

Synthesis and Characterization of Ni/Hydrotalcite and Its Application in Hydrocracking *Calophyllum Inophyllum* Oil

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ABSTRACT

This research aims to synthesize hydrotalcite as an alternatives of catalyst support of hydrocracking of vegetable oils. Hydrotalcite can be synthesized in several ways, the most common is coprecipitation method. Hydrotalcite was synthesized using Mg/Al mole ratio of 1: 1, NaOH and Na₂CO₃ as base solutions. Ni/hydrotalcite catalyst was synthesized by incipient wetness impregnation method with Ni impregnation of 10% w/w. The characterization of the crystal structure was determined by X-ray diffraction (XRD). The specific surface area (S_{BET}) was determined by adsorption-desorption of nitrogen, it were obtained 201 m²/g after impregnation and 191 m²/g before impregnation. The test of performance of catalyst was conducted by hydrocracking reaction of *Calophyllum inophyllum* oil. The liquid products were analyzed by gas chromatography mass spectrometry (GC-MS). Hydrocracking process produced gasoline, kerosene, gas oil with yield of 0.36%, 2.45%, 54.88% respectively, conversion of 96.26% and selectivity of gas oil of 84.39%.

Keywords: Ni/hydrotalcite, coprecipitation, hydrocracking, *calophyllum inophyllum* oil, biofuel

INTRODUCTION

The search and development of renewable energy become the main agenda in the Indonesia energy sector to achieve energy independence and sovereignty. The development and use of biofuels were the efforts made by government. Biofuel is an alternative renewable energy to substitute petroleum fuel. It can be obtained by hydrocracking vegetable oil into gasoline, kerosene, and diesel oil (gas oil). Cracking of vegetable oils has been done as the potential way to produce biofuel. Generally, triglycerides are composed of fatty chains of 16 to 24 carbon in length, which are ideal for the production of synthetic fuels and biochemical [1]. *Calophyllum inophyllum* oil as non edible oil is potensial source for biofuel because it has high rendement oil of about 70 % [2]. Biofuel is obtained from the saturation reaction of triglycerides and termination of long-chain triglycerides into shorter chain with hydrogen and a catalyst. The reaction pathway includes the hydrogenation of the C=C bonds of the vegetable oils and oxygen removal to produce alkanes through three different pathways: decarbonylation, decarboxylation and hydrodeoxygenation [3].

The common catalysts for hydrocracking are Ni, Pd, NiW, NiMo, CoMo that were impregnated into a support of zeolite, silica-alumina or γ alumina. The activity of the catalyst is high for hydrocracking. Hydrotalcite is promising as an alternative support catalyst because

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it can be synthesized easily and is useful in various applications [4,5]. Catalyst selectivity is not only depend on the composition of the catalyst but also on the support of the catalyst and the dispersion of the metal on the support used. Metal catalyst was impregnated into the catalyst support to maximize the performance of the catalyst so that it has a high surface area and high catalytic activity. The catalyst with large surface area and high value of acidity showed activity of hydrocracking with a high conversion, and it affects to the distribution of the liquid product [4]

Hydrotalcite was classified into mineral layered double hydroxide. It has been known as one of the interest, prospective and promising minerals because it can be synthesized easily, and it useful in various applications [5][6]. Applications of hydrotalcite are very broad as catalysts, catalyst supports, adsorbents, anion scavengers, anion exchangers, polymer stabilizers, antacids and antipeptin. Hydrotalcite can be converted into mixed oxides through thermal decomposition which posses large surface area [7]. When the material hydrotalcite is calcinated, the molecules are decomposed and leave pores thereby it increases the surface area of the particles.

