

Hydrocracking of Mefa Rubber Seed Oil into Biofuels Fraction with Co and CoMo Metals Supported on Zeolite Catalyst

Junifa Layla Sihombing^{1,2}, Herlinawati², Asep Wahyu Nugraha², Ahmad Nasir Pulungan², Moondra Zubir², Tiamina Nasution², Ary Anggara Wibowo³ and Saharman Gea⁴

¹Postgraduate School, Department of Chemistry, Universitas Sumatera Utara, Jl. Bioteknologi No. 1, Medan, Indonesia

²Department of Chemistry, Universitas Negeri Medan, Jl. Willem Iskandar Pasar V Medan Estate, Medan, Indonesia

³College of Science, Energy Change Institute, College of Science Australian National University, ANU, Australia

⁴Department of Chemistry, Universitas Sumatera Utara, Jl. Bioteknologi No. 1, Medan, Indonesia

Keywords: Rubber Seed Oil, Hydrocracking, Catalyst, Impregnation, Biofuel.

Abstract: This research was aimed to produce biofuel fraction from rubber seed oil by using synthetic Zeolite Y (ZY), Co/ZY and CoMo/ZY catalyst. The insertion of metal used a wet impregnation method. Furthermore, in order to produce a good catalyst, the oxidation and reduction process at 500°C using oxygen and nitrogen gases at approximately 2 hours were performed. Then, the effect of addition of ZY, Co/ZY and CoMo/ZY had been investigated at catalytic hydrocracking using methyl ester fatty acid (MEFA). The reaction was conducted at 450°C with ratio of catalyst:feed of 1:4 and 20 mL/sec with hydrogen gas flow. Moreover, the characterization of catalyst depicted that no significant changes in wavenumber of TO4 groups and a crystallinity of catalyst. Then, the crystal system of ZY and Co/ZY was indicated as monoclinic while CoMo/ZY was revealed as triclinic. The surface area, pore volume and mean pore of catalysts revealed an increase trend as a result of Co and Mo impregnation. These trends have also been proven with SEM analysis which was shown an equal spreading of metals in the catalysts. Furthermore, the highest result of catalytic performance among catalysts was shown by CoMo/ZY with 59.45% of bio-gasoline. To sum up, the impregnation of Co and CoMo in Zeolite Y depicted a well-effect on its selectivity into bio-gasoline product.

1 INTRODUCTION

The world's energy needs for petroleum fuels are increasing in accordance with technological and industrial developments and the growth of the world's population. Meanwhile, fossil fuel reserves continue to decrease and have a negative impact on the environment. This has encouraged a lot of research to find alternative fuel sources that are sustainable and environmentally friendly. According to the Renewable Fuel Standard, the consumption of renewable fuels currently reaches 14 billion gallons per year (BGY) and in 2022 is predicted to reach 32 BGY (Perlack et al., 2011).

Indonesia has enormous biomass potential as a renewable and environmentally friendly alternative energy sources (Sihombing, Gea, Kembaren, et al., 2018). Biomass and agricultural or plantation products such as palm oil, soybeans and rubber seed oil have been converted to biofuels (Vinh et al., 2011).

Rubber seed oil (RSO) is one of the biomass, that is widely available in Indonesia and has not been widely used. The main contents of RSO is 39% of linoleic acid and 23.52% of oleic acid (Wibowo et al., 2014), which can be converted to liquid fuel fraction by catalytic cracking process (Sihombing, Gea, Pulungan, et al., 2018).

Hydrocracking method has been commonly used to produce biofuels sourced from vegetable oils (Bezergianni et al., 2009). The use of catalysts in this process is more desirable because it can reduce the activation energy (Sriningsih et al., 2014), therefore, it will make the process more efficient and can reduce unnecessary byproducts, such as heteroatomic substances (Khowatimy et al., 2014). In the hydrocracking process, breaking the C-C bond from a long chain carbon compound to a short chain carbon compound with simultaneous or sequential hydrogenation. Heterogeneous catalyst such as Zeolite Y (De Jong et al., 2010; Pulungan et al., 2014), porous

material MCM-41 (Zubin et al., 2010) and multi porous Composite MC-ZSM-5/ MCM-41 [14] have been used in this process. The fuel products produced have low density and good physical and chemical properties as petroleum fuels.

