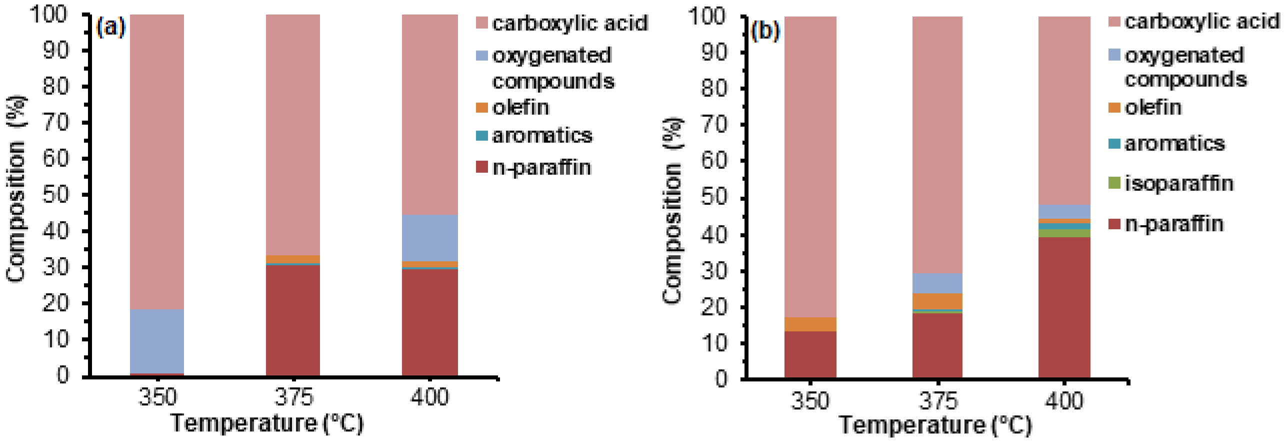

Fig 6. Effect of reaction temperature on the hydrocarbon biofuel composition using (a) HZSM-5 and (b) Ni-Fe/HZSM-5 catalyst under 30 bar in the batch reactor

successfully dispersed on the HZSM-5 surface and incorporated into HZSM-5 pore [6,10,26]. Metal content in the catalyst was determined by EDX which is shown in Table 1. Based on the EDX in Table 1, the metals content was 2.19 wt.% of Ni and 4.30 wt.% of Fe. The result of EDX measurement also proved the existence of nickel and iron in the HZSM-5.

Catalytic activity

GC-MS chromatogram of liquid products produced from hydrocracking of coconut oil over Ni-Fe/HZSM-5 catalyst at 400 °C is shown in Fig. 5. Fig. 5. shows that peaks at retention time of 0-12 min appeared and indicated the increasing a large number of hydrocarbon compounds after cracking reaction. The rise of temperature to 400 °C, the formation of n-paraffin compounds increase in the liquid products. A small peaks intensity of fatty acids such as caprylic acid and lauric acid were detected in GC-MS chromatogram of liquid product so that it can be implied that triglycerides were successfully cracked into short chain molecules by several reaction sequences by cracking, isomerization, cyclization, and aromatization at 400 °C [10,27].

The major components of hydrocarbon biofuel produced at different temperatures shown in Fig. 6. Based on the GC-MS analysis, the hydrocarbon biofuel usually mainly contained hydrocarbons and oxygen-containing compounds such as acids, alcohols, and esters. At the temperature of 350 °C, in Fig. 6a. was observed that the composition of hydrocarbon biofuel consists of

0.6% of hydrocarbons, 18% of oxygenated compounds and 81.37% of carboxylic acids using an HZSM-5 catalyst. In Fig. 6b., when using the Ni-Fe/HZSM-5 catalyst, the composition of hydrocarbon biofuel consist of 10.26% of hydrocarbons (i.e., 9.1% of n-paraffin, and 1.16% of olefin), and 89.1% of carboxylic acids. The presence of the carboxylic acids indicated that the compounds have not completely converted to hydrocarbon at the temperature of 350 °C, similar results were obtained by Simacek et al. [26] who observed that at 310 °C still more carboxylic acids were formed. It shows that cracking takes place at a temperature above 350 °C. The Increasing temperatures will lead to improve the activity of hydrocracking and help to cleavage triglycerides of coconut oil and a long chain of hydrocarbon molecules of biofuel produced into a short chain hydrocarbon molecules as reported in a previous study [9-10].

