

Effect of NiMo/Zelite Catalyst Preparation Method for Bio Jet Fuel Synthesis

Thareq Kemal Habibie¹, Bambang Heru Susanto^{1*}, and Michaele Flavin Carli¹

¹Departement of Chemical Engineering, Universitas Indonesia, Depok 16424, Indonesia

Abstract. Bio jet fuel is an alternative fuel derived from vegetable oil substitutes for conventional aviation fuel. Bio jet fuel can be synthesized through hydrodeoxygenation and catalytic cracking process pathways that influence by the catalyst. The success rates of bio jet synthesis with catalysts influence by the characteristic and activity of the catalysts. One factor that influence the catalyst characteristic and activity is the preparation method. This study focuses on the preparation method of a catalyst by comparing the conventional method of impregnation and the latest microwave polyol method. The impregnation method utilizes stirring up to 24 hours while microwave polyol utilizes a microwave for rapid heating which serves to expand the active core, but the catalyst is not yet known its character and its activity in bio jet fuel synthesis process. In this study, NiMo/Zelite was synthesized by impregnation method had 232.18 m²/gram surface area and had average crystal size of 49.35 nm. Further, the catalyst was used to synthesize bio jet fuel through a catalytic cracking process, with green diesel from the hydrodeoxygenation process of oleic acid conversion as feed. The result, obtained high enough of conversion by 84.30%, but low yield and selectivity of bio-jet fuel range by 34.77% and 36.43% respectively.

1 Introduction

Currently in Indonesia, the growing number of air transport passengers is increasing from the data of BPS (2017) an increase of 95.1 million in 2016. The increasing number of passenger aircraft impact on aviation fuel consumption. To meet the needs of jet fuel at this time, the government is still importing from other countries, such as Singapore. One of the opportunities to overcome the aviation commodity deficit is with bio jet fuel [1]. Bio jet fuel is one of the second-generation renewable fuel produced from vegetable oils (triglycerides). Vegetable oil was investigated as an affordable alternative to conventional fuel derived from petroleum. The benefits using vegetable oil for biofuel production are renewable, easy to obtain, low aromatic content, low sulfur content, and bio-degradable. Bio jet fuel can be produced by a hydrodeoxygenation process followed by a catalytic cracking process.

The reaction of bio jet fuel synthesis by hydrodeoxygenation and catalytic cracking process involve the catalyst to decrease the activation energy of the reaction and increase the reaction selectivity. The type active nucleus of the catalyst that has been shown to have high activity for this reaction is the Ni-Mo metal transition. Itthibenchapong [2] in his study used a NiMo/ γ -Al₂O₃ sulphide catalyst and obtained a

selectivity of hydrocarbon similar to jet fuel range (C₁₀ - C₁₂) from oil palm shell is 58%. From this study, it can be said that NiMo sulphide catalysts have high activity, but they do not correspond to environmental issues where sulfur content plays a role in pollution and global warming, therefore zeolite non-sulphide catalyst is required [3]. Similar studies using NiMo/H-zeolite Y non-sulphide catalysts with soybean oil feedstock managed to obtain bio jet fuel with a yield of 48.2% [4]. Prakasa [5] in his research used NiMo/ZAL converted palm oil and jathropa oil to synthesize renewable diesel gave 45.66% yields. This proves that Ni and Mo metal components distributed on the support surface such as zeolite produce bio jet fuel with high selectivity and yield due to the ability of zeolite as a cracking catalyst and that has a very porous 3-dimensional structure and has a wide pore space for the reaction which is indicated by the large volume and pore diameter of the zeolite [6]. In Indonesia there are a lot of natural zeolite sources, one of them from Malang, East Java. Setiadi [7] in his research explains that natural zeolite from Malang is a natural zeolite with mordenite type which has 44.1% crystallinity and yields 41.9% on ABE reaction to hydrocarbon. Apart from crystallinity, the particle size and dispersion of the metal active sites on support is determined by the choice of catalyst preparation method [8]. Wiyo [9] in his study using Pd/Zeolite to synthesize

* Corresponding author: bambanghs@che.ui.ac.id

renewable diesel through hydrodeoxygenation produces 90.23% conversion, 10.78% selectivity and 8.80% yield of C₁₁ - C₁₃ carbon chain.