Based on several heterogeneous catalyst types used, zeolite is the catalyst most widely used in the petroleum process, because it has a large surface area, high thermal stability and high acidity (Degnan, 2000). One type of zeolite which is very important is Y zeolite. It is widely used as a catalyst for the process of fluid catalytic cracking, hydrocracking, and alkylation in the process of oil refining and petrochemical synthesis (Choi et al., 2009). This is because Zeolite-Y has a high concentration of active acid sites, high thermal stability and high size selectivity (Sato et al., 2001).

One method to increase the activity and selectivity of the catalyst is by impregnation of transition metals into zeolites. Co and Mo metals loaded into pore of alumina have been tested in the heavy oil hydrocracking and hydrotreating process, which shows high conversion results and low coke formation (Da Silva, 2014; Parkhomchuk et al., 2013; Pashigreva et al., 2010). Sihombing, Gea, Kembaren, et al. (2018) has also been reported that loaded Co and Mo on natural zeolites as catalysts for mefa rice bran oil hydrocracking processes have increased the selectivity of biogasilen products.

Therefore, in this study a modification of the ZY catalyst character by impregnation of Co and CoMo metals and an activity test on MEFA hydrocracking from rubber seed oil to biofuel was carried out. This modification is expected to provide high conversion products and good selectivity for the biogasoline fraction.

2 MATERIALS AND METHODS

2.1 Materials

MEFA Rubber Seeds, Synthetic Zeolite Y (ZY) was obtained from Tosoh-Japan, Precursor Metal $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ were purchased from Merck. Distilled water was purchased from CV.Bratachem. Hydrogen Gases, Oxygen Gases and Nitrogen Gases were purchased from PT. Aneka Gas.

2.2 Experimental

2.2.1 Preparation of Catalysts

The impregnation of Co and CoMo on ZY according to Sihombing, Gea, Kembaren, et al. (2018). As much as 1% (w/w) of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was poured into 100 grams of zeolite Y through the wet impregnation method. Then, the mixture was refluxed for 5 hours at a temperature of 80°C to produce Co-ZY. After that, the Co-ZY mixture was oxidized with oxygen gas (± 20 mL/sec) for 2 hours at 500°C. Then, the reduction process was conducted by using hydrogen gas (± 20 mL/sec) for 2 hours at a temperature of 500°C to produce Co/ZY catalyst.

An amount of 1% (w/w) of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was poured into 100 grams of zeolite Y and treated with wet impregnation method. Then, the mixture was refluxed for 5 hours at 80°C to produce Mo-ZY. After that, a total of 1% (w/w) of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added to Mo-ZY. It was then refluxed for 5 hours at 80°C and Co-Mo-ZY was resulted. The oxygen gas (± 20 mL/sec) was flowed to Co-Mo-ZY mixture in order to perform the oxidation process. This was conducted for 2 hours at 500°C. Finally, the reduction process was carried out by using hydrogen gas (± 20 mL/sec) for 2 hours at a temperature of 500 °C to produce the CoMo/ZY catalyst.

2.2.2 Characterization of Catalysts

At last, the ZY, Co/ZY and CoMo/ZY catalysts were analyzed using the FTIR (Shimadzu-Prestige-21), XRD (shimadzu), SEM (ZEISS Mode EVO MA 10) and specific surface area measurements with Gas sorption analyzer through BET method.

2.2.3 Catalyst Activity Test

The activity test of Co/ZY and CoMo/ZY catalysts towards Catalytic Hydro Cracking process was performed. MEFA rubber seed oils in a fix-bed system reactor. The reaction temperature was set at 450 oC and with the ratio of feed:catalyst was 1: 4 with a reaction time of 2 hours [2]. The conversion yield of each product was calculated using the equation used by Sriningsih et al. (2014) and the resulting liquid product was analyzed by GC and GC-MS method (GC-FID Agilent Technologies 6890N Network).