When the temperature increase from 350 °C to 400 °C, the content of hydrocarbon biofuel increase with the increasing temperature. At the temperature of 400 °C, carboxylic acids and oxygenated compounds were completely converted to hydrocarbon compounds. The concentration of carboxylic acids decreased from 81.37 to 55.28% using HZSM-5 catalyst and 82.36 to 51.91% using Ni-Fe/HZSM-5 catalyst. It can be said that this reaction was more favorable at high temperature. The presence of oxygen in the final product reduces stability and heating value of hydrocarbon biofuel, and it also increases the acidity and corrosivity [28]. A similar report was found from Xu et al. [29] that hydrocarbon fuel produced from pyrolysis of soybean oil contained hydrocarbons and oxygenated compounds.

Fig. 6 also shows that the rise of temperature to 400 °C, the formation of n-paraffin increase. When the HZSM-5 catalyst was used at a temperature of 400 °C, the carboxylic acid was converted into 29.71% n-paraffin. It was also different found in biofuel with the Ni-Fe/HZSM-5 catalyst. At this temperature, 39.24% of n-paraffin is the most abundant hydrocarbon in the liquid product. The composition of n-paraffin formed at this temperature contained the main components of tridecane of 19.39%, pentadecane of 11.33%, and heptadecane of 4.31%. A high n-paraffins were produced at this reaction temperature condition. The results indicated that the incorporation of metal transition over HZSM-5 catalyst promotes the cracking activity of HZSM-5 and the formation of aliphatics and aromatics from the conversion of oxygenated compounds [17]. Based on this results, pentadecane and heptadecane were the most abundant hydrocarbon compounds in biofuel. These results are similar to Marlinda et al. [10] and Veriansyah et al. [30], indicated that the hydrocracking process proceeded via decarboxylation and decarbonylation was the dominant reaction pathways, not by hydrodeoxygenation [31].

Table 2. Product distribution of hydrocarbon biofuel at 400 °C using Ni-Fe/HZSM-5 catalyst

Compounds (Hydrocarbons)	Relative Content (%)
C12	2.47
C13	19.39
C14	3.77
C15	11.33
C16	-
C17	4.31
C18	0.43
C19-C22	2.37

Aromatic compounds were also found in the hydrocarbon biofuel at a temperature of 400 °C, i.e., hexyl-benzene and octyl-benzene. The Ni-Fe/HZSM-5 catalyst showed a bifunctional catalyst, which included both acid and metal sites to increase the aromatization and alkylation reaction [17]. Sotelo Boyas et al. [32] and Iliopoulou et al. [15] stated that ability of Bronsted acid of the active site on HZSM-5 catalyst provided proton (H+) can affect the rate of cycloparaffin and aromatic formation during hydrocracking process. Ni and Fe combined with acid site provided the ideal environment for oligomerization of small alkenes followed by cyclization and dehydrogenation, leading to higher levels of aliphatic and aromatic formation. On the other hand, aliphatic and aromatic compounds were desirable products due to their high calorific value properties in biofuels [17,26].

Table 2 shows the product distribution of hydrocarbon biofuel at 400 °C using Ni-Fe/HZSM-5