This work focuses on preparing hydrotalcite by coprecipitation under low supersaturation. Low supersaturation co-precipitation is a common method used in the process of preparation of hydrotalcite because the growth of particles in this condition usually success. The process is performed by slow addition of mixed salt metals solution into aqueous solution of desired interlayer anion at constant pH. In previous research [17] on hydrocracking *calophyllum inophyllum* oil reported that at a concentration of 10% CoMo/ γ -Al₂O₃ the conversion and yield higher than most other concentration. The impregnation of 10% nikel on hydrotalcite catalyst support is expected to increase the surface area and catalytic activity so that the conversion and yield of the reaction hydrocraking also increase.

EXPERIMENT

Chemicals and instrumentation

Chemicals

Magnesium Hexahydrate (Mg(NO₃)₂·6H₂O) (Merck), Aluminium Nonahydrate (Al(NO₃)₃·9H₂O) (Merck), Natrium hydroxide (NaOH), Natrium Carbonate (Na₂CO₃), Ni(NO₃)₂·6H₂O (Merck 98%) as Ni precursors.

Instrumentation

The surface area (S_{BET}) calculated by Brunauer Emmett Teller (BET) on Quantachrome NovaWin Version 10.0 based on the adsorption data with partial pressure (P/P₀) range 0.097183 - 0.30026, through recording process of isotherm BET on 5 Points. Total pore volumes calculated from the amount of nitrogen adsorbed at P/P₀=0.99789

Functional groups of catalysts were investigated by Thermoscientific Nicolet IS10 FTIR Spektrometer. X-Ray diffraction (XRD) patterns were obtained in the 2 θ range = 5-90° using PANanalytical X'Pert PRO X-ray Diffractometer operating at 40 kV and 30mA with CuK α radiation source and

The component of liquid products biofuel were analyzed 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 \times 250 μ m \times 0.25 μ m DB-5MS. The major components of hydrocarbon biofuel were identified through a National Institute of Standards and Technology (NIST02) mass spectra library and wileys275.

Procedure reaction

Preparation Of Hydrotalcite

Ni/hydrotalcite was synthesized by co-precipitation method at constant temperature and pH. It was prepared by slow co-addition of metal solution ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and NaOH into Na_2CO_3 solution under vigorous stirring. After 5 hours, the suspension was filtered and washed with aquades until pH 7. Hydrotalcite was dried at 110°C for 12 hours. Solid of hydrotalcite was calcinated for 6 hours at 600°C ,

Impregnation of Nickel

Solid hydrotalcite was impregnated with solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (10%). Ni/hydrotalcite dried in the oven at 110°C for 12 hours, and then continued with calcination for 3 hours at 400°C and reduction for 2 hours at 450°C under hydrogen atmosphere.

Catalyst Application

Catalyst performance test was conducted in a Parr USA pressure reactor equipped with mechanical stirrer at 350°C under 20 bar. The catalyst of 5 gram and *Calophyllum inophyllum* oil of 200 ml was poured into reactor, then it was purged with nitrogen. Reaction was took place for 2 hours in presence of hydrogen.

