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Hydrocracking of Nyamplung Oil (*Calophyllum inophyllum 0il*) Using CoMo/γ-Al_2O_3 and CoMo/SiO_2 Catalysts

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Abstract

The purpose of this research is to study hydrocracking process of nyamplung oil using 5% and 15% CoMo catalyst and supported on γ-Al_2O_3 and SiO_2. Catalyst was prepared using wet impregnation method and calcined at 500^{o}C for 5 hours without sulfidation process. The X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) were performed to analyze the crystalinity and surface morphology. Based on the XRD that MoO_2 was deposited on the surface of the catalysts. The hydrocracking of *nyamplung (Calophyllum inophyllum)* oil was conducted in Parr pressure reactor at 350^{o}C and 3 MP. Hydrocracking product was analyzed by using Gas Cromotography – Mass Spectrometry (GCMS). The highest catalytic activity was obtained by 15% loading CoMo over γ-Al_2O_3 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 nvironmen 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-$C_{16}H_{34}$ and n-$C_{28}H_{58}$ using Pt/ SiO_2 – Al_2O_3 (Rossetti et al., 2009), meanwhile, hydrocracking of vacuum gas oil applying zeolite catalyst (Cui et al., 2013).

Generally, hydrocracking uses bifuctional 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 H_2S/H_2 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.

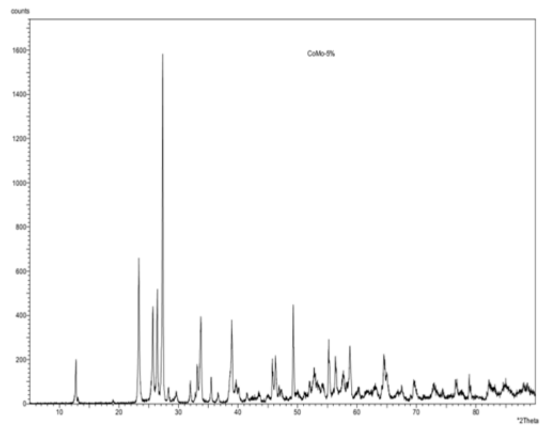
The purpose of this research was aimed to study hydrocracking process of nyamplung oil using 5% and 15 % CoMo catalyst and supported by γ-Al_2O_3 and SiO_2. The present catalyst preparation did not employed the sulfidation process on CoMo catalyst. The advantages of this method were 43nvironmentally friendly and more economical.

2. Method

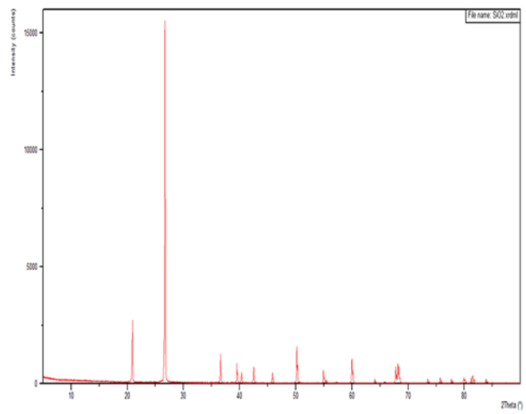
The catalysts were prepared by wet impregnation method. The five and 15 % CoMo catalysts derived from $Co(NO_3)_2{\cdot}6H_2O$ and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, which were p.a 99% (Merck). The CoMo was impregnated into the catalyst support γ-Al_2O_3 (p.a ,Merck) or SiO_2 (p.a, Sigma Aldrich) and referred to methods proposed by authors (Anderson and Garcia, 2005). The catalyst was dried at 110^{o}C for 8 h and calcined at 500^{o}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 of 350°C for 2 h. The products were analyzed by GC-MS (Gas Cromotography – Mass Spectrometry).