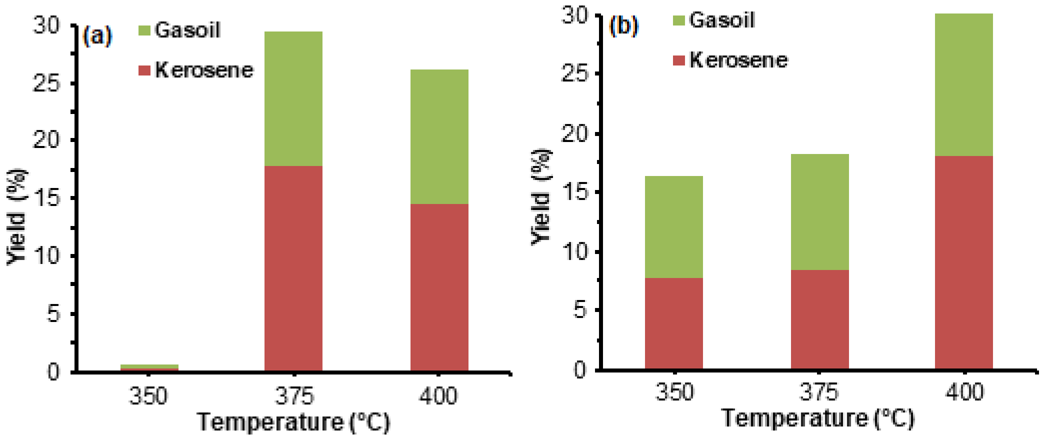

Fig 7. Effect of reaction temperature on kerosene/gasoil yields of hydrocarbon biofuel product produced using (a) HZSM-5 and (b) Ni-Fe/HZSM-5 catalyst, under 30 bar in the batch reactor

catalyst. Based on this results, the product distribution resulting from lauric acid as the feedstock were the hydrocarbon fraction mainly comprised straight chain alkanes n-C13, n-C15 and n-C17, with the maximum of C13 chain length. At high temperature, decarboxylation and decarbonylation were favored; lead to the formation of n-alkanes with an odd number of carbon atoms chain length [33].

Fig. 7 shows the yield of hydrocarbon biofuel over HZSM-5 and Ni-Fe/HZSM-5 catalyst with the metals content Ni of 2.19wt.% and Fe of 4.30wt.% at a different temperature. During the hydrocracking process, the conversion of vegetable oil was observed from 350 °C to 400 °C. In Fig. 7a., the yield of gasoil was increased from 0.2% at a temperature of 350 °C to 11.6% at a temperature of 400 °C. The yield of kerosene changed from 0.4% at a temperature of 350 °C to 14.5% at a temperature of 400 °C. Fig. 7b. shows that the yields of hydrocarbon biofuel were an only small amount at the temperature of 350 °C. However, when the temperature increased from 350 °C to 400 °C, the yield of hydrocarbon biofuel increased from 7.7 to 18.1% for kerosene, and 8.7 to 18.4% for gasoil. These yields suggest that at a low- temperature reaction (350 °C) did not affect the cracking reaction. Based on the above results, it can be concluded that the hydrocracking at a temperature of 400 °C produced high yields of kerosene and gasoil. As shown in Fig. 7, it suggested that the temperature significantly influence the yields of hydrocarbon biofuel, as reported by Mo and Savage [34]. Liu et al. [33] also reported that the level cracking also depended on the acid strength and amount of the catalyst. Catalyst containing transition metal such as Ni and Fe could change the strength of the acidity of HZSM-5 as support and exhibited higher catalytic activity on C-C bond scission [35].

■ CONCLUSION

The Ni-Fe/HZSM-5 catalyst was prepared by incipient wetness impregnation and applied for hydrocracking of coconut oil to produce hydrocarbon biofuel. The effect of Ni-Fe/HZSM-5 catalyst on the yields and distribution of liquid product was investigated using GC-MS. Hydrocarbon biofuel mainly contains hydrocarbon and oxygenated compounds. The highest amounts of n-paraffin produced were 39.24% at a temperature of 400 °C, i.e., pentadecane and heptadecane were the most abundant hydrocarbon compounds in biofuel. The highest yield of hydrocarbon biofuel was 18.1% for kerosene and 18.4% for gasoil, respectively. The experiment resulted that the reaction temperature affects the yield and distribution of hydrocarbon biofuel. The hydrocracking process proceeded via decarboxylation and decarbonylation was the dominant reaction pathways, not by hydrodeoxygenation.

■ ACKNOWLEDGMENTS

The authors acknowledge to DRPM, Directorate General of Research and Development, the Ministry of research, Technology and Higher Education of Indonesia for the research grant supporting in this research. The authors also would like appreciate to the head of chemical reaction engineering laboratory for the facilities, and also thanks for the crews of the laboratory, i.e., Afrida Nur Aini, Irene Fransisca Theresia, Faisal Arifin and Davi Khoirun Najib, Department of Chemical Engineering, Faculty of Industrial Technology, Sepuluh Nopember Institute of Technology.

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