3 RESULTS AND DISCUSSIONS

3.1 The Characterization of Catalyst

The catalyst used in this study was synthetic zeolite Y (ZY). It is a synthetic zeolite which is included in the classification of faujasite. The cell unit is cube-shaped with large cell dimensions approaching 25Å and consists of 192 tetrahedral of (Si, Al)O₄. Zeolite Y is very good for carrying various types of metals in catalytic hydrocracking reactions since it has a uniform pore structure and a high concentration of active sites, so it has excellent thermal stability and selectivity (Htay & Oo, 2008). In this research, the ZY catalyst was used by inducing the Co metal and CoMo metal combination using the wet impregnation. Then, it was followed by the process of calcination, oxidation and reduction in the presence of hydrogen. The calcination process, oxidation and reduction were carried out to produce strong interactions between metal and carrier (Schwarz et al., 1995). From the series of processes, a uniform distribution of catalyst metal will be obtained on the surface of the carrier. In addition, the calcination, oxidation and reduction processes affect the metal dispersion in the carrier. Metal preparation of the carrier and the basic properties of the carrier can affect the physical structure and chemical properties of metal deposits. The significant changes to the catalytic properties of a metal can occur with variations in the composition of the carrier from different metal development preparations. To analyze the success of the treatment given, several analysis of catalyst material were performed with FTIR, XRD, BET and SEM methods.

3.1.1 FT-IR Analysis

Based on Figure 1, it can be seen that the wave numbers that show the adsorption of FTIR spectra on protonated zeolite is at 4000 to 400 cm⁻¹. All spectra display great intensity at 3451-3442 cm⁻¹ which indicates the vibration of O-H stretching from Si-OH and Al-OH groups. The spectra recorded at 1642-1635 cm⁻¹ correspond to a buckling vibration of Si-OH. Then, the peak at 1049-1180 cm⁻¹ indicates the presence of internal and external asymmetric vibrations of the TiO₄ group, while the peak at 816-817 cm⁻¹ shows the TiO₄ symmetrical stretching vibration. The intensity of the band around 591-590 cm⁻¹ indicates the internal buckling of the tetrahedron while the band around 456-454 cm⁻¹ shows the D4R ring. It can be seen that all

peaks reveal no significant change in the catalyst after the metal addition. So it can be concluded that metal development does not contribute damage to the framework of zeolite.

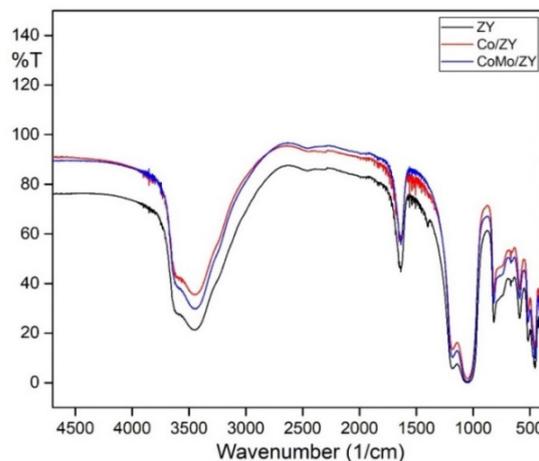


Figure 1: The comparison of FTIR spectra of ZY, Co/ZY and CoMo/ZY catalysts.

3.1.2 XRD Analysis

The XRD characterization results are spectra with abscissa which shows the diffraction and ordinate angles indicating the intensity.

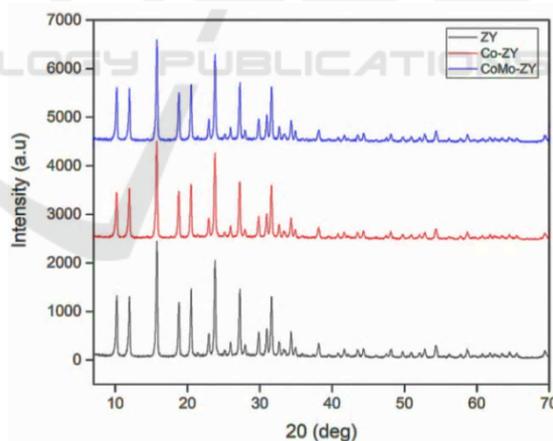


Figure 2: The XRD diffractogram of ZY, Co/ZY and CoMo/ZY catalysts.

Based on the comparison of the intensity shown in Figure 2, it can be inferred that the process of Co and CoMo metals addition in zeolite Y (ZY) carrier results in a decrease of some ZY diffraction main peaks intensity in the range 10-30 θ degrees, yet it still has the same diffractogram shape. This indicates that the addition of metal does not damage the crystal structure and the spread of the metal occurs even-

ly on the surface of the ZY pore. The results of this analysis correlate with the results of the surface area analysis as shown in Table 2. Further analysis was carried out using the Expo 2014 method to determine the catalyst crystal structure. The results of the analysis are described in Table 1.