There are several NiMo/Zelite catalyst preparation processes including the conventional method of impregnation method, which is the easiest method, but requires more than 24 hours preparation times and large energy consumption [10]. Huali [11] in his study using ZSM-5 zeolite that was polymerized with 1.1% ruthenium in catalytic cracking reaction of hydrocarbons equivalent to jet fuel produces 16% of yield. The use of a long time spent so much energy makes this method inefficient in synthesizing a catalyst. For that, there needs to be a modification method that can reduce the time of synthesizing and energy consumption. The latest preparation method is using microwave polyol process method. This method utilizes microwaves and homogeneous processes using ultrasonication. Modification with a microwave is a simple, efficient and fast method that takes about 3 to 5 minutes to synthesize the catalyst [12]. Both of these methods have been tested to produce a catalyst with a nanoparticle size. The smaller particle size gives higher activity to the catalytic cracking reaction [13].

In this study, NiMo/Zelite catalyst synthesis by comparing two preparation methods. The impregnation method used a long agitation while the microwave polyol method, utilizing microwave rapid heating and the activation process will be carried out under optimum conditions to produce surface area, high activity and selectivity of bio jet fuel.

2 Method

2.1. Materials

This study used natural zeolite from Malang as catalyst support, metal salt precursors nickel nitrate hexahydrate (Ni(NO₃)₂.6H₂O) and ammonium heptamolybdate tetrahydrate (NH₄)₆Mo₇)₂₄.4H₂O as active nucleus bought from Toko Ilmu Kimia, Jogjakarta, 3M HCl solvent for natural zeolite activation, ethylene glycol as polyol solvent, potassium bromide (KBr) as stabilizer compound, 1M NaOH solvent as pH regulator.

2.2. Catalyst Preparation Procedures

Zeolite activation as support – natural zeolite from Malang with type of mordenite soaked with demineralized water and stirred for 24 hours. Then, natural zeolite was filtered and dried by oven at 100°C for 1 hour. Subsequently natural zeolite was soaked and stirred with 3M HCl solution at 50°C for 1 hour. After that, natural zeolite was filtered and rinsed again to pH 7 and then heated with furnace at temperature 300°C for 1 hour.

Catalyst synthesis – impregnation method. NiMo as precursor with determined loading dissolved with 10 ml of distilled water and mixed with 10 ml of ethylene

glycol. 10 grams of activated zeolite were introduced into the mixture and then stirred for 24 hours without heating. After that set the pH of solution until 8 with NaOH. Used KBr to stabilize the solution then dispersed with ultrasonicator bath for 100 minutes. The solution then filtered and rinsed with ethanol and demineralized water and heated to 500°C for 3 hours.

Catalyst synthesis – microwave polyol method. The different between this method and impregnation are the mixture (NiMo, ethylene glycol and activated zeolite) was not stirred for 24 hours and there is an additional step after the KBr addition process, the solution heated in microwave at specified power for 1 minute. The synthesized catalysts were given term to facilitate the naming according to Table 1.

Table 1. Synthesized Catalyst

Catalyst (%Loading)	Impregnation	Microwave Power (Watt)
NMZ-IMP (10%)	√	-
NMZ-MWP (10%)	-	800

Catalyst characterization – the results of the synthesized catalyst, characterized by several tests such as BET to obtain the surface area, pore size (diameter and volume), SEM-EDX to determine surface morphology and catalyst composition, and XRD to determine the crystallite size of the metal precursor.

2.3. Catalyst Activation

The catalytic cracking reaction performed in autoclave batch reactor integrated with condenser and furnace. Renewable diesel converted from oleic acid used as feed and NiMo/Zelite as catalyst with feed ratio 100:1 wt, stirred at 800 rpm and atmospheric pressure. The reaction is kept at temperature 375°C for 1.5 hours.

