



Research Article

## Hydrocracking of *Calophyllum inophyllum* Oil with Non-Sulfide CoMo Catalysts

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### Abstract

This research was aimed to convert *Calophyllum inophyllum* kernel oil into liquid fuel through hydrocracking process using non-sulfide CoMo catalysts. The experiment was carried out in a pressurized reactor operated at temperature and pressure up to 350 °C and 30 bar, respectively. The CoMo catalysts used in the experiment were prepared by 10 wt.% loading of cobalt and molybdenum solutions over various supports, i.e.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> through impregnation method. It is figured out from the experiment that non-sulfide CoMo based catalysts have functioned well in the hydrocracking conversion of *Calophyllum inophyllum* kernel oil into fuels, such as gasoline, kerosene, and gasoil. The CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst resulted higher conversion than CoMo/SiO<sub>2</sub> and CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. The fuel yields were 25.63% gasoline, 17.31% kerosene, and 38.59% gasoil. The fuels obtained in this research do not contain sulfur compounds so that they can be categorized as environmentally friendly fuels. ©2015 BCREC UNDIP. All rights reserved

**Keywords:** *Calophyllum inophyllum* oil; hydrocracking; non-sulfidecatalysts; fuels

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### 1. Introduction

Among other sources of energy like gas, solar and electricity, oil fuels are the most common used energy sources for the transportation sectors. In 2004, the demand for the oil was up to 82 million barrels per day; and is predicted to rise up to 111 million barrels per day in 2025 [1]. This significant rise of demand would affect the amount of the petroleum supplies that consequently affects the prize of the oil that would probably increase. However, this problem can be overcome by finding alternative supplies,

like vegetable oils. It is worth to consider these types of oil due to a renewable production process, and that at the same time yield lower pollutant emissions than the fossil fuels [2].

Both, non-saturated and saturated fatty acids contents of vegetable oils, such as: palm, soybean, rape-seed, woody oils and the like, can be converted into fuels [3-7]. Among those vegetable oils, *Calophyllum inophyllum* kernel oil is the most favorable oil to be converted into fuels [8]. Unlike other vegetable oils, say palm oil, the oil is non-edible so it would not affect the food supplies when it is used for producing the fuel.

In the moment, a process for converting *Calophyllum inophyllum* kernel oil into fuels in-

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volves esterification and transesterification reactions and followed by the process of purification [9, 10]. However, this process brings a complicated separation process and yields only a biodiesel. In order to have more developed process, cracking and hydrocracking process seems to be more enhancing .

Instead of employing the foregoing process, hydrocracking is thus far a more promising employed as the process is comprised from two processes, namely catalytic cracking and hydrogenation. These processes are conducted in high pressure and temperature and using bifunctional catalysts as well. To facilitate that function, the catalysts have two functions, as acids and metal catalysts. The former would function in the process of cracking and isomerization, while the latter is used in the process of dehydrogenation and hydrogenation [11]. Hydrocracking process yields more than one types of fuels, say for example gasoline, kerosene, and gasoil [12].

In hydrocracking process, metal transition catalysts, cobalt (Co) and molybdenum (Mo), has high selectivity. The catalysts can also be used in the process of hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) [13, 14]. Both HDS and HDN processes are methods used to reduce nitrogen and sulfur contents found in the common oil fuels [15, 16]. Other process is the process of hydrotreating using CoMo catalysts with the temperature up to 380 oC and pressure up to 40-60 bar, which may successfully achieved 100 % conversion of sun flower oil [17].

Before used, metal catalysts, like cobalt (Co) and molybdenum (Mo) or NiMo, are subjected to sulfidation using gas mixtures  $H_2S/H_2$  or  $S/H_2$ , for activating the metal sites on the surface of catalysts [18, 19]. The use of catalysts in sulfidation process may yield non environmentally friendly products as a result of sulfur contamination [20]. One of the unfavorable impacts for the catalysts (deactivation) is sulfur where the sources are derived from gases,  $H_2S$  [21]. Therefore, it is necessary to develop a catalyst to obtain products that are environmentally friendly.

