Research Article

Hydrotalcite Catalyst for Hydrocracking *Calophyllum inophyllum* Oil to Biofuel: A Comparative Study with and without Nickel Impregnation

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Abstract

This research aims to study the effect of nickel impregnation into hydrotalcite catalyst that use to convert *Calophyllum inophyllum* oil into biofuel through hydrocracking process. Hydrocracking process was carried out under mild condition (350 °C and 20 bar) for two hours in a slurry batch reactor. The adding nickel affected the reaction conversion, yield, and selectivity of gasoil. The process of oxygen removal from the compounds in the oil was characterized by Fourier Transform Infrared Spectroscopy (FTIR), and the compositions of the products were determined by Gas Chromatography-Mass Spectrometry (GC-MS). The results of the study successfully proved that nickel impregnated into hydrotalcite catalyst increased the conversion, yield, and selectivity of gasoil up to 98.57 %, 54.15 %, and 81.31 %, respectively. Copyright © 2017 BCREC Group. All rights reserved

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1. Introduction

Energy has become the basic needs of peoples in the world. It is necessary to find the renewable sources of energy that can be optimized. Various methods are used to fill up the increasing energy needs around the world. One concern is biofuel; where the biofuels are characterized by good cold flow properties, the proper ratio of hydrocarbons (n-alkanes, isoalkanes, cycloparaffins, and aromatics) and high-energy density [1]

The use of non-edible oils, such as jatropha oil, rubber seed oil, and *Calophyllum inophyllum* oil as a source of biofuel, can be the best option in order not conflict with food needs. The compounds of triglycerides contain hydrocarbon chains that similar to petroleum. The removal of oxygen needs to be done in the form of CO, H_2O, and CO_2 to produce paraffin liquid biofuel that can be used directly in the existing infrastructure without modification [2,3].

Through the hydroprocessing process, it can be used to remove oxygen from triglyceride oils to obtain diesel range hydrocarbons. There are three pathways in the process, i.e. (1) the first pathway, decarbonylation produces CO and

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H2O, (2) the second pathway, decarboxylation produces CO_2, and (3) the last pathway, hydrodeoxygenation produces H_2O [4,5]. After removal of oxygen, the process was followed by hydrocracking that breaks carbon-carbon bonds and reduces average molecular weight and produces higher yields of fuel. The type of catalyst can control the route and products from the reaction [6]. Scheme of simple reaction is shown in Figure 1 [7].

Hydrotalcites, magnesium - aluminum hydrocarbonate $(Mg_6Al_2(OH)_{16}CO_3.4H_2O)$ are minerals from anionic clays family. It contains M^{2+} and M^{3+} metal cation in hydroxide layers and anion in the interlamellar space. Hydrotalcite exhibited high surface area after thermal degradation by calcination and formed MgO [8]. It has great variety and was used as heterogeneous catalyst and adsorbents. The common method to prepare the hydrotalcite is by coprecipitation at low supersaturation because it produces more crystalline compare to high supersaturation. Romero *et al*. [9] tested decarboxylation of *Jatropha curcas* oil under a nitrogen atmosphere by hydrotalcite (Pural MG70) catalyst at 350 °C and 400 °C with a reaction time of 6 h, in which the yield of C_8-C_{18} was about 83 %.

Calophyllum inophyllum seed productivity is higher compared to other plants, such as jatropha and palm, where *Calophyllum inophyl-lum* plant productivity reached 20 tons/ha/year while the jatropha only five tons/ha/year and palm six tons/ha/year. Therefore, *Calophyllum inophyllum* are potentially used as an alternative fuel in the future [11]. In addition to that, *Calophyllum inophyllum* seeds have an oil content of 55-75 % [12,13], kernel seeds contain of 3.3 % water, and 71.4 % of oil, when fresh seeds contain 55 % of oil whereas the dry seeds about 70.5 % of the oil.