3 Result and Discussion

3.1. BET Surface Area Characterization

Table 2. BET Characterization Result

Catalyst	Surface Area (m ² /g)	Pore Volume (cc/g)	Pore Diameter (nm)
Malang Activated Natural Zeolite*	99.10	0.02	0.80
NMZ-IMP	232.18	0.16	2.67
NMZ-MWP	39.21	0.05	5.24

*Funky [18]

Can be seen from the BET surface characterization test results in Table 2, there are differences in surface area between each catalyst with the activated natural zeolite support from Malang. Based on the results of the

test, NMZ-IMP or NiMo/Zelite by Impregnation method catalysts have a larger surface area than the activated natural zeolite and NMZ-MWP or NiMo/Zelite by Microwave Polyol method. This indicates that, there are not many NiMo metals are adhered and dispersed throughout the zeolite surface.

MWP, thus causing the formation of an imperfect crystal. The intensity of the peak represents the crystallinity, the sharper peaks tend to be better crystallinity. The higher crystallinity has a high catalytic activity and stable at high temperatures.

Table 3 is the result of catalyst crystallite size using

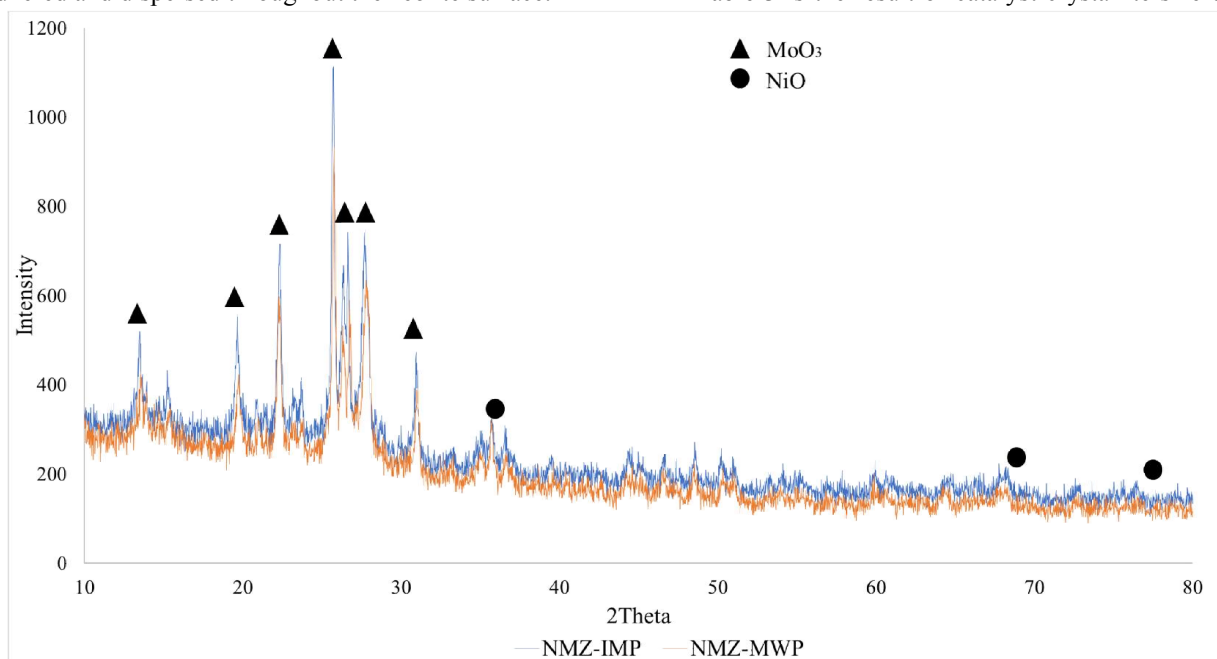


Figure 1. XRD Diffractogram. (A) NMZ-IMP and (B) NMZ-MWP

In contrast, NMZ-MWP catalysts have a smaller surface area compared to activated zeolite and NMZ-IMP, indicating that the causes of decreasing catalyst surface area of NiMo metal are not evenly distributed and there is an indication it accumulates to form agglomeration in several regions on the surface of the support because sintering by a volatile solvent such as ethylene glycol in the microwave heating process. Another possibility, there is damage on the NMZ-MWP catalyst support structure due to the rapid heating of the microwave with the power of 800W for 1 minute. With high power produces high microwave intensity, resulting in high heating rate.