Table 1 reveals that the addition of Co metal does not change the ZY carrier crystal system. How-

ever, the crystal system change was occurred in CoMo / ZY. This is probably the result of strong interaction of Co and Mo metals on the pore surface. The Interactions between metals can cause the formation of alloys. Moreover, alloy formation in the ZY carrier pore will cause a geometric change due to the limitation of the size of each component.

Table 1: The result of XRD data analysis on ZY, Co/ZY and CoMo/ZY catalysts via EXPO method.

Catalysts	A (Å)	B (Å)	C (Å)	a (°)	b (°)	g (°)	Vol (Å ³)	Crystal System
ZY	8.14904	8.98075	12.48393	117.9507	122.3303	91.5312	633.1	Triclinic
Co/ZY	10.26336	11.39037	10.24643	60.73391	67.99091	48.9241	785.11	Triclinic
CoMo/ZY	14.33625	8.65771	7.50814	89.99995	100.0584	89.99995	917.58	Monoclinic

3.1.3 BET Method Analysis

Table 2 shows the results of determining the catalyst surface area using the Bruener-Emmer-Teller (BET) method. From these data, it can be seen that the addition of Co and CoMo metals on ZY increases the total pore volume of ZY catalyst. This indicates that the metals were spread evenly on the pore surface of the ZY carrier. In contrast to the results of the measurement of the pore spacing, the addition of metal into the pore of the ZY carrier results in a greater average pore radius. This is possible since the more metals are impregnated into the pores of the carrier, and then the pores of the carrier with smaller fingers will be more clogged so that the average pore radius increases. Meanwhile, the catalyst surface area after metal Co has increased from 342.651 m²g⁻¹ (ZY) to 491.246 m²g⁻¹ (Co / ZY), but it has decreased with CoMo/ZY metal addition with the value of 435.239 m²g⁻¹. However, when it is compared to basic ZY catalysts, the addition of Co and CoMo increases the catalyst specific surface area. Similar results were reported by Semeykina et al. (2016), showing that Co, Mo and Ni metals in mesoporous alumina (Al₂O₃) carriers increased the catalyst specific surface area. Surface area, pore volume and mean pore size are important characteristics of the catalyst which greatly affect the activity and selectivity of the catalyst. The scheme of metal loaded to the ZY catalyst presented in figure 3.

Table 2: The result of BET analysis on ZY, Co/ZY a CoMo/ZY catalysts.

Catalysts	Area (m ² g ⁻¹)	Pores Volume (cc/gr)	Average Pore Size (Å)
ZY	342.651	0.24	13.78
Co/ZY	491.246	0.40	16.38
CoMo/ZY	435.239	0.66	30.43

3.1.4 SEM Analysis

SEM (Scanning Electron Microscopic) analysis is used to determine the catalyst surface topology. Moreover, it aims to determine the dispersion level of the metal which is applied to ZY. The visualization of the Co and CoMo addition on the ZY carrier pliers was evenly distributed on the surface of the ZY carrier pore illustrated in Figure 4. The result of SEM analysis is shown in Figure 4, which shows that the distribution of metals in ZY is evenly distributed and does not show sintering metals on the pore surface of the ZY carrier. This is indicated by the shape of the surface morphology of each catalyst which is relatively homogeneous. This SEM data correlates with previous XRD and BET data.

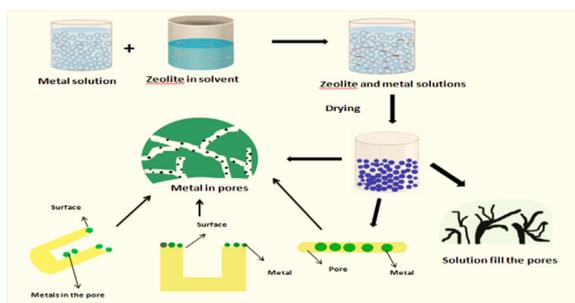


Figure 3: The scheme of metal loaded to the ZY catalyst.