This research is aimed to convert Calophyllum inophyllum kernel oil to environmentally friendly oil fuels through hydrocracking process using CoMo/CoMo/ $\gamma$ - $Al_2O_3$ , CoMo/ $SiO_2$ , and CoMo/ $\gamma$ - $Al_2O_3$ - $SiO_2$  catalysts. The 10 wt.% CoMo promoters are employed in the impregnation of the support during catalyst preparation without sulfidation process.

## 2. Materials and Methods

Prior to the research, catalysts preparations, catalysts characterizations and catalysts testing have been carried out in the pressurised reactors. Then, CoMo catalysts was produced with the 10 wt.% loading of the support material. The catalysts are made by means of impregnation methods, whereas the raw materials for the catalysts  $Co(NO_3)_2 \cdot 6H_2O$  and  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ . All chemicals were provided with p.a 99% (Merck) grade. Solution of  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$  and  $Co(NO_3)_2 \cdot 6H_2O$  is impregnated in the support of  $\gamma$ - $Al_2O_3$  (p.a. Merck) with 10 wt.% loading, and into other supports such as  $SiO_2$  (p.a., Sigma Aldrich) and support of  $\gamma$ - $Al_2O_3$ - $SiO_2$ . The mixture of the catalysts would be dried under the temperature 110 °C within 8 hours, then calcined under the temperature of 500 °C within 5 hours.

The characterization of catalysts was conducted using X-ray diffraction (XRD) to identify the compositions of the catalysts and to recognize the forms of crystal catalysts. The catalyst samples were placed on the sampling container, using a Philips PN-1830 with  $CuK\alpha$  radiation 1.5406 Å at 40 kV and 30 mA. Samples were scanned in the range  $2\theta$  of 5-90o with a step size 0.017 and step time 10.15 s.

The following Brunauer Emmett Teller (BET) analysis method was employed for identifying the surface of the catalysts volume. Sample was added to the sample cell with 3 hours of outgas time and 573 K of outgas temperature. Nitrogen has been used in this analysis and bath temperature is 77.3 K. Pressure tolerance for ads/des is 0.100/0.100 with equil time = 180/180sec (ads/des), equil timeout = 360/360 sec (ads/des) where time analysis is approximately 67.4 mins.

Reactions were carried out with Parr USA pressure reactor, while nitrogen and hydrogen gases were used in the reaction process. This was proceeded under the pressure of 30 bar and catalyst weight percent up to 5% from the volume of the oil, while the process is done under the temperature of 350 °C. The reaction product would be analyzed by GC-MS (Gas Chromatography-Mass Spectrometry). It can analyze both qualitatively and quantitatively as well; whereas, the components comprised would be able to be detected by means of the instrument with capillary column model number of Agilent 19091 S-493, HP-5MS 5% Phenyl Methyl Siloxane, nominal length: 30.0 m, nominal diameter: 250 um, nominal film thickness: 0,25 um, and nominal initial pressure of 10,5 psi.

### 3. Results and Discussion

#### 3.1. Characterization of Catalyst

As shown in Figure 1, the XRD results from CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, CoMo/SiO<sub>2</sub>, CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> catalysts are elucidated based on the JCPDS data. The CoMo catalyst describes the patterns of diffraction at the peak of 23°, 26° with 100 % relative intensity at 27.31° and peak height 1593.36 counts. The CoMo/SiO<sub>2</sub> catalyst shows that the peaks at 20.85° and 23°, with the height 9899.55 counts at 26.64 and at 27.32°, whereas the catalysts of CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> serves peak height at relatively 100% intensity at the 26.62° angle. Such a pattern could shows that synchronized peak at the CoMo catalysts exhibiting the structure of the crystal.

While CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts gives amorf pattern (Figure 2), this is different from the other non amorf supports. Catalysts with support  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, have the composition of MoO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> different at the peak 26°, 37°, 45.9°, 66° and 67° based on reference code of 00-013-0373 and 00-032-0671, while the catalysts with SiO<sub>2</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> supports has SiO<sub>2</sub> active sites.