The metal catalyst transition has an important role in the process of hydrocracking. The metals, i.e. Ni, NiMo, CoMo, Pd, and Pt, are the common catalysts for hydrotreating vegetable oil. Rasyid *et al*. [14] studied the hydrocracking of *Calophyllum innophylum* kernel oil over non-sulfide CoMo. It converted into fuels, such as gasoline, kerosene, and gasoil, under temperature of 350 °C, pressure of 30 bar, and catalyst weight of 5 %. The study resulted in the conversion of 99.9 % and selective to gasoil. Wang *et al*. [5] studied hydrotreatment of soybean oil to produce diesel alkanes ranged over Ni/Zeolite, the conversion of soybean oil was 100 % over 8 wt% Ni/SAPO-11 catalyst at 370 °C, 4 MPa, and 1 hour reaction time. The method of impregnation of Ni has been selected because it has good activity in hydrogenation, and the cost of Ni is ~1000 and ~2500 times lower than Pd and Pt [15]. Morgan *et al*. [16] also proved that Ni-based catalysts were highly
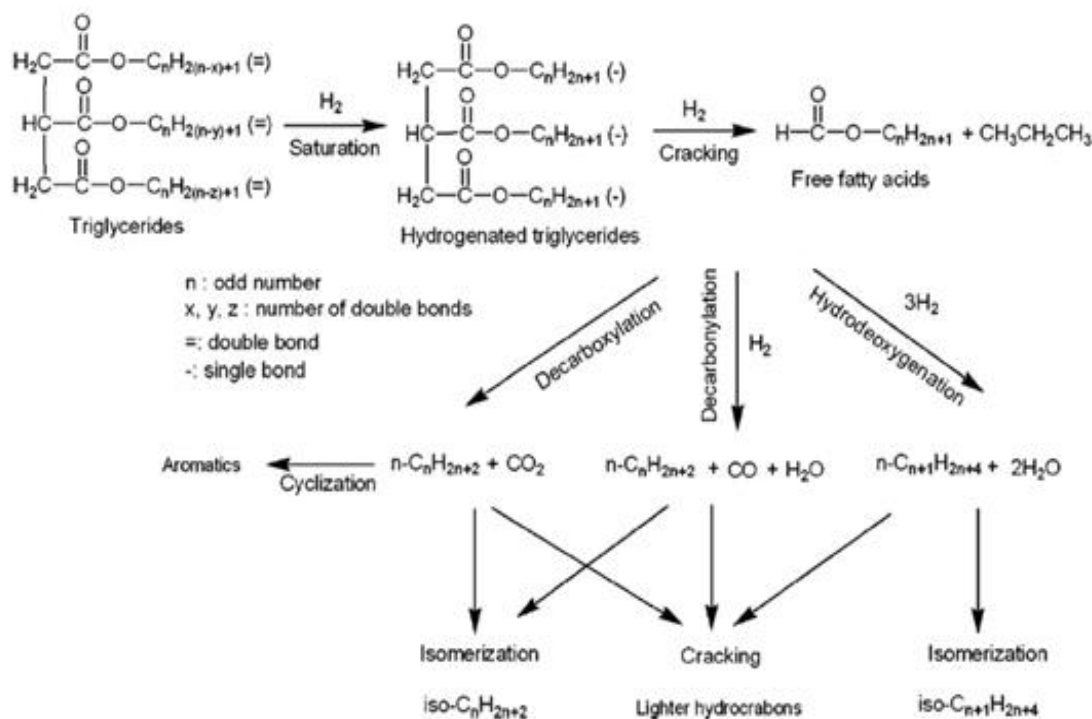

Figure 1. The possible pathways to produce biofuel [7]

active for upgrading vegetable oil in batch reactors.

In the view of above, there has been no study of hydrocracking that uses pure hydrotalcite and nickel impregnated into hydrotalcite catalysts. The last previous study reported hydrocracking over hydrotalcite (MG70) at high temperature (400 °C) and without hydrogen in the process [9]. In this study, hydrocracking of *Calophyllum inophyllum* oil was conducted in a slurry batch reactor at mild temperature of 350 °C under hydrogen atmosphere over hydrotalcite and Ni/Hydrotalcite catalysts. This research intends to study the effect of nickel impregnation towards the effectiveness of hydrocracking process.