3.2 Catalytic Performance of Catalyst

The catalyst activity test was carried out on the hydrocracking reaction of rubber seed oil. The feed solution used was MEFA from rubber seed oil with the ratio of catalyst and feed used was 1:4 (w/w). Rubber seed oil MEFA hydrocracking reaction was carried out at a temperature of 450°C with hydrogen gas flow of 20 mL/minute for 2 hours. The products which were produced are gas, liquid and coke. The resulting liquid product was analyzed by GC and GC-MS. The coke formation can be seen from changes in the color of the catalyst which tends to be darker after the reaction process takes place. The results of the activity and selectivity test of each catalyst are presented in Figure 5 and figure 6. Figure 5 show that the metal addition of the Co/ZY catalyst gives a larger gas product than the ZY catalyst which was 26.60%. This is caused by the entry of Co metal in the carrier pore gives more active sites which play a role in the reaction process. Zhang et al., 2003 reported that homogeneously distributed metals on zeolite surfaces and pores had increased catalytic active sites. In addition, the Co/ZY catalyst has a larger surface area, so the probability of the reaction occurring in the active site is greater. However, in CoMo/ZY Catalyst, it provides a larger gas product than Co/ZY catalyst. This was considered from the role of the combination of Mo metal as a catalyst promoter which showed a performance in increasing catalyst activity in the MEFA hydrocracking reaction of rubber seed oil. The conversion of liquid products produced from each ZY, Co/ZY and CoMo/ZY catalysts were 39%, 32.4% and 26.4% respectively. The selectivity of liquid products to the gasoline and diesel fractions is displayed in Figure 6.

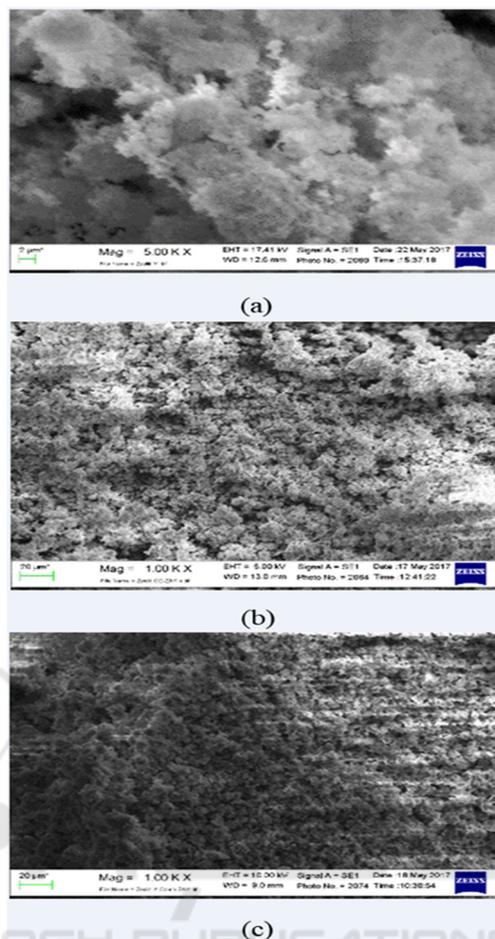


Figure 4: The SEM analysis result of (a) ZY, (b) Co/ZY and (c) CoMo/ZY catalysts.

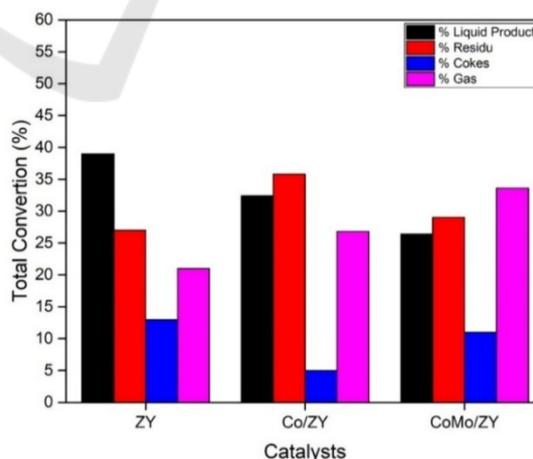


Figure 5: The catalytic activity of MEFA hydrocracking of rubber seed oil with ZY, Co/ZY and CoMo/ZY catalyst at a temperature of 450 oC with the ratio of 1:4.