In this present research, CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts configurates oxide metal (MoO<sub>2</sub>), at the same time, a study on sulfide catalysts, the oxide metals configured is MoO<sub>3</sub> [22, 23]. This could happen due to Co in the periodical system which has an empty *d*-orbital 1-3, and Mo which gas an empty *d*-orbital 4-5. Based on that finding, it can be inferred that Co has been fully absorbed during the impregnation.

Metal oxides existing in the surface of the catalysts function to bond hydrogen so that the olefin compounds undergo hydrogenation to form saturated bonds. Hydrocracking process is able to yield better quality products than those usual cracking process. Hydrogenation is one of the existing processes in hydrocracking that enhances higher quality product. The support of the catalyst functions to elucidate ion carbenium for cutting off long bonds of carbon chains.

Hydrocracking reactions require good catalysts, indicated by the wide of the surface area; thus, in the present study it is figured out that the wide of the surface areas range from CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> then CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> and further CoMo/SiO<sub>2</sub> (see Table 1). Hence, based on the analysis using XRD and BET method, the surface area required to employ cracking process is 100 m<sup>2</sup>/g minimum [24]. The research is conducted by making CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> going with the criteria of catalysts cracking.

#### 3.2. Hydrocracking Reaction

The raw materials were analyzed with GC-MS, *Calophyllum inophyllum* oil contains fatty acids compositions as explained in Table 2. Non saturated fatty acids like oleat and linoleat acids are more dominant than other composition, they range up to 70.394 % out of total contents of the fatty acids in *Calophyllum inophyllum* oil. The *Calophyllum inophyllum* oil has four dominant fatty acids components, i.e. 39.1% oleic acids, 13.7% palmeic acids, 31.1% linoleic acids, and 14.3% stearic acids [25].

Results of product analysis are compared to the results of GC-MS commercial fuel sold to the public refueling unit. The main components existing in the gasoline (Figure 3a) are, among others, methylcyclohexane, toluene, cyclooctane, 3-octane, ethylbenzene, 1,3-dimethylbenzene, 1-ethyl-2-methylbenzene. While retention time (RT) shown from chromatogram around RT 1.6 to 4.28. Kerosene fuel containing main components as seen in Figure 3b includes 1,2-dimethyl benzene; 1,2,4-trymethyl benzene, 4-ethyl-1,2-dimethyl benzene, naphthalene; kerosene owes RT 1,61-7,6. Chromatogram of diesel fuel (gasoil) serves RT 2,05 - 14,67 (Figure 3c) and have nonane, decane, pentadecane, and octadecane components.

Catalysts of CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> yield fuel products in the Retention Time (RT) dispersed within the range of gasoline, kerosene and diesel fuel (gasoil) (Figure 4). Constituent element of gasoline components are comprised by some compounds of 2-octane, methyl cyclohexane, ethyl cyclohexane, ethyl benzene, toluene, xylene. Kerosene compounds are comprised from varied constituent elements, namely: nonane; 1,4-dimethylbenzene; 1-methyl-2-methylbenzene, octylbenzene, naphthalene, 1-methyl-naphthalene, 2-ethyl-naphthalene; 1,7-dimethyl-naphthalene; 1,2,4-trimethylbenzene. Constituents elements of gasoil compounds is comprised from: decane, undecane, dodecane,

Table 1. BET test of catalysts

Catalysts	Surface area (m <sup>2</sup> /g)	Pore diameter (nm)	Pore volume (cc/g)
CoMo/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	116.467	4.633	0.211
CoMo/SiO <sub>2</sub>	0.72	0.005	3.017
CoMo/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub>	60.6	0.117	4.646

Table 2. Fatty acids of *Calophyllum inophyllum* oil

Fatty acids	Chemical name	Chemical formula	wt%
Oleic acid	Cis-9- Octadecenoic	$C_{18}H_{34}O_2$	58.131
Palmitic acid	Hexadecanoic	$C_{16}H_{32}O_2$	18.466
Linoleic acid	Cis-9,cis-12-Octadecadienoic	$C_{18}H_{30}O_2$	12.263
Stearic acid	Octadecanoic	$C_{18}H_{36}O_2$	11.141