3. Results

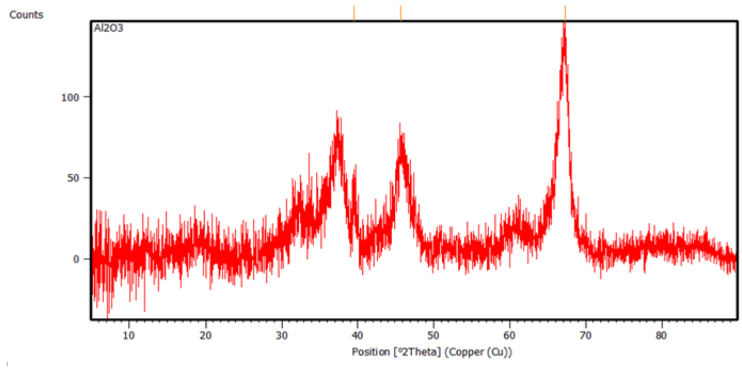
3.1 XRD Characterization of Catalysts



(a). XRD of CoMo catalyst



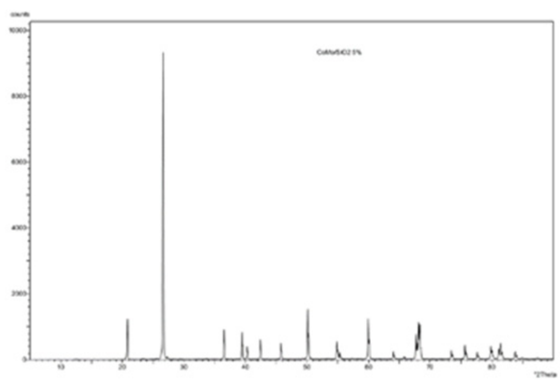
(b). XRD of SiO_2 catalysts

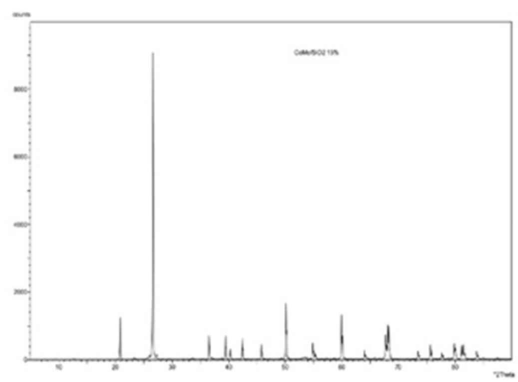


(c). XRD of Al_2O_3 catalyst

Figure 1. XRD pattern CoMo, SiO_2 and γ-Al_2O_3 catalysts

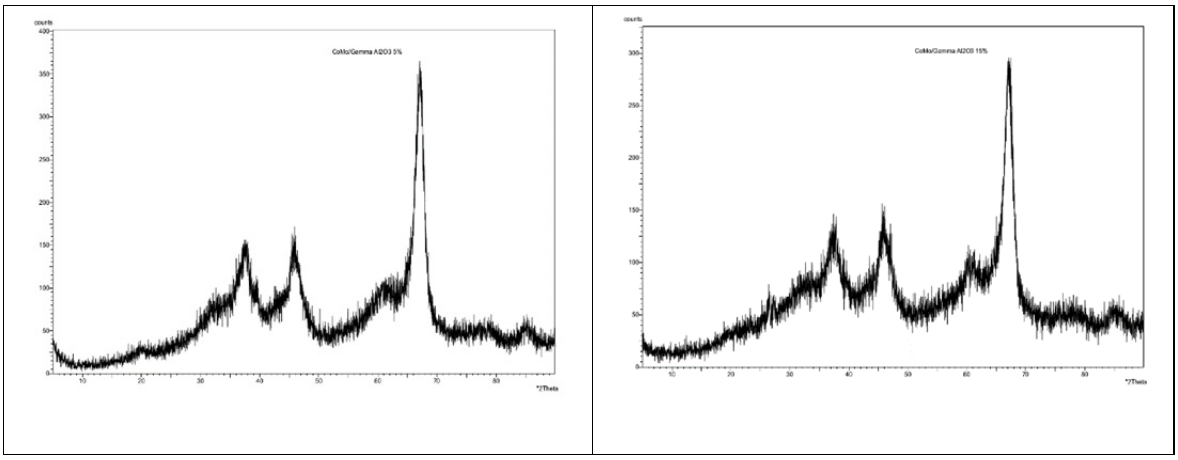
a.





XRD Pattern of CoMo (5%)/SiO_2 Catalyst b. XRD Pattern of CoMo(15%)/SiO_2 Catalyst

Figure 2. XRD pattern of CoMo/SiO_2 catalyst

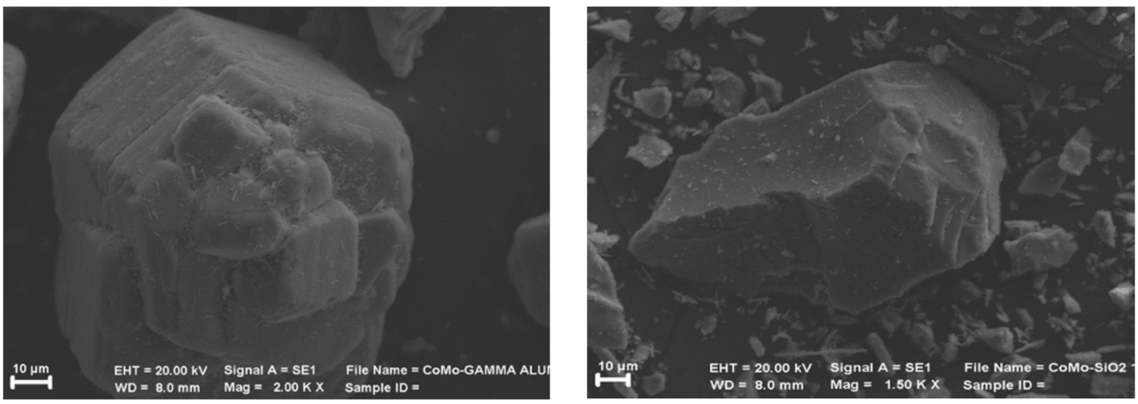


(a) (b)

