Hydrocracking process of coconut oil using Ni-Zn/HZSM-5 catalyst for hydrocarbon biofuel production

M Al Muttaqi1, F Kurniawansyah1, D H Prajitno1 and A Roesyadi1

1Department of Chemical Engineering, Faculty of Industrial Technology, Sepuluh Nopember Institute of Technology, Surabaya 60111, Indonesia
2Research Unit for Mineral Technology, Indonesian Institute of Sciences, South Lampung 35361, Indonesia

Corresponding author’s email: almuttaqimuhammad@gmail.com

Abstract. Renewable hydrocarbon biofuel was produced by hydrocracking of coconut oil using a bifunctional catalyst. Hydrocarbon biofuel is promising for production of future fuels from vegetable oil. The advantage of the hydrocracking is the formation of hydrocarbon biofuel products at the conventional fuel range. The purpose of this work is to produce hydrocarbon biofuel by hydrocracking of coconut oil using the catalyst of Ni-Zn/HZSM-5. The processes of hydrocracking processes were performed in a vessel reactor by stirring with magnetically at 350 °C and the reaction pressure of 15 bar for 2 h under flowing H2 with Ni-Zn/HZSM-5 catalyst. The effect of Ni-Zn/HZSM-5 catalyst was evaluated by determining the composition of products (hydrocarbon biofuel). The hydrocarbon biofuel was determined by Gas Chromatography-Mass Spectrometry (GC-MS). The GC-MS results of hydrocarbon biofuel show the aliphatic compounds in the range C12-C22. The presence of C17-C18 in the hydrocarbon biofuel was relatively low. Hydrocarbon biofuel composition consists of 0.11 cycloparaffins, 5.33 normal paraffins, 7.85 olefin, and 0.08 aromatics based on area%. The total amount of detected oxygenated compounds was 86.63 area% carboxylic acid. These compounds are responsible for the low quality of the hydrocarbon biofuel. However, the reaction must be carried out at above 350 °C to eliminate the oxygenated compounds in the hydrocarbon biofuel, as an important step to replace non-renewable fossil fuels.

Keywords: Coconut oil, hydrocarbon biofuel, hydrocracking, Ni-Zn/HZSM-5 catalyst

1. Introduction
The combustion of fossil fuel has led to the increase of environmental pollutions, such as water pollution, air pollution, and soil pollution. The increasing emission causes the greenhouse effect and global warming. Fossil fuel is non-renewable resources, so it is necessary to develop clean renewable energy to replace fossil fuels sources and minimize the increasing environmental problems. To overcome this problems, biofuels play a crucial role as an alternative and promising potential in the development of renewable energy.

Among the potential feedstock for production of hydrocarbon biofuel is coconut oil. It can be applied to produce biofuel. Some methods to produce biofuel such as transesterification, hydrocracking, and cracking. The prior research reported an application of the transesterification method on vegetable oils to generate biodiesel known as fatty acid methyl ester (FAMEs). Biodiesel...
still contain oxygenated compounds and make the properties of fuel is poor energy and low heating [1, 2]. It is difficult to use biodiesel directly in the transport fuel application. In order to use biofuel for transport fuel application, upgrading technologies by hydrocracking process using catalyst are interesting in order to reduce the oxygen contents via dehydration and decarboxylation reaction [3]. Hydrocracking is one of the most promising biofuel processing methods that can directly convert vegetable oil into liquid biofuel hydrocarbons. The hydrogen application is beneficial to eliminate oxygen atoms in the H₂O, CO, and CO₂ forms [4]. Hydrocarbons have been produced by HDO technology and some studies recorded the application of vegetable oils, namely palm, soybean, sunflower, and etc. [5, 6].

