Hydrocracking of Nyamplung Oil (Calophyllum inophyllum oil) 
Using CoMo/γ-Al2O3 and CoMo/SiO2 Catalysts

Rismawati Rasyid1, Adrianto Prihartantyo1, Mahfud1 & Achmad Roesyadi1

1Department of Chemical Engineering, Sepuluh Nopember Institute of Technology, Indonesia

Correspondence: Achmad Roesyadi, Department of Chemical Engineering, Sepuluh Nopember Institute of Technology, Surabaya, 60111, Indonesia. E-mail: aroesyadi@yahoo.com

Received: May 4, 2015 Accepted: June 5, 2015 Online Published: June 30, 2015
doi:10.5539/mas.v9n7p43 URL: http://dx.doi.org/10.5539/mas.v9n7p43

Abstract
The purpose of this research is to study hydrocracking process of nyamplung oil using 5% and 15% CoMo catalyst and supported on γ-Al2O3 and SiO2. Catalyst was prepared using wet impregnation method and calcined at 500°C for 5 hours without sulfidation process. The X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) were performed to analyze the crystallinity and surface morphology. Based on the XRD that MoO2 was deposited on the surface of the catalysts. The hydrocracking of nyamplung (Calophyllum inophyllum) oil was conducted in Parr pressure reactor at 350°C and 3 MP. Hydrocracking product was analyzed by using Gas Chromatography – Mass Spectrometry (GCMS). The highest catalytic activity was obtained by 15% loading CoMo over γ-Al2O3 and the highest yields were 39.58% gasoil, 31.32% gasoline and 7.44% kerosene.

Keywords: nyamplung oil, hydrocracking, gasoil, gasoline, kerosene

1. Introduction
Biofuel is an alternative energy source that can nvironment the part of fossil based oil. Therefore, the amount of raw material should be able to meet those needs. One of raw material that can be used as alternative energy resources is non-edible oil. Nyamplung oil, as non-edible oil contains saturated and unsaturated fatty acid which can be converted into biofuel and consists of 75% oil of total components. It was found that nyamplung oil contained 71% of unsaturated fatty acids, such as oleic acid and linoleic acid (Ong et al., 2011).

This work used hydrocracking and employing bifunctional catalysts. Hydrocracking followed two processes, i.e. hydro-dehydrogenation and catalytic cracking. Bifunctional catalyst has two active sides, metal and acid, which serves to accelerate the reaction of hydrogenation, dehydrogenation and cracking, (Tayeb et al., 2010). The previous studies were the hydrocracking of soybean oil employing NiMo (Ishihara et al., 2014); hydrocracking of n-C16H34 and n-C28H58 using Pt/ SiO2 – Al2O3 (Rossetti et al., 2009), meanwhile, hydrocracking of vacuum gas oil applying zeolite catalyst (Cui et al., 2013).

Generally, hydrocracking uses bifunctional catalysts as previously reported investigations (Regali et al., 2013; Puron et al., 2014; Burnens et al., 2011). Catalyst preparation of CoMo for reaction had followed through sulfidation of H2S/H2 as proposed by authors (Yang et al., 2009; Anand et al., 2012; Loricera et al., 2011). However, those methods produced catalyst contained sulfuric compound, which accelerated the deactivation and more expensive.

The purpose of this research was aimed to study hydrocracking process of nyamplung oil using 5% and 15% CoMo catalyst and supported by γ-Al2O3 and SiO2. The present catalyst preparation did not employed the sulfidation process on CoMo catalyst. The advantages of this method were environmentally friendly and more economical.

2. Method
The catalysts were prepared by wet impregnation method. The five and 15 % CoMo catalysts derived from Co(NO3)2·6H2O and (NH4)6Mo7O24·4H2O, which were p.a. 99% (Merck). The CoMo was impregnated into the catalyst support γ-Al2O3 (p.a, Merck) or SiO2 (p.a, Sigma Aldrich) and referred to methods proposed by authors (Anderson and Garcia, 2005). The catalyst was dried at 110°C for 8 h and calcined at 500°C for 5 h. Catalysts prepared were analyzed by Scanning Electron Microscopy (SEM) with Ma Evo 10 instrument. The analysis determining the crystallinity of the catalyst was performed X-Ray Diffraction (Philips Analytica with scan
description: EI-0725). Hydrocracking process was conducted reactor (Parr pressure reactors, USA), which operated at 350°C for 2 h. The products were analyzed by GC-MS (Gas Chromatography – Mass Spectrometry).

3. Results

3.1 XRD Characterization of Catalysts

![XRD Pattern of CoMo catalyst](image1)

![XRD Pattern of SiO2 catalysts](image2)

![XRD of Al2O3 catalyst](image3)

Figure 1. XRD pattern CoMo, SiO2 and γ-Al2O3 catalysts

![XRD Pattern of CoMo (5%)/SiO2 Catalyst](image4)

![XRD Pattern of CoMo(15%)/SiO2 Catalyst](image5)

Figure 2. XRD pattern of CoMo/SiO2 catalyst
3.2 SEM Characterization of Catalysts

The characteristics of surface morphology of CoMo/γ-Al₂O₃ and CoMo/SiO₂ catalysts are presented in SEM images as shown in Figure 4.