Figure 3. The XRD patterns of Catalyst of 5% CoMo /γ-Al_2O_3 (a) and 15% CoMo /γ-Al_2O_3 (b)

3.2 SEM Characterization of Catalysts

The characteristics of surface morphology of CoMo/γ-Al_2O_3 and CoMo/SiO_2 catalysts are presented in SEM images as shown in Figure 4.



a. SEM analysis of CoMo/γ-Al_2O_3 b. SEM analysis of CoMo/ SiO_2

Figure 4. SEM analysis of CoMo/γ-Al_2O_3 dan CoMo/SiO_2 catalysts

3.3 Hydrocracking Results

Table 1. Product yield (in %) of hydrocracking of nyamplung oil

Type of Catalyts	Yield (%)		
	Gasoline	Kerosene	Gasoil
5%CoMo /SiO_2	9.54	10.54	27.84
15%CoMo /SiO_2	4.24	-	15.50
5%CoMo /γ-Al_2O_3	10	8.52	36.75
15%CoMo /γ-Al_2O_3	31.32	7.44	39.58

4. Discussion

The original CoMo XRD patterns showed the clear peaks at angles (2θ) 12.7, 13, 19, 23 and 25, meanwhile, γ-Al_2O_3 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 SiO_2 catalyst (Figure 1).

There were indicative that there were other elements deposited on the surface of the catalyst and for the catalyst

CoMo/SiO_2 is presented in Figure 2. Catalyst 5% CoMo/SiO_2 showed peaks at 2θ = 20.84, 26.62, 39.45, 50.11, 59.92, 67.71 and 68.2°. Catalyst 15% CoMo/SiO_2 was 2θ = 20.84, 26.62, 36.52, 39.44, 50.11, 59.93, and 68.11°.

The five percent CoMo/γ-Al_2O_3 catalysts have a clear peaks at 2θ = 20.8, 26.6, 50.1, 59.9, 68.1 and 68.2°, while 15% CoMo /γ-Al_2O_3 catalysts were at 2θ = 26.51, 27.2, 37.78, 60.2, 60.55, and 67° shown in Figure 3. The MoO_2 and Al_2O_3 were deposited on the surface of catalyst γ-Al_2O_3 as its support.

After SiO_2 and γ-Al_2O_3 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 SiO_2 and $CoMoO_4$ were deposited on CoMo/SiO_2 the catalyst surface. Catalysts without sulfidation was formed MoO_2 through depositing on the catalyst surface of CoMo /γ-Al_2O_3 since Mo has an empty d orbital at periodical system. Free electrons on the 4d and 5s orbit of Mo atom can form Mo^{4+} that composed MoO_2, while MoO_3 is formed from Mo^{6+}. The CoMo catalysts prepared via sulfidation, MoO_3 deposited on the surface of the catalysts (Nava et al., 2011). Other research using CoMoW was detected in some peakes at 2θ = 25, 28, 32.5, 38, 43, 48, 57, and 59.5° and β-$CoMoO_4$ was deposited on the surface of catalyst (Huirache-Ancuña et al., 2009).

It showed that addition of CoMo at above 5 % over SiO_2 support gave the lower yields of product. The ability of catalyst with γ-Al_2O_3 support gave greater yields than that of SiO_2. 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 m^2/g. The ratio of metal and acid catalysts affected the performance of catalyst (Rayo Patricia et al., 2012).

The images CoMo/γ-Al_2O_3 and CoMo/SiO_2 showed the different morphological shapes (Figure 4). The CoMo/γ-Al_2O_3 catalyst has octahedral shape, while SiO_2 catalyst was irregular shape. An octahedral shape on CoMo/γ-Al_2O_3 was due to the MoO_2 deposited on the surface of catalyst forming Mo^{4+} ions. The MoO_2 significantly influenced to activity of catalyst so the yields obtained was higher than those of SiO_2.

After employing Catalyst CoMo/γ-Al_2O_3 and CoMo/SiO_2 without sulfidation for hydrocrackyng of nyamplung oil, it was found that CoMo/γ-Al_2O_3 resulted the highest yield. The highest yields of product in hydrocracking of nyamplung oil with catalyst 15%CoMo/γ-Al_2O_3 were 39.58% gas oil, 31.32% gasoline and 7.44% kerosene. The five percent CoMo/SiO_2 catalysts produced product yield of hydrocracking greater than 15% CoMo/SiO_2. Both catalysts are more selective on gas oil products than kerosene and gasoline shown in Table 1. While, 5%CoMo /γ-Al_2O_3 was more selective for gasoil compared to gasoline and kerosone. On other hand, the yield of gasoil using15%CoMo /γ-Al_2O_3 resulted 39.58 %, which slightly increased from gasoline recorded at 31.32%. It was discovered that 15% CoMo /γ-Al_2O_3 employed yielded the biggest gasoline of others catalysts.

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