3.2. XRD Characterization

XRD characterization was performed to determine the crystallite size on NMZ-IMP and NMZ-MWP catalysts, which can be seen in Figure 1. From the diffractogram, it can be seen that the peaks appearing on both catalysts are at the similar 2θ. Yaser [14] in his study conduct diffraction of NiO phase are detected on 2θ = 37.2; 43.4; 63; 75.6; and 79.6 (JCPDS card no. #47-1049), and Palcheva [15] has conduct of MoO₃ phase on 2θ = 24.2; 27.3; 47.4; and 57.2 (JCPDS card 35-0609).

Each peak has different characteristic, for NMZ-IMP diffractogram having a higher intensity than NMZ-MWP. This suggests that crystals formed on NMZ-IMP catalysts are more crystalline than NMZ-MWP. This can be due to the rapid heating of the microwave for NMZ-

Scherrer equation below

$$L = \frac{0,89\lambda}{\beta \cos\theta} \quad (1)$$

Where,

L = Crystallite size (nm)

λ = X-ray Wavelength (nm) [Cu K Kα = 0,15406 nm]

β = Full Width at Half Maximum [FWHM] (rad)

θ = Peak

The size of each crystal can be seen in Table 3. From the results it is found that both methods produce crystals of nano size, this can be caused by the ultrasonification process.

Table 3. Catalyst Crystallite Size

Catalyst	Crystal Size (nm)		
	NiO	MoO ₃	Average
NMZ-IMP	42.85	55.85	49.35
NMZ-MWP	51.68	56.16	54.29

3.3. SEM-EDX Characterization

Characterization with SEM aims to look at the surface morphology of the catalyst, which is visualized as a reflection of electron from the shooting of electron light. The following pictures of SEM test with 1000x

magnification (Figure 2) and 10000x magnification (Figure 4).

From Figure 2 at 1000x magnification, there can be seen morphological differences on the surface of the catalyst, wherein Figure 2, NMZ-IMP does not form clumps which indicate that the NiMo metal particles formed are distributed evenly on the surface, this is supported by mapping of particle spreading or mapping, the buildup of particles by in a small part of the area.

Whereas in Figure 2, NMZ-MWP there are clumps with variant size, indicates the existence of the particle accumulation in the area. This is supported by the results of mapping, where in most areas of the surface there are particles with a large intensity that formed clumps. This proves that the NMZ-MWP catalyst produced by microwave polyol process method does not distributed evenly. Another difference between these two catalysts is the number of particles attached to the surface, where in the NMZ-IMP catalyst mapping the intensity of the