![SEM analysis of CoMo/γ-Al₂O₃](image-a)

![SEM analysis of CoMo/SiO₂](image-b)

Figure 4. SEM analysis of CoMo/γ-Al₂O₃ dan CoMo/SiO₂ catalysts

3.3 Hydrocracking Results

<table>
<thead>
<tr>
<th>Type of Catalysts</th>
<th>Gasoline</th>
<th>Kerosene</th>
<th>Gasoil</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%CoMo /SiO₂</td>
<td>9.54</td>
<td>10.54</td>
<td>27.84</td>
</tr>
<tr>
<td>15%CoMo /SiO₂</td>
<td>4.24</td>
<td>-</td>
<td>15.50</td>
</tr>
<tr>
<td>5%CoMo /γ-Al₂O₃</td>
<td>10</td>
<td>8.52</td>
<td>36.75</td>
</tr>
<tr>
<td>15%CoMo /γ-Al₂O₃</td>
<td>31.32</td>
<td>7.44</td>
<td>39.58</td>
</tr>
</tbody>
</table>

4. Discussion

The original CoMo XRD patterns showed the clear peaks at angles (2θ) 12.7, 13, 19, 23 and 25, meanwhile, γ-Al₂O₃ displayed at 39.5, 45.7 and 67. On the other hand, peaks 20.9, 26.68, 36.58, 39.50, 50.17, 59.9, 67.78, 68.17 and 68.35 appeared for SiO₂ catalyst (Figure 1).

There were indicative that there were other elements deposited on the surface of the catalyst and for the catalyst
CoMo/SiO₂ is presented in Figure 2. Catalyst 5% CoMo/SiO₂ showed peaks at 2θ = 20.84, 26.62, 39.45, 50.11, 59.92, 67.71 and 68.2°. Catalyst 15% CoMo/SiO₂ was 2θ = 20.84, 26.62, 36.52, 39.44, 50.11, 59.93, and 68.11° shown in Figure 3. The MoO₂ and Al₂O₃ were deposited on the surface of catalyst γ-Al₂O₃ as its support.

After SiO₂ and γ-Al₂O₃ were impregnated by CoMo, the crystalinities were measured by XRD. The catalysts obtained showed the particular peaks on XRD patterns. In general, the peaks of prepared catalysts slightly shifted from those of original catalysts. The SiO₂ and CoMoO₄ were deposited on CoMo/SiO₂ the catalyst surface. Catalysts without sulfidation was formed MoO₃ through depositing on the catalyst surface of CoMo /γ-Al₂O₃ since Mo has an empty d orbital at periodical system. Free electrons on the 4d and 5s orbit of Mo atom can form Mo⁴⁺ that composed MoO₃, while MoO₃ is formed from Mo⁶⁺. The CoMo catalysts prepared via sulfidation, MoO₃ deposited on the surface of the catalysts (Nava et al., 2011). Other research using CoMo/W was detected in some peakes at 2θ = 25, 28, 32.5, 38, 43, 48, 57, and 59.5° and β-CoMoO₄ was deposited on the surface of catalyst (Huirache-Ancuña et al., 2009).

It showed that addition of CoMo at above 5 % over SiO₂ support gave the lower yields of product. The ability of catalyst with γ-Al₂O₃ support gave greater yields than that of SiO₂. It was caused by the presence of oxide metal on the surface of catalyst functioning to bind hydrogen. This is also attributed with the surface area range at from 165 – 186 m²/g. The ratio of metal and acid catalysts affected the performance of catalyst (Rayo Patricia et al., 2012).

The images CoMo/γ-Al₂O₃ and CoMo/SiO₂ showed the different morphological shapes (Figure 4). The CoMo/γ-Al₂O₃ catalyst has octahedral shape, while SiO₂ catalyst was irregular shape. An octahedral shape on CoMo/γ-Al₂O₃ was due to the MoO₂ deposited on the surface of catalyst forming Mo⁴⁺ ions. The MoO₂ significantly influenced to activity of catalyst so the yields obtained was higher than those of SiO₂.

After employing Catalyst CoMo/γ-Al₂O₃ and CoMo/SiO₂ without sulfidation for hydrocracking of nyamplung oil, it was found that CoMo/γ-Al₂O₃ resulted the highest yield. The highest yields of product in hydrocracking of nyamplung oil with catalyst 15%CoMo/γ-Al₂O₃ were 39.58% gas oil, 31.32% gasoline and 7.44% kerosene. The five percent CoMo/SiO₂ catalysts produced product yield of hydrocracking greater than 15% CoMo/SiO₂. Both catalysts are more selective on gas oil products than kerosene and gasoline shown in Table 1. While, 5%CoMo /γ-Al₂O₃ was more selective for gasoil compared to gasoline and kerosene. On other hand, the yield of gasoil using15%CoMo /γ-Al₂O₃ resulted 39.58 %, which slightly increased from gasoline recorded at 31.32%. It was discovered that 15% CoMo /γ-Al₂O₃ employed yielded the biggest gasoline of others catalysts.

Acknowledgments
The authors would like to thank members of the Chemical Engineering & Reaction and Process Technology Laboratories, Sepuluh Nopember Institute of Technology.

References


Copyrights
Copyright for this article is retained by the author(s), with first publication rights granted to the journal.
This is an open-access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/3.0/).