2. Materials and Methods

2.1. Materials

Calophyllum inophyllum oil was obtained from local farmer in Kroya, Cilacap, Central Java, Indonesia. It was directly used for hydrocracking without any pretreatment. The raw materials for synthesis hydrotalcite were grade PA of Magnesium Nitrate Hexahydrate ($Mg(NO_3)_2.6H_2O$) (Merck, 99 %), Aluminium Nonahydrate ($Al(NO_3)_3.9H_2O$) (Merck 98.5 %), Natrium hydroxide (NaOH) (Merck, 99 %), Natrium Carbonate (Na_2CO_3)(Merck, 99.5 %). Nickel Nitrate Hexahydrate ($Ni(NO_3)_2.6H_2O$) (Merck, 98 %) solution for impregnation.

2.2. Methods

2.2.1. Preparation of catalyst

Hydrotalcite catalyst was prepared by low supersaturation coprecipitation method, followed by incipicient wetness impregnation methods to produce Ni/Hydrotalcite catalyst. In the impregnation method, the solution of nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) (10 %) was used appropriate with pore volume of the support catalyst. The Ni/Hydrotalcite was dried in an oven at 110 °C for 12 hours and followed by calcination for 3 hours at 400 °C and reduction for 2 hours at 450 °C with hydrogen.

2.2.2. Catalyst characterization

X-Ray diffraction (XRD) patterns for hydrotalcite were obtained in the 2θ range = 5-90° using PAN Analytical X'Pert PRO X-ray Diffractometer with Cu-Kα radiation source and operating at 40 kV and 30 mA. The XRD patterns were compared with JCPDS data for material identification. The N_2 adsorption isotherms at 77.3 K analyzes the textural parameter of supports and catalysts such as surface area, pore volume, and average pore diameter. The surface area (S_{BET}) was calculated by Brunauer Emmett Teller (BET) using Quantachrome NovaWin Version 10.0 based upon the adsorption data with partial pressure (P/Po), range of 0.0990-0.3006 through recording process of isotherm of BET on 5 points. Pore size distribution was calculated by Barret-Joyner Halenda (BJH) and total pore volumes was calculated from the amount of nitrogen adsorbed at P/Po = 0.99789.

2.2.3. Hydrocracking process

The reactions were conducted in slurry batch reactor equipped with mechanical stirrer under mild condition at temperature of 350 °C and pressure of 20 bar. The 200 mL of *Calophyllum inophyllum* oil was introduced into the reactor with 5 g of catalyst and then purged with nitrogen to remove remaining oxygen from reactor. The reaction took time about 2 h in the presence of hydrogen.

2.2.4. Characterization of *Calophyllum inophyllum* oil and the liquid products

The chemical composition of liquid products was investigated by Thermoscientific Nicolet IS10 FTIR Spectrometer. The component of liquid products biofuel was analyzed by using Gas Chromatography-Mass Spectrometry (GC-MS, Agilent HP 6890 and models 19091S-433, HP-5MS) with a hydrogen flow rate of 1.0 mL/min. The capillary column was a 30 m × 250 µm × 0.25 µm DB-5MS. The 1.0 µL of hydrocarbon biofuel was introduced to the GC-MS through an injection port operated in a splitless mode at 300 °C. The gas chromatograph was programmed at nominal initial pressure of 13.3 psi and temperature at 150 °C for 2 min, then it increased to 240 °C at the rate of 10 °C/min for 11 min. The major components of hydrocarbon biofuel were identified through a National Institute of Standards and Technology (NIST02) mass spectra library and wileys 275. The relative content of the components was determined based on the GC-MS peak area.

The effectiveness of hydrocracking *Calophyllum inophyllum* over hydrotalcite catalyst can be seen from conversion as the percentage of the oil feed product which has been converted into biofuel products (Equation 1).

$$Conversion(\%) = \frac{Feed_{Cbx.acid} - Product_{Cbx.acid}}{Feed_{Cbx.acid}} x100$$

(1)

where $Feed_{Cbx.acid}$ and $Product_{Cbx.acid}$ are the area % of the feed and product, which are carboxylic acids. The yields of the three different products of biofuel, gasoline, kerosene, and gasoil, were estimated from area% of liquid product that has carbon number C_5-C_8 (gasoline), C_9-C_{13} (kerosene), C_{14}-C_{22} (gasoil). Furthermore, the effectiveness of hydrotalcite and nickel to produce a particular product were calculated based on selectivity (Equation 2).