Figure 6 shows that the ZY catalyst produced by liquid hydrocarbons is dominated by diesel fractions with 74.18%. However, for both the Co/ZY and CoMo/ZY catalysts, the selectivity of liquid hydrocarbon products produced on the gasoline fraction increased significantly with the percentage of selectivity to gasoline with 55.58% and 59.45% respectively. The metal catalyst system of Co/ZY and CoMo/ZY is able to increase the product selectivity to the gasoline fraction to be more than 2 times that of using a metal-free catalyst (ZY). This is due to the increase in catalyst surface area and pore volume. Trisunaryanti et al. (2013) reported that by using zeolites which is containing metal, it will produce liquid products with the C7-C12 fuel fractions. This phenomenon may occur due to the presence of the Bronsted acid site and as an active metal site causing the solids to have catalytic properties. The empty d orbitals owned by the metal, is functioning as Lewis acid sites which can accept electron pairs from the reactants. Therefore, the breakdown of the C-C bonds occurs through the carbocation mechanism. The CoMo/ZY catalyst shows the role of a combination of Co and Mo metals, where Mo acts as a promoter on the catalyst which contributes to the increase in catalyst activity in the MEFA rubber seed oil hydrocracking reaction. This causes the Co-Mo/ZY catalyst to produce gas and gasoline products that are larger than the ZY and Co/ZY catalysts. The mechanism of the hydrocracking reaction on the metal-carrying system catalyst (bifunctional catalyst) has been described by Weitkamp (2012), as described in Figure 7.

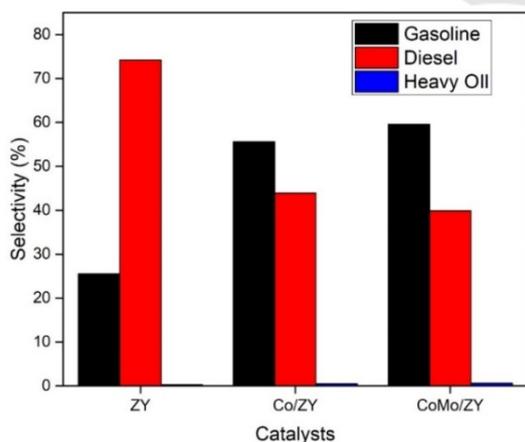


Figure 6: The selectivity of liquid product of MEFA hydrocracking of rubber seed oil with ZY, Co/ZY and Co-Mo/ZY catalyst at a temperature of 450°C with the ratio of 1:4.

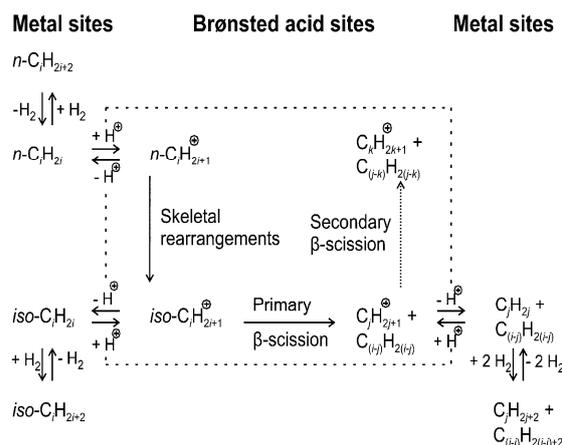


Figure 7: The classical reaction mechanism of n-alkane hydrocracking process on metal addition catalytic system.

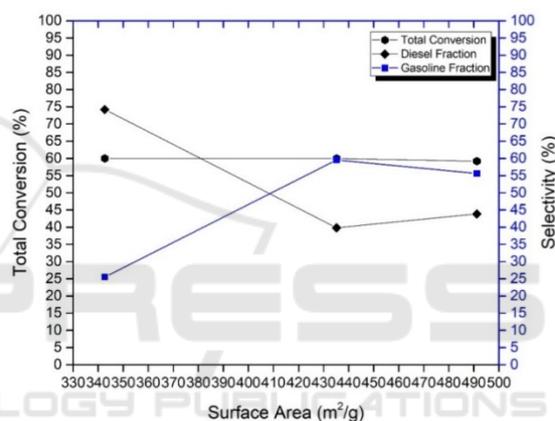


Figure 8: The relation between surface area of catalyst to the total conversion and selectivity level.