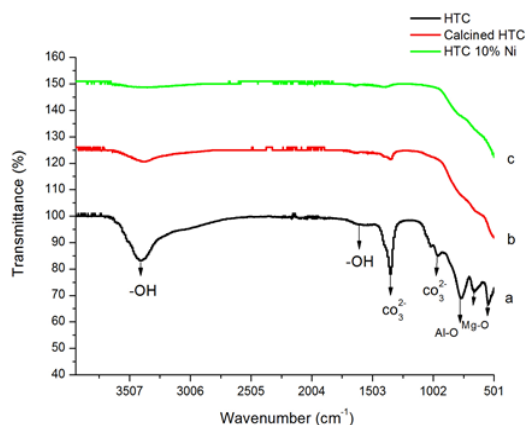
RESULT AND DISCUSSION

Catalyst Characterization

FTIR spectra for Ni/hydrotalcite are shown in Fig.1. The absorption bands 548, 1354 and 3419 cm^{-1} which is the main character of hydrotalcite looks quite strong. It shows that hydrotalcite is already formed. Davydov [8] reported that the presence of stretch vibration of Al-O and Mg-O present in the region of $500\text{--}600\text{ cm}^{-1}$. From the analysis of absorption band at 3 samples of hydrotalcite component before calcination, after calcination and after impregnation, there are a number of material changes of hydrotalcite when the calcination was processed. The first change is increasingly weak absorption bands at 548, 655.769 and 966 cm^{-1} and the spectrum for uncalcined hydrotalcite. It shows a large band at $3300\text{--}3400\text{ cm}^{-1}$ and 1300 cm^{-1} indicates vibration OH group and CO_3^{2-} respectively. These bands disappear when catalyst is calcinated at 600°C , the loss of water and carbonate ionic during calcination process is a mechanism of loss during thermal decomposition of the hydrotalcite.

Figure 1. IR Spectra of hydrotalcite (right) :

- a) before calcination,
- b) after calcination,
- c) after impregnation.



The addition of nickel metal causes two absorption bands at 1900 and 2042 cm^{-1} . This fits with previous research conducted by Mette [9] who reported that the main contribution of metallic Ni was between 2100 and 1800 cm^{-1} .

Hydrotalcite synthesis show a high match with diffractogram of commercial hydrotalcite as shown in Fig.2. It can be concluded that the hydrotalcite synthesis was successful, because of high compatibility of hydrotalcite synthesis and commercial hydrotalcite.

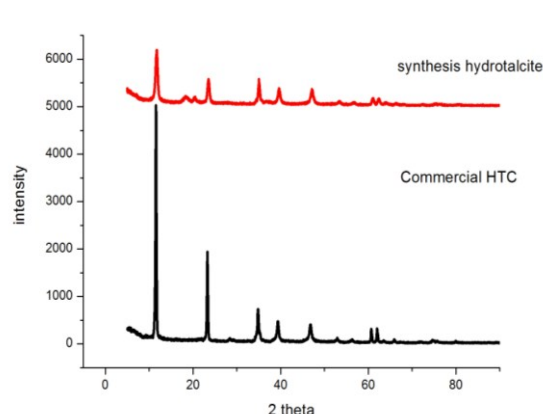


Figure 2. Diffractogram of synthesis hydrotalcite compare to commercial hydrotalcite

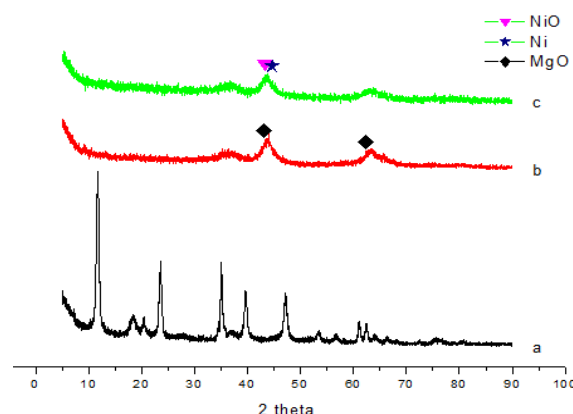


Figure 3. Diffractogram of hydrotalcite: a. before calcination, b. after calcination, c. after impregnation

XRD patterns of uncalcined, calcined, and Ni impregnated hydrotalcite are shown in Fig.3. Uncalcined hydrotalcite has seven high peaks located at 2θ : 11.74°; 23.55°; 35.07°; 39.59°; 47.11°; 60.99° and 62.50°. A typical hydrotalcite structure is often very poorly crystallized. Diffraction shows a broad and low intensity line at high value of 2θ , a sharp and high intensity line at low value of the 2θ [10]. The intense peaks at 11.74°, 23.55° and 34.59° are characteristic of a layered structure and correspond to the 003, 006 and 009 reflections respectively. As reported by Heraldry [11] the most intense peak at 2θ of 11.4°-11.7° (d003); 23.0-23.6° (d006); 34.9°-35.1° (d009) and 61.0°- 62.0° indicates that the interlayer of hydrotalcite are carbonate anion. After hydrotalcite was calcined and nikel was impregnated, it has 3 main peaks at 43,26°, 43,93° dan 62,93°. Meira [12] found the same peak that correspond to MgO (Magnesium Oxide). Comelli [13] reported that hydrotalcite is calcined at 600°C a form of magnesium oxide is observed, as shown at Fig.3.