$$Selectivity(\%) = \frac{Product_A - Feed_A}{Feed_{Cbx.acid} - Product_{Cbx.acid}} x100 \quad (2)$$

3. Results and Discussion

3.1. Catalyst characterization

Textural properties of hydrotalcite employed in this hydrocracking reaction were summarized in Table 1. Besides of analysis of surface area, nitrogen adsorption-desorption method was also conducted to determine the type of adsorption-desorption isotherm to describe the pores of the catalyst. The adsorption-desorption isothermal curves are shown in Figure 2. Based on the classification of IUPAC (International Union of Pure and Applied Chemistry in) adsorption-desorption of hydrotalcite shows the isothermal type IV. In Figure 2, the adsorption starting at P/P_0 = 0 to 1, it appeared that at P/P_0= 0 very little gas was adsorbed, and the area has not been a full in monolayer. When

the pressure was raised again until the P/P_0 = 0.5 multilayer adsorption was taking place, but the amount not much that's why the increase in the graph was still not too sharp. After the application of higher pressure, P/P_0=1, caused gas molecules fulfilled the mesoporous, and isothermal curve sharply rose because of the large amount of adsorbed gas.

Figure 3 shows the pore size distribution of hydrotalcite with BJH method (Barret, Joiner, Halenda). It observed that the bimodal peaks showed the presence of two groups that each pore size was the pore diameter of about 3.42 and 4.27 nm with a percentage of 34.75 % of the total volume. Overall, it can be concluded that the pore diameters of the samples were in the size range of mesoporous (2-50 nm), so that the hydrotalcite samples was mesoporous solids.

Catalyst with large pore size, such as mesoporous, has better thermal stability compare to microporous size, because it posses thick walls, uniform and hexagonal structured channel [15]. The mesoporous catalyst performance in hydrocracking gives high selectivity to diesel, low gas products, and high cokes because of low acidity and high pore volume.

XRD pattern of calcined hydrotalcite with metal (nickel) in Figure 4 shows two main peaks at 2θ of 36.95° and 42.91° corresponded to the diffraction of MgO, while peak of NiO

Table 1. Textural properties of hydrotalcite

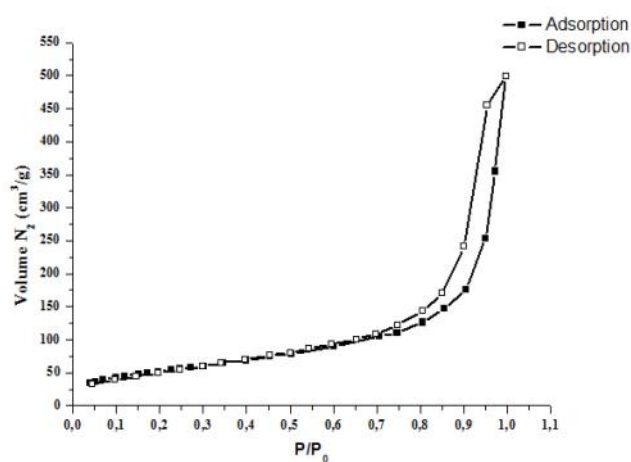| Sample	S_{BET} (m²g⁻¹)	Pore Volume (cm³ g⁻¹)	Average Diameter Pore (nm)
Hydrotalcite	190.166	0.7714	16.226

Figure 2. N₂ adsorption/desorption isotherms of hydrotalcite after calcination
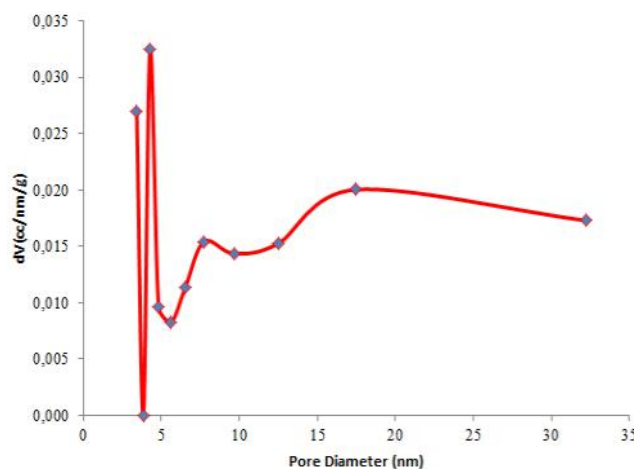

Figure 3. Pore size distribution of hydrotalcite after calcination

was detected at 2θ of 37.25° and 43.27°, and Ni at 44.6°. In fact, the most intense diffraction data of NiO almost overlaps at about 37.25° and 43.27° with the most intense peak of MgO, but the presence of diffraction peak of Ni at 44.6° was detectable with small intensity.

