Conversion of Nyamplung Oil into Green Diesel through Catalytic Deoxygenation using NiAg/ZH Catalyst

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Abstract

Nyamplung oil (Calophyllum inophyllum L) can be converted into green diesel by the catalytic deoxygenation method. Bimetallic catalyst NiAg supported by hierarchical natural zeolite (NiAg/ZH) can be used in this method. This study aims to determine the characteristics of the NiAg/ZH catalyst and the optimal conditions for the catalytic deoxygenation of nyamplung oil into green diesel. The NiAg/ZH catalyst was synthesized by wet impregnation with a total metal concentration of 10% and a mass ratio of Ni/Ag of 4. X-Ray Diffraction, Surface Area Analyzer and NH_3-TPD characterized the catalyst. Catalytic deoxygenation of Nyamplung oil was carried out by varying the temperature (325, 350 and 375 °C) and reaction time (1, 2 and 3 hours) with a catalyst dosage of 5%. The composition of the product was analyzed using Gas Chromatography-Mass Spectroscopy. The catalyst XRD spectrum showed a peak at $2\theta = 22.38°$ (clinoptilolite zeolite), 44.42° (Ni) and 38.21° (Ag). The surface area of the catalyst is 46.7024 m^2/g, the pore volume is 0.0813 cc/g, the average pore diameter is 6.9632 nm, and the deposit is 1.6882 mmol/g. The optimum catalytic deoxygenation of nyamplung oil was obtained at 350 °C and 3 hours with a gasoline selectivity of 3.51%, kerosene 4.73%, and 62.02% green diesel.

Keywords: Catalytic deoxygenation, green diesel, hierarchical natural zeolite, nyamplung oil,

1. INTRODUCTION

The primary energy source generally used is petroleum. Because it is non-renewable so decreases its reserves. The data on petroleum reserves in Indonesia reported that in 2016, reserves reached 7250 Million Stock Tank Barrels (MMSTB), while in 2020, they fell to 4170 MMSTB (Adriawan *et al.,* 2020). Fossil energy is also one of the most significant contributors to greenhouse gas emissions (CO_2) that cause global warming and climate change (Hongloi *et al.,* 2021). In addition, gas emissions like nitrogen, sulfur, volatile compounds and other particles are also produced (Karavalakis *et al.,* 2016). This condition is a trigger to develop alternative energy that is renewable and environmentally friendly. Biofuels are one of the most promising alternative energy. The renewable standards (especially those derived from plants) and the resulting gas emissions are more environmentally friendly than petroleum. Plants in photosynthesis can reuse CO_2 gas resulting from combustion. Gas emissions like nitrogen, sulfur, and volatile compounds are almost non-existent.

First-generation biofuels such as biodiesel have begun to be developed and have even been commercialized. In Indonesia, biodiesel is marketed as a mixture of diesel with a concentration of 30% (B30). Biodiesel is produced from the reaction of vegetable oil transesterification or fatty acid esterification. Structurally, biodiesel is classified as an oxygenate compound (Zhang *et al.,* 2022). It leads to lower quality than petroleum diesel,

such as calorific value and low thermal stability, high NOx emissions, and compatibility with limited diesel (Kordulis *et al.,* 2016; Hosseinzadeh-Bandbafha *et al.,* 2018; Murnieks *et al.,* 2016). Using biodiesel in diesel engines also causes problems such as clogged filters, corrosion, and sediment buildup in fuel pumps due to chemicals used during the transesterification reaction (Kordulis *et al.,* 2016; Gamal *et al.,* 2020). Green diesel is emerging as the second generation of biofuels that can overcome the disadvantages of biodiesel. Green diesel has properties that are very similar to diesel from petroleum because it is a hydrocarbon compound. The oxygen element is almost absent, and the cetane number and thermal stability are higher (Kamaruzaman *et al.,* 2020). Green diesel can be used entirely in diesel engines without requiring engine modification (Khalit *et al.,* 2022).

One raw material that can be converted into green diesel is nyamplung oil (Trisunaryanti *et al.,* 2020). This oil is extracted from nyamplung fruit seeds, where the oil content is quite high, around 40-73% (Atabani & César, 2014). In addition, the productivity of nyamplung seeds is higher than other plants, namely around 20 tons/ha/year, where the castor is only 5 tons/ha/year and palm 6 tons/ha/year (Leksono *et al.,* 2012). It causes nyamplung oil to be potentially used as a raw material for green diesel. Synthesis of green diesel from vegetable oils can be carried out by the catalytic deoxygenation method. This method can use hydrogen (hydrodeoxygenation, HDO) or without hydrogen (deoxygenation, DO). In terms of economy, deoxygenation is more profitable than HDO because additional reactants in the form of hydrogen gas are not used (Gamal *et al.,* 2020). The energy required is also lower than HDOs that use high temperatures to ensure the reaction takes place perfectly. In addition, the reactor needed does not require high pressure like HDO (Baharudin *et al.,* 2020). In deoxygenation, all oxygenate compounds (vegetable oils) are converted into hydrocarbons through decarboxylation and decarbonylation reactions (Hafriz *et al.,* 2018). The role of catalysts is decisive in this conversion.