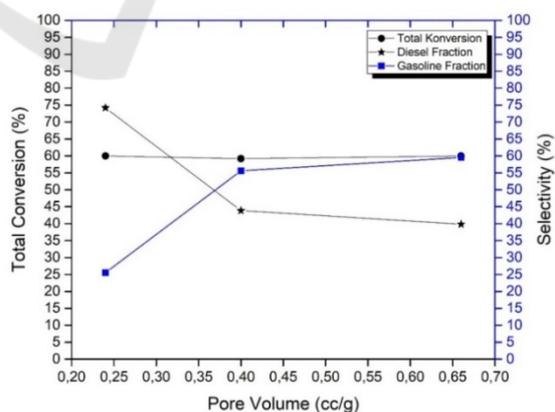


Figure 9: The relation between pore volume of catalyst to the total conversion and selectivity level.

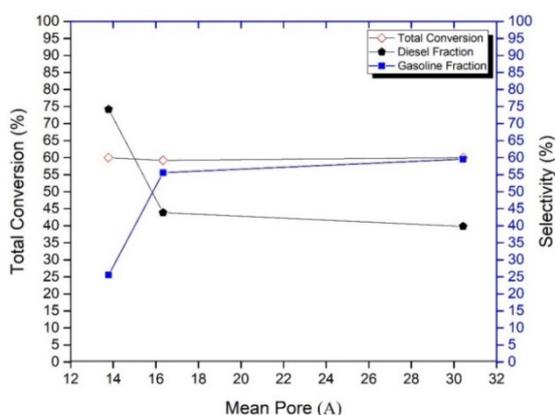


Figure 10: The relation between mean pore of catalyst to the total conversion and selectivity level.

The relationship between specific surface area, pore volume and mean of pore catalyst to the total conversion and product selectivity are shown in Figure 8, 9 and 10. Figure 8 shows that the increase in catalyst surface area, will not giving a significant effect on the total conversion results. In the other hand, increasing the catalyst surface shows a tendency to produce a higher gasoline fraction. This condition is inversely proportional to the selectivity of the diesel fraction. This is possible since the wide catalyst surface provides a higher chance of adsorption and cracking reactions to produce lighter fractions of gasoline or hydrocarbons. The same trends are also shown in Figure 9 and 10. In Figure 9 and 10, it can be observed that the increase in pore volume and the mean of the catalyst pore range does not contribute large influence on the total conversion value, but shows the trend of increasing the selectivity of liquid products to the gasoline fraction. Increased pore volume as a result of the widening of the pore size of the catalyst, so that the diffusion process of the molecules resulting from cracking MEFA can penetrate the pore, no further reaction occurs, resulting in hydrocarbon compounds which is equal to gasoline fractions in higher amounts. This phenomenon may also be caused by the suitability of the pore size of the catalyst at the time of cracking reaction, including the process of reactant adsorption, catalytic cracking process, and desorption of cracking molecules from the catalyst surface.

4 CONCLUSIONS

The Co and CoMo metal supported on ZY carriers exhibit characteristics in increasing catalyst specific surface area, total pore volume and mean catalyst

pore rate. The data obtained illustrate that Co metal and CoMo metal presences do not damage the crystal structure of ZY and are evenly distributed on the pore surface of the carrier. From the processing of XRD data using expo-2014 method, it was found that ZY and Co/ZY catalysts were formed with a triclinic crystal system, while for CoMo/ZY catalysts showed a monoclinic crystal system. Moreover, in the rubber seed oil MEFA hydrocracking reaction, ZY catalyst showed a 74.18% higher selectivity for biodiesel products. The presence of Co and CoMo metals loaded on ZY increases the activity and selectivity to the formation of the gasoline fraction. To sum up, the highest gasoline product was produced by CoMo/ZY catalyst with 59.45% w/t, followed by Co/ZY catalyst with 55.58% w/t.

ACKNOWLEDGEMENT

Authors would like to acknowledge Rector Universitas Negeri Medan and LPPM-Unimed for financial support via "Hibah Penelitian KDBK-2019" scheme. Moreover, a grateful acknowledgement is addressed to Universitas Negeri Medan Research Center, Indonesia, for facilitating the research.

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