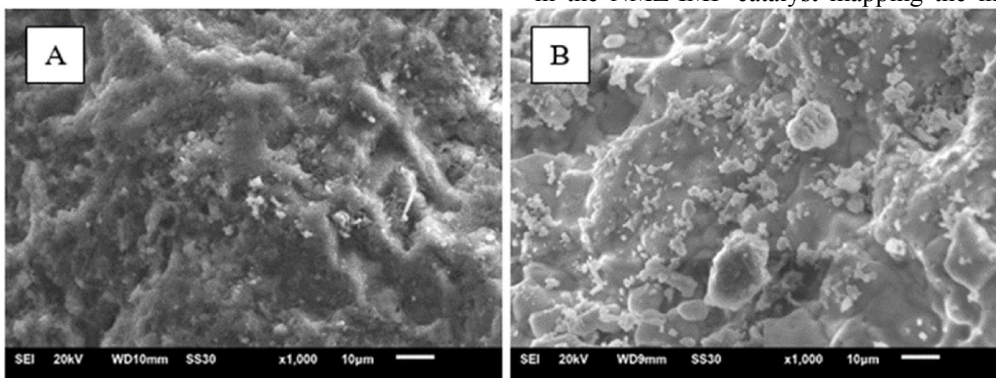


Figure 2. SEM Characterization, 1000x Magnification. (A) NMZ-IMP and (B) NMZ-MWP

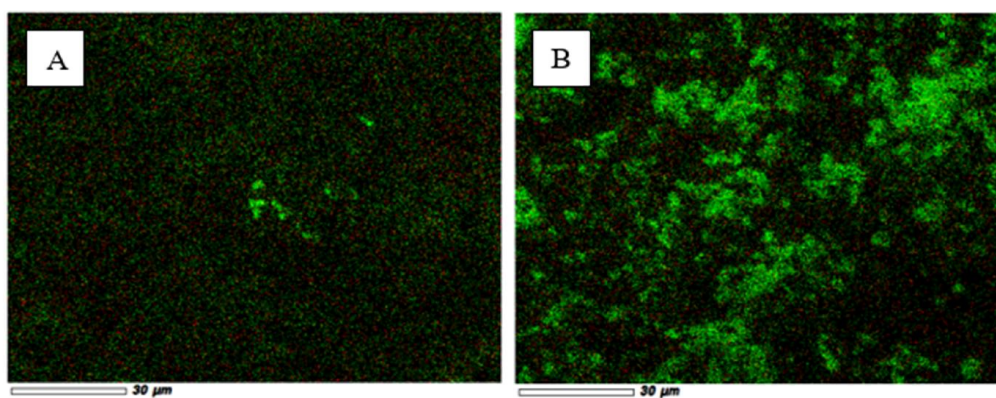


Figure 3. SEM Mapping, 1000x Magnification. (A) NMZ-IMP and (B) NMZ-MWP

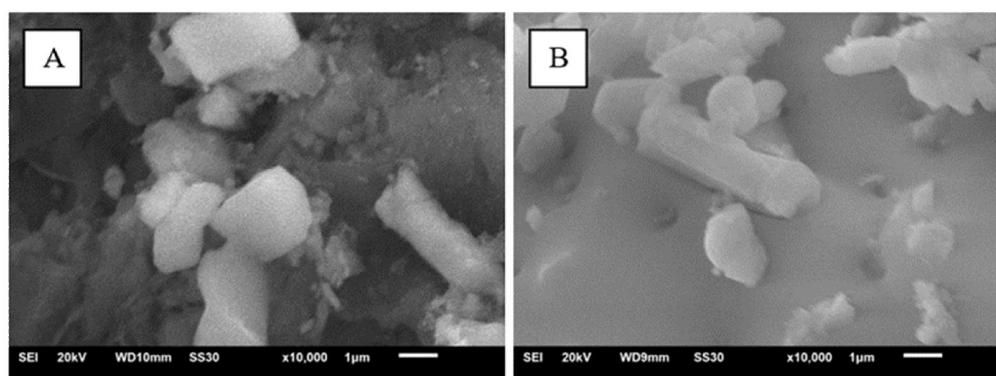


Figure 4. SEM Characterization, 10000x Magnification. (A) NMZ-IMP and (B) NMZ-MWP

number of particles attached to the surface is less than the NMZ-MWP catalyst, this indicates that the rapid heating from the microwave makes the metal active core stick more to support surface than NMZ-IMP.

In Figure 4 at 10000x magnification, it appears that in both catalysts the size between the particles are not too much different. The two catalysts have the same shape of the particles, which is indicating the effect of the stabilizing compound, potassium bromide (KBr), which has the ability to control the size and shape of the metal particles [16].

To confirm the loading count has been as expected, an EDX test was performed together with the SEM test. EDX test results can be seen in Table 4.

Table 4. EDX Characterization Result

Element	% Weight	
	NMZ-IMP	NMZ-MWP
Si	79.56	11.56
Al	10.66	49.61
Ni	1.20	0.34
Mo	8.58	38.48

From the two catalysts characterized by EDX it can be seen that NMZ-IMP catalysts have weight percentage of Ni and Mo metal of 9.78% while for NMZ-MWP catalyst 38.82%. The NMZ-IMP catalyst loading results are closer to the expected loading during catalyst preparation of 10%, while the NMZ-MWP catalyst has loading that exceeds from the expectation during preparation, demonstrated that the use of microwaves that utilize rapid heating generates particle spreading which is uneven in other words the possibility of some part of NiMo metal particles embedded in the support, collected on the area detected by the EDX instrument, so another possibility that in the area that is not analyzed has fewer number of NiMo particles.