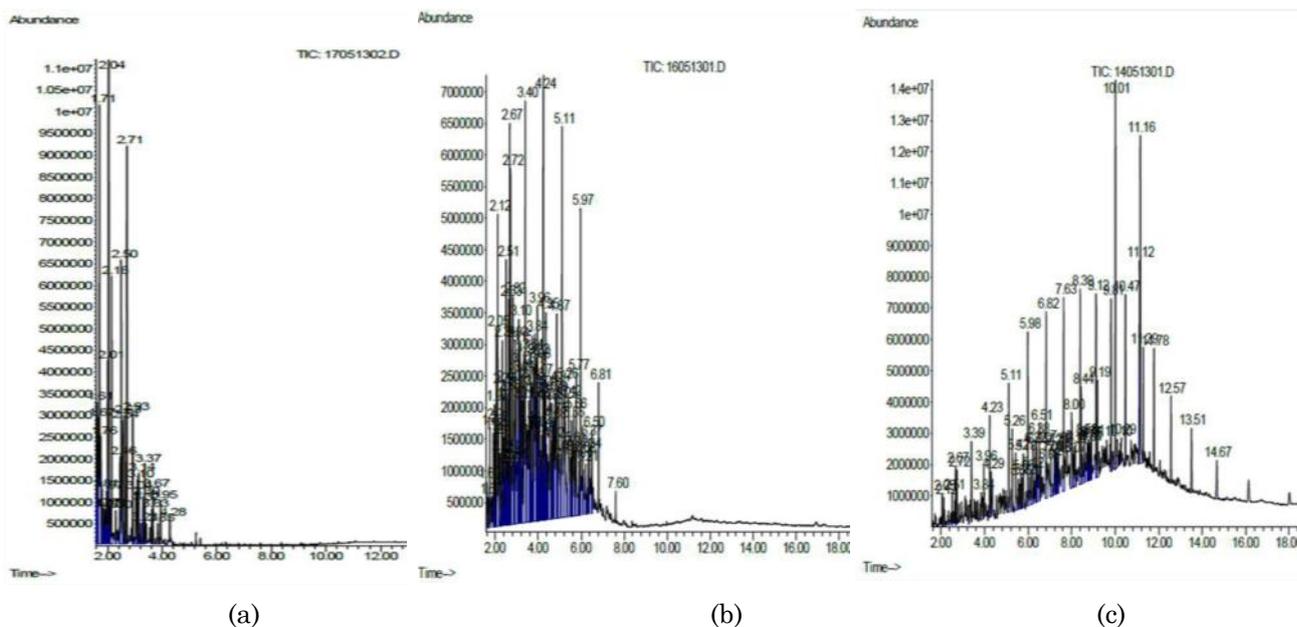


Figure 1. XRD pattern of non sulfide catalysts at angle (0 – 90 °) and calcined sampels at 500 °C within 5 h : (a). CoMo, (b). CoMo/SiO<sub>2</sub>, (c). CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>