The conversion of vegetable oils using a variety of catalyst into hydrocarbon biofuel have been reported by researchers. Wang et al. [7] reported the hydrocracking of soybean oil over NiMo/HZSM-5 (the molar ratio of Ni to Mo was 0.5) catalyst to produce hydrocarbon fuel. They found that hydrocarbon fuel has the content of fractions of gasoline (C₅-C₁₂), jet fuel (C₈-C₁₀), and diesel fuel (C₁₂-C₂₂). The greatest hydrocarbon fuel result was obtained around 50 %. The ZSM-5 catalyst was an important catalyst support in industry due to its specific micro-structure and strong acidity properties. Al Muttaqi et al. [8] investigated the hydrocracking of sunan candlenut oil over Co-Ni/HZSM-5 catalyst. The operation condition was at temperature of 350 °C and pressure of 10 bar for 2 h. The results showed the hydrocarbon contained of 34 area% hydrocarbons (i.e. 0.14 isoparaffins, 12.29 cycloparaffins, 6.87 n-paraffins, 4.18 olefins, and 10.52 aromatics based on area%), and oxygenated substances covering 35.03 area% carboxylic acids. It showed the existence of oxygenated substances covering carboxylic acids need the temperature higher than 350 °C to cleavage C=O bonds to produce hydrocarbon compounds such as n- and iso-paraffin, cycloparaffin and aromatic.

The goal of this study is to convert vegetable oils into hydrocarbon biofuel and aromatic by hydrocracking process using Ni-Zn/HZSM-5 catalyst. The preparation of catalyst was prepared by dry impregnation. The purpose of addition of metals solution (Nickel and Zinc) into HZSM-5 is to improve the activity of catalyst. It can be eliminated the oxygenated compounds and increasing hydrocarbon and aromatic compounds. The products of hydrocarbon biofuel were determined by using Gas Chromatography-Mass Spectrometry (GC-MS). In this study, the possibility of the coconut oil for producing biofuel can be investigated to be a good commercial fuel.

2. Materials and method

2.1. Raw material
The coconut oil was purchased from local market in Surabaya, East Java Province, Indonesia. It was used as raw material to produce hydrocarbon biofuel.

2.2. Catalyst preparation and characterization
The zeolite powders were purchased from Zeolyst International, USA (SiO₂/Al₂O₃ mole ratio: 40). The metal solution was purchased from Merck, such as nickel (II) nitrate hexahydrate and zinc (III) nitrate nonahydrate with 98 % purity. The 5 wt.% Ni-Zn/HZSM-5 catalyst doped with nickel (II) nitrate hexahydrate and zinc (III) nitrate nonahydrate were prepared by dry impregnation method. After impregnation 5 wt.% metal loading of nickel and zinc salts, the catalyst was dried at temperature of 120 °C for 12 h. The catalyst was calcined at temperature of 500 °C in the air for 3 h and it was reduced by hydrogen gas at temperature of 550 °C for 2 h to become active metal phase in the catalyst. The Ni-Zn/HZSM-5 catalyst was put in a sealed vial in desiccator before used in hydrocracking process. It was used to minimize the adsorption of the atmospheric moisture in the rooms. Then, the catalyst was characterized by X-Ray Diffraction (XRD) to determine the crystallinity of Ni-Zn/HZSM-5 catalyst, using a PANalytical X’Pert PRO X-ray diffractometer. It was operated at 40 kV and 30 mA and registered on 2θ of 5° to 70° with a Cu Kα radiation source.
2.3. Hydrocracking reaction
The reaction process of hydrocracking was conducted using a batch reactor (produced by Parr USA, volume of reactor of 600 mL), with a mechanical device used for stirring, respectively [8]. The experiment for the hydrocracking of coconut oil was conducted under the reaction condition. The hydrocracking experiments were conducted at temperature of 350 °C for 2 h using a nitrogen for 10 min to purge and remove the air inside the reactor. About 2 gr of 5wt% Ni-Zn/HZSM-5 catalyst and 200 mL of coconut oil were used. Then, the reactor was flowed with hydrogen gas (H₂) for 1 h and the pressure of reactor of 15 bar. After the reaction, the liquid product of hydrocarbon biofuel was collected and analyzed. The analysis of the liquid product was performed using a gas chromatograph-mass spectrometry (GC-MS) (standard GC: Agilent HP 6890 with models 19091S-433, HP–5MS capillary column 30 m × 250 μm × 0.25 μm).