Another difference of the two catalysts, the Si/Al ratio, on the Si/Al catalyst NMZ-IMP ratio of 7.46 this proves that an increase in ratio when compared with Estiaty [17] for natural zeolite Malang amounting to 5.77 this is due to the dealumination process at the time of activation of the catalyst. Different results were obtained on the NMZ-MWP catalyst which had a Si/Al ratio of 0.23. For NMZ-IMP and NMZ-MWP catalysts using simultaneously activated zeolite support. Thus, there is an indication that, the area on the NMZ-MWP catalyst support surface detected by the SEM-EDX instrument is an area having a greater number of Al particles than the Si particle, so that produced data of the catalyst with a low ratio.

3.4. Catalyst Activation

Based on the characterization result, NMZ-IMP have large surface area, better characteristic such as small crystallite size, have NiMo loading close to expected.

So, NMZ-IMP is selected to be used to test the activity for synthesizing bio jet fuel. Table 5 show data obtained from bio fuel synthesis with optimum operating conditions.

Table 5. Catalyst Activation Result

Synthesis Condition	
Temperature	375°C
Pressure	Atmospheric
Reaction Time	1.5 hours
Biofuel Component	%wt (percentage)
Biogasoline (C ₅ -C ₁₀)	23.08
Bio Jet Fuel (C ₉ -C ₁₅)	36.43
Renewable Diesel (C ₁₄ -C ₂₀)	47.82
Lubricant (C ₁₉ -C ₂₅)	9.86

These conditions with activated NMZ-IMP led to 84.30% of conversion, 34.77% yield of bio jet fuel range, and selectivity of 36.43%.

4 Conclusion

The conclusion that can be drawn from this study are the best catalyst prepared by compare two methods is NMZ-IMP catalyst that prepared by impregnation method which had 49.35 nm average crystallite size, and had surface area, pore diameter and pore volume 232.18 m²/g, 2.67 nm and 0,16 cc/g respectively. The activity catalyst test by using catalytic cracking reaction showed that the catalyst NMZ-IMP at condition 375°C and atmospheric pressure was able to synthesize bio jet fuel product with high enough conversion of 84.30%, but low bio jet fuel range selectivity and yield 36.43% and 34.77% (wt) respectively.

Director of Research and Community Service through International Indexed Publication Grant for Student Thesis (PITTA) Universitas Indonesia 2018 with contract: No. 2388/UN2.R3.1/HKP.05.00/2018 is acknowledged for the financial support to carry out the present study.

References

- 1 Widayatno, R. L., Datumaya, A., & Abidin, Z. *Jurnal Pertahanan: Analisis Bioavtur for Energy Security*. ISSN : 2087-9415. Vol. 2. 243-256. (2015).
- 2 Itthibenchapong, V., Srifa, A., Kaewmeesri, R., Kidkhunthod, P., dan Faungnawakij, K. *Deoxygenation Of Palm Kernel Oil To Jet Fuel-Like Hydrocarbons Using Ni-MoS₂/γ-Al₂O₃ Catalysts*. *Energy Conversion and Management* 134. 188–196. (2017).
- 3 Shahinuzzaman, M., Yaakob, Z., Ahmed, Y. *Non-Sulphide Zeolite Catalyst for Bio-Jet-Fuel Conversion*. *Renewable and Sustainable Energy Reviews*. (2017).