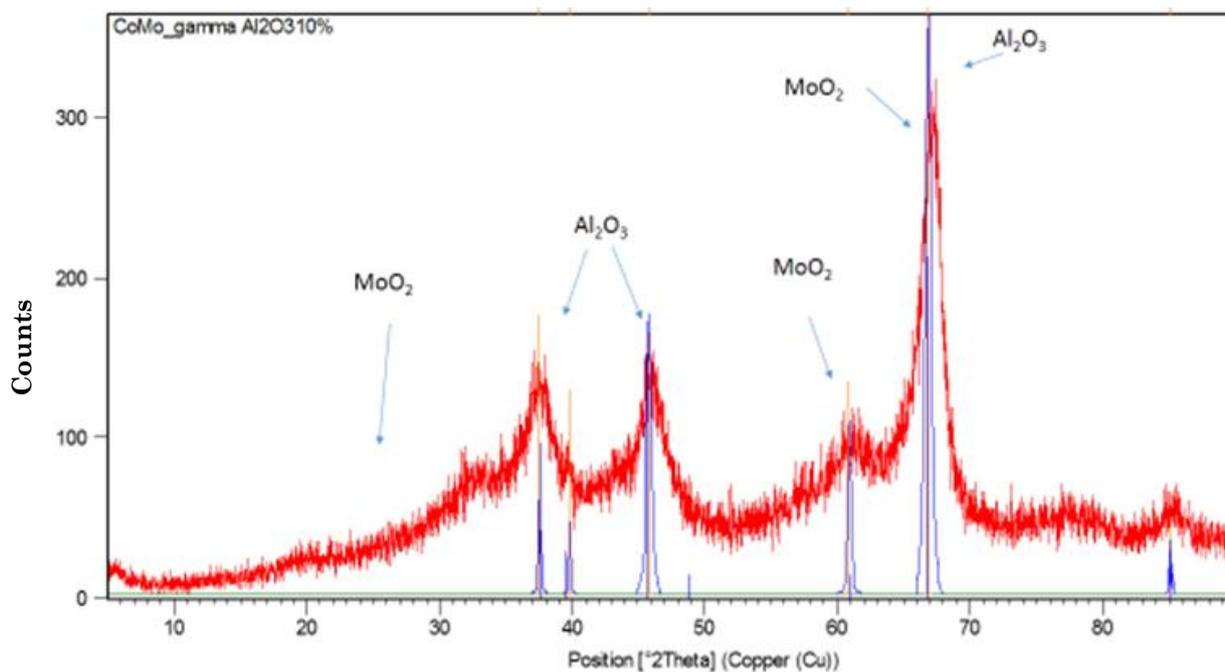


Figure 2. XRD of catalyst CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

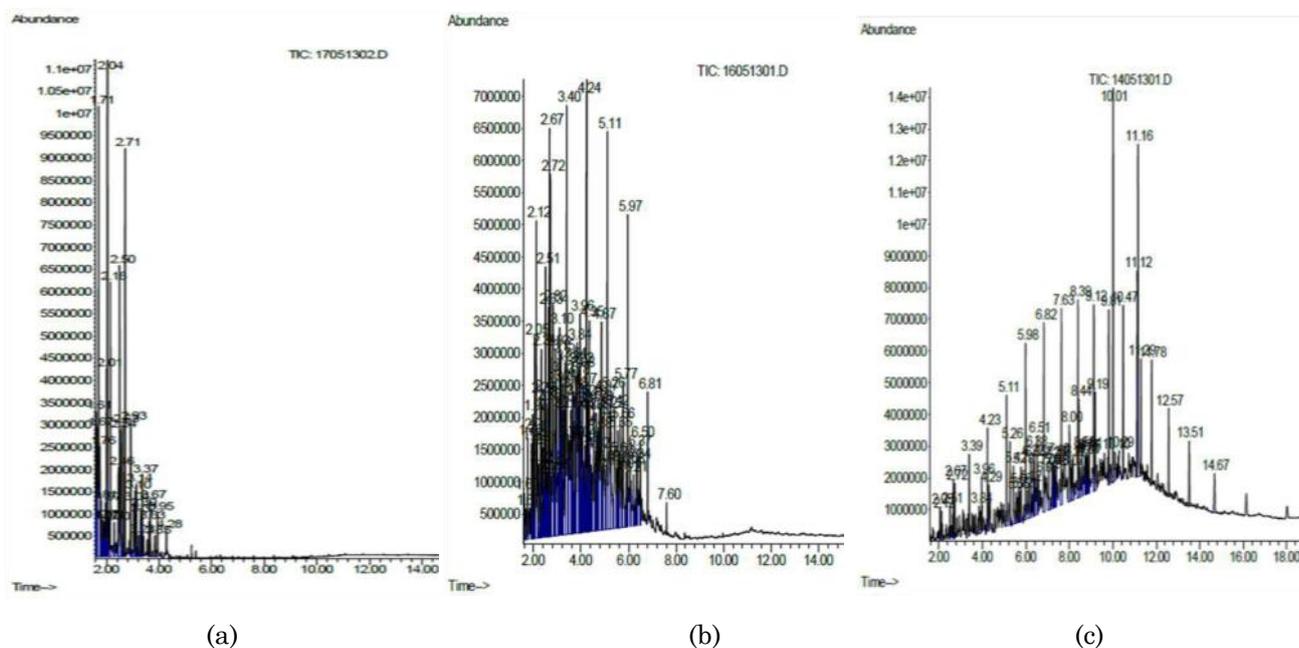
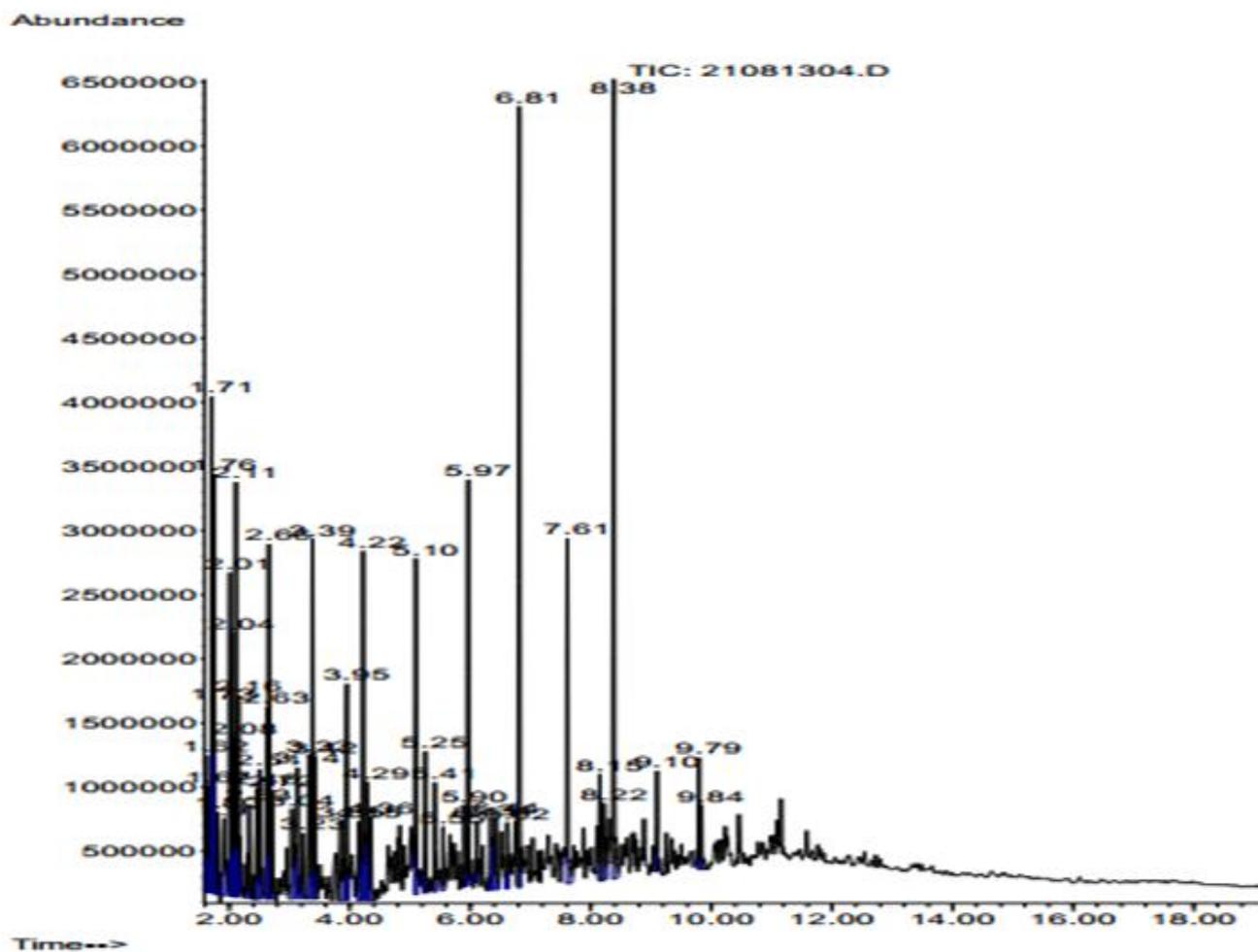


Figure 3. Chromatogram of GCMS for various commercial fuel: (a). Gasoline, (b). Kerosene, (c). Gasoil





tridecane, tetradecane, pentadecane, hexadecane, octadecane, nonadecane.