3. Results and discussion
3.1. Characterization of catalyst
The XRD patterns of Ni-Zn/HZSM-5 catalyst are presented in figure 1. The Ni-Zn/HZSM-5 catalyst showed the type and specific peaks of MFI (2θ = 7–9° and 23–25°). These indicated that the catalyst maintains the structure of HZSM-5 zeolite, similar information to the previous studies [1, 8]. The XRD peaks of NiO particles at (37.6° and 63.6°), ZnO particles at (31.2° and 34.3°) were detected. Furthermore, no nickel and zinc phases were detected, implying that the metal was well dispersed on the catalyst and did not affect the structures of HZSM-5 zeolite [9, 10]. In addition, NiO and ZnO particles have been found on Ni-Zn/HZSM-5 catalyst [3, 11, 12].

3.2. Chemical composition of hydrocarbon biofuel
The major chemical compounds of hydrocarbon biofuel from analysis of GC-MS at temperature of 350 °C over Ni-Zn/HZSM-5 catalyst (showed in figure 2) were carboxylic acid compounds (86.63 area%) mainly dodecanoic acid (39.53 area%) and ketone (1.7 area%). Because high-carboxylic acid compounds, it is responsible for making low quality of the hydrocarbon biofuels. The valuable compounds of hydrocarbon biofuel were 13.37 % such as n-paraffin (5.33 area%), cycloparaffins (0.11 area%), olefin (7.85 area%), and aromatics (0.08 area%).

Figure 1. The diffraction peaks of Ni-Zn/HZSM-5 catalyst analyzed by XRD.
The presence of transition metals such as nickel and zinc on/into HZSM-5 showed a bifunctional character in Ni/Zn-HZSM-5 catalyst [13]. It showed two functions, including acid- and metal sites to contribute in hydrocracking process (oligomerization and aromatization reaction). The presence of transition metals is also to develop the oxygenated conversion compounds to (n-paraffin, olefin) and aromatics [8]. During the process of hydrocracking on the coconut oil, the reaction pathways can remove oxygen in the original feedstock by different pathways. The reactions into hydrocarbons such as cyclization (converted into alkenes) and dehydrogenation (lead to small aromatics) [14]. In addition, Ni-Zn/HZSM-5 catalyst could eliminate oxygenated compounds in hydrocarbon biofuel such as carboxylic acid and ketone. As reported in previous study [8], the activity of hydrocracking needs the temperature above 350 °C to produce biofuel and cleavage of oxygenated compounds (C=O) in coconut oil into a short-chain hydrocarbon molecules. The hydrodeoxygenation was occurred at temperatures above 350 °C.

The major chemical components of the hydrocarbon biofuel are presented in table 1. The identified chemical groups consists of ketones, carboxylic acid, and hydrocarbons. The highest compounds is carboxylic acid which of 86.63 area%. The presence of this compounds are responsible for the quality in the products. It made the low heating value, the chemical instability, high viscosity, and acidity in the product, comparing with the normal fuel. The amount of valuable hydrocarbon biofuel was 13.37 %, there is no sulfur containing in hydrocarbon biofuel products were detected. In this work, the product in the range of C_{12–C_{22}} contains aliphatic compounds. The existence of C_{17–C_{18}} in the hydrocarbon biofuel is only in small amount of area%. The formation of hexadecene and octadecene were supported by the initial hydrogen pressure. As reported by Simacek et al. [12], at temperatures lower than 310 °C, over Ni-Mo/Al_2O_3 catalyst with hydrogenated of rapeseed oil, the formation of product consists fatty acid and triglycerides. When the temperature reaction is high, hydrocarbons such as C_{17} and C_{18} n-alkanes were detected. It was about 40 wt.% of i-alkanes C_{16–C_{18}}. The amount of aromatic compounds (i.e. hexylbenzene) 0.08 area% was formed.
Table 1. Chemical composition of hydrocarbon biofuel identified by GC-MS at temperature of 350 °C.