The physical and chemical properties of catalyst Ni/hydrotalcite was summarized in Table.1

Table 1. Component, S_{BET} and Total pore volume of the Ni/hydrotalcite sample

Sample	Ni ^a (%)	Ratio Mg/Al	S_{BET}^b (m ² /g)	Total pore volume ^b (cm ³ /g)
Hydrotalcite	-	1:1	190.166	-
Ni/Hydrotalcite	7.56	1:1	201.340	0.7714

^aThe elemental composition was determined by AAS

^b S_{BET} and Total pore volume was determined by Nitrogen Adsorption-Desorption.

The AAS result show the actual content of active metal nickel 7.56% is smaller than nominal content of 10%. Because the dispersion of nikel on hydrotalcite support during process of impregnation was not spread evenly. S_{BET} and total pore volume of the Ni/hydrotalcite sample are 201.340 m^2/g and 0.7714 cm^3/g respectively. Before Ni impregnated, hydrotalcite has surface area as catalyst support material of 190,166 m^2/g .

After impregnation 10% of Ni and reduced for 3 hours with H_2 at temperature of 450°C, the surface area of the catalyst to increase to 201.340 (m^2/g). It's indicating the reconstruction of the surface of the catalyst. According to Song, 2014 [14] the salt of nickel decomposed when the reduction take place, resulting a larger surface area of the hydrotalcite before impregnated. This result is similar to Qi [7] that impregnation of Ni can increase the surface area of the catalyst.