3.2. Hydrocracking reaction of *Calophyllum inophyllum* oil over hydrotalcite and Ni/hydrotalcite

3.2.1. Characterization of the feeds and liquid products

The results of GC-MS analysis of *Calophyllum inophyllum* oil showed two dominant fatty acids as shown in Table 2. Palmitic acid appeared in retention time 9 minutes and oleic acid at the retention time of 11-12 minutes (Figure 5). A high content of oleic acid is potential to be converted into biofuel through hydrocracking. Results of analysis of *Calophyllum inophyllum* oil was similar to the studied by other researchers [17,12], stated that the *Calophyllum inophyllum* oil contains unsaturated fatty acid (oleic acid) in an amount greater than other fatty acids. Liquid product of hydrocracking *Calophyllum inophyllum* oil appeared in a dark, turbid, and distinctive smell liquid. It is because of the carbon deposit formation
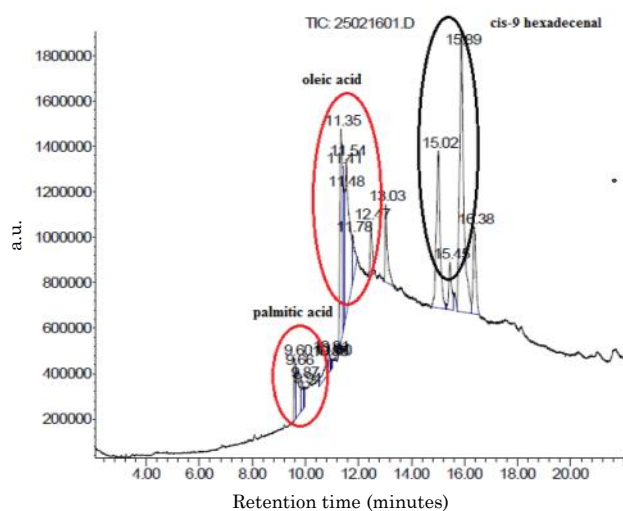
during high temperature of hydrocracking. Carbon deposits, known as a coke, was a product from the cation intermediates that more stable and accumulates in the catalyst during the reaction.

3.2.2. FTIR analysis

Figure 6 shows the spectra of *Calophyllum inophyllum* oil as feedstock, biofuel products over hydrotalcite, and 10 % Ni/Hydrotalcite catalysts. The FTIR analysis observed the
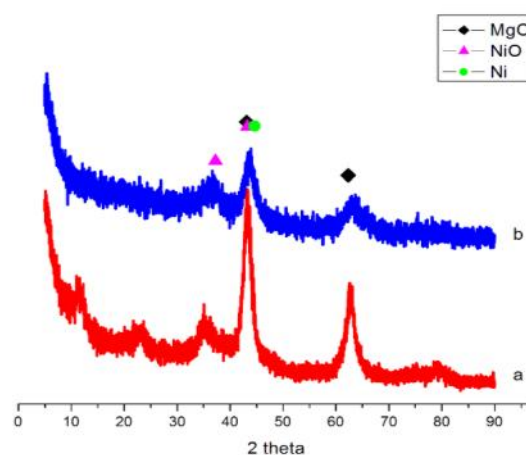

Figure 4. Powder X-ray diffraction patterns of a) Hydrotalcite, b)10 % Ni/Hydrotalcite