| Compound/Formula                  | Structure | Abundance (area%) |
|-----------------------------------|-----------|------------------|
| **n-paraffin**                    |           |                  |
| Trimethyloctane/C_{11}H_{36}      |           | 0.09             |
| Tridecane/C_{13}H_{28}            |           | 1.05             |
| Tetradecane/C_{14}H_{36}          |           | 1.21             |
| Pentadecane/C_{15}H_{32}          |           | 0.71             |
| Hexadecane/C_{16}H_{34}           |           | 1.97             |
| Heptadecane/C_{17}H_{36}          |           | 0.3              |
| **Cycloparaffin/naphthene**       |           |                  |
| Cyclotetradecane/C_{14}H_{28}     |           | 0.11             |
| **Aromatic**                      |           |                  |
| Hexylbenzene/C_{12}H_{28}         |           | 0.08             |
| **Olefins**                       |           |                  |
| Dodecene/C_{12}H_{24}             |           | 0.52             |
| Tridecene/C_{13}H_{26}            |           | 0.05             |
| Tetradecene/C_{14}H_{28}          |           | 0.8              |
| Pentadecene/C_{15}H_{32}          |           | 0.71             |
| Hexadecene/C_{16}H_{32}           |           | 0.27             |
| Heptadecene/C_{17}H_{36}          |           | 0.53             |
| Octadecene/C_{18}H_{36}           |           | 5.18             |
| Nonadecene/C_{19}H_{38}           |           | 0.27             |
| Docosene/C_{22}H_{24}             |           | 0.12             |
| Tricosanone/C_{23}H_{40}O         |           | 1.7              |
Table 1 (continued). Chemical composition of hydrocarbon biofuel identified by GC-MS at temperature of 350 °C.

| Compound/Formula Structure | Abundance (area%) |
|---------------------------|-------------------|
| Carboxylic acid           |                   |
| Nonanoic acid/C₉H₁₈O₂     | 0.2              |
| Decanoic acid/C₁₀H₂₀O₂    | 6.19             |
| Undecanoic acid/C₁₁H₂₂O₂  | 0.36             |
| Dodecanoic acid/C₁₂H₂₄O₂  | 39.53            |
| Tetradecanoic acid/C₁₄H₂₈O₂| 19.16            |
| Octanoic acid/C₈H₁₆O₂     | 6.01             |
| n-Hexadecanoic acid/C₁₆H₃₂O₂| 12.98            |
| Octadecanoic acid/C₁₈H₃₄O₂ | 0.26             |

As reported in previous study by Prajitno et al. [15] and Marlinda et al. [16], they have investigated using Sunan candlenut oil and Cerbera manghas oil as a feedstock for producing the biofuel via hydrocracking process with Co-Ni/HZSM-5 catalyst. The products contain aromatics compounds i.e. n-hexylbenzene, n-heptylbenzene, octylbenzene, and etc, which called as monocyclic aromatic hydrocarbons. Other researchers have studied the hydrogenation of rapeseed oil over Ni-Mo/Al₂O₃ catalyst. The liquid products contained single branched of C17 and C18 alkanes under the operating conditions 3h at 350 °C and with initial hydrogen pressure of 8–9 MPa. During the reaction, the initial hydrogen pressure and reaction temperature contribute in the hydrocracking process. The main reaction products of hydrocarbon biofuel were C18 (5.18 area%) hydrocarbons, as reported by previous study [17]. From the results, high temperatures are needed for the conversion of feedstock into long paraffins, then into light paraffins which simply took place at high temperatures through by decarboxylation/decarbonylation reactions [2].

4. Conclusion

Hydrocracking of coconut oil at 350 °C using Ni-Zn/HZSM-5 catalyst produced the hydrocarbon (13.37 area%) such as n-paraffin (5.33 area%), cycloparaffins (0.11 area%), olefin (7.85 area%), aromatics (0.08 area%) and carboxylic acid compounds (86.63 area%) mainly dodecanoic acid.
(39.53 area%) and ketone (1.7 area%). The presence of the carboxylic acid and oxygenated compounds indicates that the compounds have not completely converted to hydrocarbon compound at temperature of 350 °C. Temperature over 350 °C was needed.

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