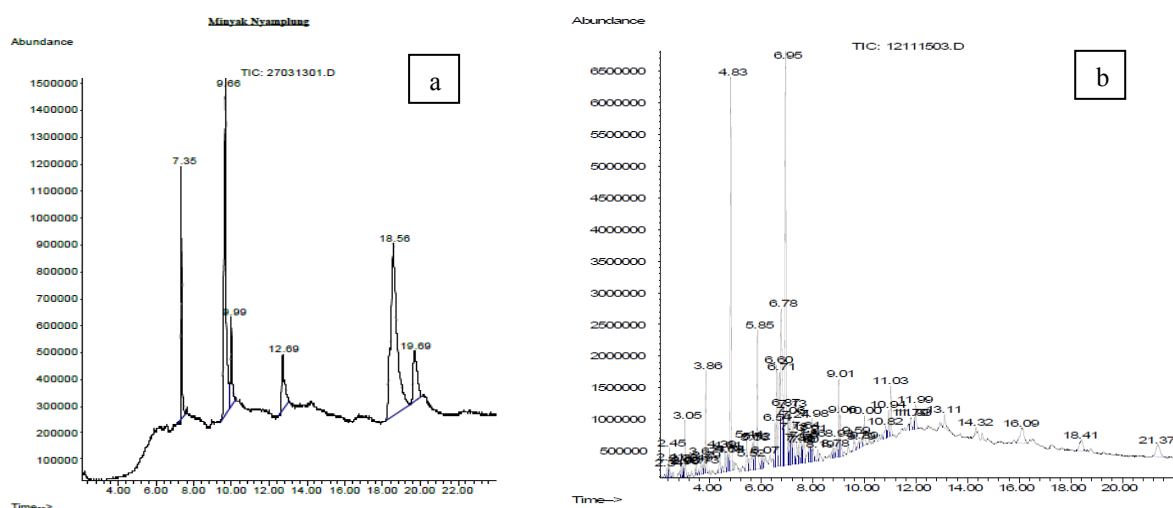


Figure.4 GC-MS chromatograms of a). *calophyllum inophyllum* oil b). biofuel

Fig.4.a shows the chromatogram of GC-MS of *calophyllum inophyllum* oil [15] and hydrocracking product at a temperature of 350°C under 20 bar. Components with retention time of 7-19 minutes in the *calophyllum inophyllum* oil disappear after hydrocracking reaction take place. Triglyceride of *calophyllum inophyllum* oil is converted into short-chain molecules through hydrocracking process as shown in table 2. As described by Sotelo-Boyas et al, 2012 [16] in order to convert the triglycerides into biofuel through a complex reaction. The reaction consists of several steps starting from the saturation of the double bonds of triglycerides and the removal of oxygen through a different reaction, decarboxylation, decarbonylation, and hydrodeoxygenation. As shown in Fig 4.b, the number of components of the product in retention time of 2-13 minutes increases. Biofuel products contain paraffin compounds in large quantities, olefins, cycloparaffins and alcohols. Paraffin compounds were over 40%, consisted of heptadecane and pentadecane. As reported by Rasyid [15], Biofuel from *calophyllum inophyllum* oil is approaching the characteristics of hydrocarbons including gasoline fractions, diesel oil, kerosene and aromatic fraction with operating conditions at a temperature of 350 °C using a catalyst CoMo with various support catalysts. The fatty acids as the raw material components that not successfully converted in the form of oleic acid by 1.43% area. Carboxylic acid as an intermediate product in the form n, 2,3 -trimethyl-2-butenic acid, cycloparaffins in the form as cyclohexane (4.45%) and cyclopentane (4.65%).

Table 2. Compounds of *Calophyllum inophyllum* oil and biofuel

No.	Compounds of <i>Calophyllum inophyllum</i> oil [15]	Area (%)	Compounds of biofuel	Area (%)
1	C ₁₈ H ₃₄ O ₂	58,13	Gasoline (C ₅ -C ₈ , cycloalkane,aromatics)	0,54
2	C ₁₈ H ₃₆ O ₂	11,14	Kerosene (C ₉ -C ₁₃)	3,62
3	C ₁₈ H ₃₀ O ₂	12,26	Gas oil C ₁₄ C ₁₅ C ₁₆ C ₁₇ C ₁₈ C ₁₉ C ₂₂ C ₂₃ Olefin Cycloalkane Aromatics Total of gas oil	2,12 11,73 4,62 22,73 1,54 0,94 0,34 1,02 18,81 9,18 8,2 81,23
4.	C ₁₆ H ₃₂ O ₂	18,47		

Based on the analysis of biofuels, conversion was 96.26%. This conversion is smaller than the conversion of 10% CoMo/ γ -alumina catalyst in the same conditions of hydrocracking [15]. The actual amount of nickel only 7.56%. It makes less effective to convert triglycerides. Yield of gasoline, kerosene, and gas oil 0.36%, 2.45%, 54.88% respectively, and the selectivity of gas oil 84.39%. The selectivity of Ni is greater than CoMo to gas oil as reported by Rosyadi [17]. The increasing concentration of Ni in the catalyst of NiMo, the activity of catalyst will lead to products gas oil than gasoline or gas products. This indicates that the catalytic hydrocracking reaction with catalyst Ni/hydrotalcite occurred successfully and selective to gas oil. It is possible if the reaction is carried above the temperature of 350°C and reaction time over 2 hours will obtain greater conversion and yield.

CONCLUSION

Based on the discussion, Ni/hydrotalcite as hydrocracking catalyst of *Callophyllum inophyllum* oil can be synthesized by low supersaturation co-precipitation method and incipient wetness impregnation, it resulted high surface area of catalyst about 201.340 m²/g. Hydrocracking reaction with 7.56 % Ni/hydrotalcite catalyst at 350°C gave the conversion of 96.26%, yield of gasoline, kerosene, gas oil 0.36%, 2.45 % and 54.88% respectively and the selectivity of gas oil was 84.39%. The main product was paraffins which consist of heptadecane and pentadecane.

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