- 4 Cheng, J., Li, T., Huang, R., Zhou, J., Cen, K. *Optimizing Catalysis Conditions to Decrease Aromatic Hydrocarbons and Increase Alkanes for Improving Jet Biofuel Quality*. *Bioresource Technology* 158, 378–382. (2014).
- 5 Prakasa M.B., Susanto B.H., Nasikin M., Sukirno. *Synthesis of Renewable Diesel from Pal Oil and Jathropa Curcas Oil through Hydrodeoxygenation Using NiMo/ZAL*. *International Journal of Technology* 7 (8), 1404-1411, 2. (2016)
- 6 A. Faisal, B. H. Susanto, and M. B. Prakasa, *Preparation And Characterization of Nimo/Zeolite Catalyst Using Microwave Polyol Method for Synthesizing Renewable Diesel from Jatropha Oil*, ICCEIB 2016 on 28th November – 30th November 2016 in Melaka, Malaysia. (2016)
- 7 Setiadi dan A. Pertiwi. *Preparasi dan Karakteristik Zeolit Alam untuk Konversi Senyawa ABE menjadi Hidrokarbon*, 2nd National Proceeding Congress and Symposium MKICS, ISSN: 0216 – 4183, pg. 5-6. (2007).
- 8 Chuang, K.H., Shih, K., Wey, M.Y. *The Influences of Microwave Irradiation and Polyol Precursor pH on Cu/AC Catalyst and its CO Oxidation Performance*. *J Nanopart Res.* 14:1178. (2012).
- 9 Wiyo A., Susanto B.H., Nasikin M., Sukirno. *Synthesis of Renewable Diesel through Hydrodeoxygenation Using Pd/zeolite Catalysts*, *Procedia Chemistry*, Volume 9, 2014, Pages 139–150, Elsevier. (2014)
- 10 Boyás, R. S., Yanyong, L., & Tomoaki, M. *Production of Green Diesel by Hydrocracking of Canola Oil on Ni-Mo/ γ -Al₂O₃ and Pt-Zeolitic Based Catalysts*. *Instituto Politécnico Nacional*, 1-7. (2011).
- 11 Huali W., Shuli Y., Manhoe K., Steven O. Salley, K. Y. Simon Ng. *Jet Fuel Hydrocarbons Production from Catalytic Cracking and Hydrocracking of Soybean Oil*. *Current Catalysis: Volume 1, Issue 2* pg. 132-139, 2012. DOI: 10.2174/2211544711201020132. (2012).
- 12 Chuang, K.H., Lu, C.Y., Wey, M.Y. *Effects of Microwave Power and Polyvinyl Pyrrolidone on Microwave Polyol Process of Carbon-Supported Cu Catalysts for CO Oxidation*. *Materials Science and Engineering B* 176. 745–749. (2011).
- 13 Mortensen, P. M., Gardini, D., de Carvalho, H. W. P., Damsgaard, C. D., Grunwaldt, J.D., Jensen, P. A., Wagner, J. B., Jensen, A. D. *Stability and Resistance of Nickel Catalysts for Hydrodeoxygenation: Carbon Deposition and Effects of Sulfur, Potassium, And Chlorine In The Feed*. *Catalysis Science & Technology*, 4(10), 3672-3686. DOI: 10.1039/c4cy00522h. (2014).
- 14 Yaser, V., Haghigi M, Sogand A. *Ultrasound Assisted Dispersion of Different Amount of Ni Over ZSM-5 Used as Nanostructured Catalyst for Hydrogen Production Via CO₂ Reforming of Methane*. *Energy Conversion and Management* (8), 1093-1103. (2013).
- 15 Palcheva R, Kaluza L., Spojakina A., Jiratova K., Tyuliev G., *NiMo/ γ -Al₂O₃ Catalyst from Ni Heteropolyoxomolybdate and Effect of Alumina Modification by B, Co, or Ni*. (2012).
- 16 Li, H. Zhang, S., Lin, Y. *Pd/C Catalyst Synthesized by Microwave Assisted Polyol Method for Methanol Electro-Oxidation*. *International Journal of Electrochemical Science* (8), 1-16. (2012).
- 17 Estiaty, L.M., Fatimah, D., and Goto, Y. *Improvement of Animal Manure by Mixing with Natural Zeolite*. *Jurnal Zeolit Indonesia* Vol. 2 No.1. pg. 37-44. Research Center for Geotechnology, Bandung. (2003).
- 18 Funky. *Penggunaan Katalis Nikel-Zeolit Alam Aktif Pada Hidrolisis Selulosa Menjadi Glukosa Dengan Bantuan Ultrasonik*. Universitas Malang, East Java. (2016).