Sulfur contents as the pollutant of some fuels like methyl propyl sulfide and 3-methylthialcyclohexane, mercaptane, sulfide, disulfide, cyclo-pentana-tial, cyclo-hexane-tial, tiasiclo-hexane, thiophene, benzo-tiophena, benzo-tiophene and di-benzo-tiophena [26]. Hydrocracking over non-sulfide catalysts CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has yielded the non sulfuric products.

The products involving the main components of aromatic compounds are as yielded from the CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts, including the components required by gasoline due to their high octane numbers [27]. Components of hexadecane found in gasoil are able to reduce NOx gas emission up to 15.7% and particulate emission up to 45%. While, dodecane reduces NOx gas emission up to and particulate emission up to 49.5% [28].

Visually, as seen in Figure 5, chromatogram made shows the peak that is remarkably significant as it is identified chromatogram peak of fuel from the public refueling unit. Gasoline occupies wide range of 1.62% area and 0.48% kerosene, whereas the gasoil has 37% wide of the are. Gasoil has some main components, namely: pentadecane, 8-heptadecane, heptadecane, and cyclopentadecanone. Raw materials are not well converted due to the palmitic acids and oleic acids components in the products.

In chromatogram of hydrocracking products (Figure 6), the figure is not far different from that of the raw materials. This can be inferred that the final products are still contained some of the components of the raw materials that are not yet converted. In such a product, gasoline and kerosene yielded would not reach 0.38 % while the gasoil would be less than 16.47%. Then, the component of raw material obtained from the product would presumably reach 83 %.

Reaction results of hydrocracking using CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts give higher conversion than those using CoMo/SiO<sub>2</sub> and CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-

SiO<sub>2</sub> catalysts. The catalysts of CoMo/SiO<sub>2</sub> is more dominantly existing in gasoil product, whereas the catalysts of CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> does not contain gasoline product (Table 3).

Oxide metals composition existing on the surface of the catalysts that can absorb hydrogen and at the same time, has support with the widest rage of areas has enabled catalysts with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support to yield the highest conversion. An experiments done throughout the rection of Mo 12 (wt%) dan Co (4%), then it is used to load Mo (12 wt%) and Ni (4 wt%) would derive conversion reaction of 26.5 % [29]. At the same vein, methyl heptanoate and methyl hexanoate use catalysts CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with sulfidation process can yield reaction conversion up to 46.6 % (250 °C), 78.4 % (275 °C) and 100% (300 °C); while catalysts of CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> that is in the form of oxide would yield conversion up to in the temperature 300 °C [30].

Fuels derived from the present research are gasoline, kerosene andgasoilthat all have the non hydrocarbon constituent elements, such as sulfur; therefore, they are categorized to be enviromentally friendly.

#### 4. Conclusions

The findings of this research have brought us to the following conclusions: (a). the newly developed non-sulfide CoMo based catalysts are able to convert *Callophyllum innophyllum* kernel oil into fuels such as gasoline, kerosene, and gasoil; (b). the best catalysts is obtained from 10 wt.% loading of CoMo over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support which converts the vegetable oil up to 99.9 % and is selective towards gasoil; (c). the fuel products obtained from this conversion method are environmentally friendly.

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**Table 3** . Hydrocracking of *Callophyllum inophyllum* oil with non-sulfide catalysts

Type of catalysts	Conversion (%)	Yield		
		Gasoline	Kerosene	Gasoil
CoMo/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	99.9	25.63	17.31	38.59
CoMo/SiO <sub>2</sub>	42.33	1.11	0.33	25.77
CoMo/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub>	17.47	-	0.38	16.47

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