Figure 5. Chromatogram of *Calophyllum inophyllum* oil
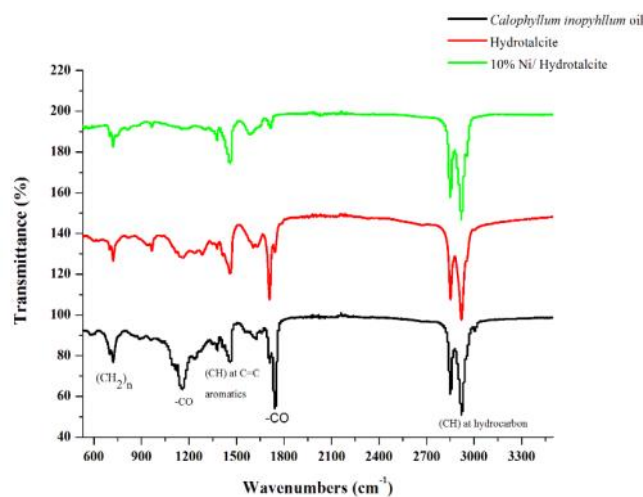
Figure 6. Comparison of FTIR spectra of *Calophyllum inophyllum* oil, biofuel over hydrotalcite, and 10% Ni/hydrotalcite

Table 2. Fatty acid composition of *Calophyllum inophyllum* oil

Fatty Acids	Name	Formula	Relative abundance (%)
1. Saturated			
Palmitic Acid (C16:0)	Hexadecanoic	$C_{16}H_{32}O_2$	7.93
2. Unsaturated			
Oleic Acid (C18:1)	Cis-9-Octadecenoic	$C_{18}H_{34}O_2$	50.25

change of the spectra after hydrocracking reaction occurs. The absorbance changed significantly at any kinds of bond between *Calophyllum inophyllum* oil and biofuel. There were significant changes in the molecular structure.

In analyzing the infrared spectrum of biofuels sample, first observe was focused on the carbon skeleton, because the biofuel was expected to have compounds approaching fraction of petroleum. Hydrocarbon chain appears in the infrared spectrum at various kinds of absorption that caused by the presence of carbon-carbon bonds. As mentioned by Pavia *et al.* [18], the hydrocarbons have a main absorption in the C–H area near 3000 cm^{-1} and was also simple absorption spectrum, which appeared at 1460-1375 cm^{-1}. If there were C = C, the medium to strong absorption would have detected on the area in 1600-1450 cm^{-1}. This value usually indicates a double bond or aromatic rings. The appearance of the tape at the wave number region of 750-720 cm^{-1} that are precisely the wave number of 721 cm^{-1} showed that the alkyl group might contain three neighboring methylene group (–CH$_2$–CH$_2$–CH$_2$–CH$_2$).

The spectrum reported in Figure 6 shows that the carbon skeletons can be directly seen in the area of the wave number of 3000-2700 cm^{-1}, which were the characteristic for the absorption of alkanes. An increasing trend in the alkane compounds, suggesting the formation of paraffin products in biofuels, and –CO bond spectra on biofuel products weakened due to removal of oxygen in the hydrocracking reaction, as well as the C=O bond order to show a decline.

3.2.2. GC-MS analysis

Table 3 showed the distribution of liquid products after 2 hours reaction time under 20 bar at temperature of 350 °C over catalyst of hydrotalcite and with nickel impregnation. The composition products over hydrotalcite catalyst was still an intermediate products in the form of carboxylic acids and fatty acid as constituent of oil, such as stearic acid, which is derived from the saturation of oleic acid as stated by Alwan [19] that the presences of stearic acid were hydrogenated products from some of the oleic acid and linoleic acid. The composition of hydrocarbons were only about 1.62 % and 2.03 % for gasoline and gasoil, respectively (Table 4), while aromatics and cycloparaffins were not formed, due to that aromatization and cyclization reaction has not occurred yet.

Table 3. Hydrocarbon composition of hydrocracking of *Calophyllum inophyllum* oil under the condition of 350 °C, 20 bar, 5 g catalyst, and 200 mL oil

Catalyst	Composition, % Area					
	n-paraffin	Cycloparaffin/ Naphtene	Aromatics	Olefin/ Alkene	Carboxylic Acid	Alcohol, C=O, C–O, C–OH
Hydrotalcite	1.53	0.82	0.16	1.6	91.15	3.55
10% Ni/Hydrotalcite	46.95	10.86	9.38	19.36	3,74	8.6

Table 4. Product yield of hydrocracking *Calophyllum inophyllum* oil under the condition of 350°C, 20 bar, 5 g catalyst, and 200 mL oil

Catalysts	Yield, wt (%)		
	Gasoline C$_5$-C$_8$	Kerosene C$_9$-C$_{13}$	Gasoil C$_{14}$-C$_{22}$
Hydrotalcite	0	1.62	2.03
10% Ni/Hydrotalcite	0.97	2.66	54.15

Table 5. The influence of the catalyst on conversion, selectivity, and product ratio of hydrocracking *Calophyllum inophyllum* oil

Catalyst	Conversion (%)	Selectivity to gasoil (%)	C$_{17}$/C$_{18}$ Ratio	C$_{15}$/C$_{16}$ Ratio
0/HTC	41.99	7.07	0	2.47
10Ni/HTC	98.57	81.31	14.76	2.54

The biofuels contain hydrocarbon and a certain amount of oxygenated compounds, such as acids, alcohols, and aldehyde. It shows low activity of hydrotalcite as hydrocracking catalysts due to the low acidity of hydrotalcite and also lack at the time needed to assist reaction hydrocracking over hydrotalcite. This finding is consistent with Romero *et al*. [9] that reported high conversion of more than 80% by using hydrotalcite with reaction time of six hours. Morgan *et al*. [14] used Ni-Al LDH and 20 % Ni/Al_2O_3 to convert stearic acid into hydrocarbons with conversion of 42 % and 80 %, respectively. The selectivity of Ni-Al LDH and 20% Ni/Al_2O_3 of the C_{10}-C_{17}, were 43 % and 85 %, respectively.

The different results were obtained when hydrotalcite was impregnated with nickel and used as a catalyst in the same operation condition. The composition of liquid products shows a large increase on the number of n-paraffin, cycloparaffin, olefin, aromatics. The composition of hydrocarbon contains gasoline (0.97 %), kerosene (2.66 %), and gasoil (54.15 %) (Table 4). These results suggest that the reaction of hydrogenolysis, cyclization, and aromatization were already occurred, while the reaction of isomerization was not happened. It is caused by the low reaction temperature, low acidic catalyst, and longer need of the reaction time. It agrees with Mohammad *et al*. [1] stated that the hydrocracking reaction was strongly influenced by reaction temperature, pressure, liquid hourly space velocity, and the catalyst. The number of carboxylic acids were also significantly reduced after the addition of nickel showing the removal of oxygen through the reaction of hydrodeoxygenation, decarboxylation, and decarbonylation.

The catalytic performances of hydrotalcite and Ni/Hydrotalcite catalysts are shown Table 5. Conversion reaction of hydrocracking *Calophylum Inophyllum* oil increased with the addition of nickel in support of hydrotalcite from 41.99 % over hydrotalcite catalyst, and increased to 98.57 % while over 10 % Ni/Hydrotalcite catalyst. This results agreed with Roesyadi [20] as the previous researcher proved that impregnation of Ni, Cu, and Zn into HZSM-5 catalyst could increase the active site and surface area of the catalyst. Its due to the higher cracking activity of catalyst. The Ni/Hydrotalcite catalyst has a high selectivity to gasoil, and the adding 10 wt% nickel to hydrotalcite increased the selectivity up to 81.31 % from 7.07 % when using the hydrotalcite.

The main component of gasoil was unsaturated C_{17}, which rose sharply after the addition of nickel into hydrotalcite. The ratio of product of hydrocarbon with an odd carbon number is presented in Table 5, which was derived from the decarboxylation and decarbonylation reactions. As the reaction scheme in Figure 1, it shows that decarboxylation produces hydrocarbon with an odd carbon number at hydrodeoxygenation of even carbon number. In agreement with the results of Roesyadi [20] that nickel tailored a diesel product and decarboxylation reaction.

4. Conclusions

Calophyllum inophyllum oil can be converted to produce hydrocarbon biofuel over hydrotalcite catalyst. Impregnation of nickel into the catalyst could increased the conversion, yield, and selectivity of gasoil up to 98.57 %, 54.15 %, and 81.31 %, respectively. The increasing conversion reaction and the yield of gas oil showed that the nickel addition could increase the active sites at the catalyst surface and increase the yield of biofuel products, especially gas oil.

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