Various types of catalysts have been used in the conversion of nyamplung oil into biofuels, such as CoMo with SiO_2 and γ-Al_2O_3 supports (Rasyid *et al.,* 2015), CoMo/γ-Al_2O_3 oxides

(Trisunaryanti *et al.,* 2020) and NiMo/γ-Al2O3 (Prasetyo *et al.,* 2018; Febriyanti *et al.,* 2020). In general, the catalysts used are transitional metal groups that have been proven to have the best catalytic activity due to the presence of unfilled d orbitals that can increase the acidity of the catalyst. This study used a natural zeolite-backed NiAg catalyst to deoxygenate nyamplung oil (without hydrogen gas) into green diesel. Nickel catalysts have high catalytic activity and almost match precious metal catalysts, with low prices and long lifetimes (Zheng *et al.,* 2019). Nickel is also smaller than other transition metals, making it easier to distribute within the catalyst support. Adding silver (Ag) promoters is expected to increase the catalytic activity of Ni. Silver has high chemical stability, excellent optical properties, and conductivity. Furthermore, it enhanced antibacterial properties (Tsuji *et al.,* 2006). The price of silver is also lower than other precious metals (gold, platinum, ruthenium, and palladium).

Using natural zeolite as a support is expected to reduce process costs because it is cheaper than synthetic supports such as γ-Al_2O_3 and SiO_2. Natural zeolite has also been shown to be capable of various catalytic deoxygenation reactions due to its porous surface that can be modified into a hierarchy and the availability of acidic sites on its surface (Aziz *et al.,* 2021; Zikri *et al.,* 2021). Natural zeolite's weakness is its small surface area and pore size (Susanto et al., 2014), but this can be overcome by desilication (Fauzi *et al.,* 2019). Desilication can produce hierarchical zeolite with two pore sizes (micro and meso) and a larger surface area (Xiao *et al.,* 2015; Kadja *et al.,* 2013). NiAg/ZH catalysts were synthesized using wet impregnation and characterized using XRD, SAA, and NH_3-TPD. Catalytic deoxygenation of nyamplung oil is carried out in batches by varying the temperature and reaction time to produce optimum green diesel selectivity.

2. MATERIALS AND METHODS
Materials and Tools

Natural zeolite is obtained from CV. Minatama Lampung, nyamplung oil from CV. Akuna Jaya Sejahtera, all precursors are derived from Merck (nickel nitrate hexahydrate pa, silver nitrate pa, sodium hydroxide pa, and ammonium acetate pa). The pieces of equipment used are a set of stainless steel reactors, X-Ray Diffraction (XRD) Shimadzu type 7000, Surface Area Analyzer (SAA)

Quantachrome NovaWin, NH_3-TPD type Chemisorb 2750 (USA), and Gas Chromatography-Mass Spectroscopy (GC-MS) Shimadzu QP 2010.

Synthesis of NiAg/ZH Catalyst

Natural zeolite is mashed, then washed using distilled water until the water is clear, and dried at 100 °C for 12 hours. The obtained zeolite took as much as 10 grams mixed with 200 mL of NaOH 0.5 N and heated for 2 hours at 75 °C. Then zeolite was washed to neutral pH using distilled water and dried at 100 °C for 12 hours (Fauzi *et al.,* 2019). The zeolite was mixed with an NH_4CH_3COO 1 M in a three-neck flask and crushed for 4-5 hours at 90 °C. The resulting zeolite is washed with distilled water to a neutral pH and dried at 100 °C overnight. The zeolite was then calcined for 3 hours at 450 °C to produce a hierarchical natural zeolite (ZH) (Aziz *et al.,* 2021). Nickel nitrate and silver nitrate with a total metal content of 10% w/w and a ratio of Ni/Ag of 4, dissolved in 20 mL of aqueous. Then added into the zeolite hierarchy, stirred for 3 hours at room temperature, dried at 60 °C for 12 hours, and calcined at 450 °C for 5 hours. Then it was reduced with H_2 gas for 4 hours at 500 °C so that a NiAg//ZH catalyst was formed (Estephane et al., 2015). The catalyst was characterized using the Shimadzu 7000 X-Ray Diffraction (XRD) with CuKα monochromatic radiation (λ = 1.54056) at a speed of 2°/min and an angle of 2θ from 2-80°. The acidity of the catalyst was analyzed using NH_3-TPD type Chemisorb 2750 (USA), and surface area, pore diameter, and pore volume using a Surface Area Analyzer (Quantachrome NovaWin).

Catalytic Deoxygenation of Oil into Green Diesel (Aziz et al., 2021)

10 mL of nyamplung oil and 0.5 g of NiAg/ZH catalysts is fed into the reactor. The reactor heater is turned on, and when the temperature reaches 350 °C, the reaction time begins to be calculated. The first parameter to vary is the temperature (325, 350, and 375 °C) with a constant parameter of 2 hoursreaction time. After the reaction, the heater is turned off, and the reactor is cooled. The resulting product (liquid) is removed from the reactor, filtered to separate the catalyst, and then analyzed using GC-MS Shimadzu QP 2010. From the results of GC-SM, biofuel compounds can be grouped into gasoline (C 5-12), kerosene (C13-14), and green diesel (C15-18) (Istadi *et al.,* 2020). The selectivity of the resulting biofuel fraction was determined using equation (1) (Ashokkumar *et al.,* 2018).

$$\text{Selectivity} = \frac{\text{Area of product}}{\sum \text{Areas of all product}} \text{ x } 100\% \quad (1)$$

3. RESULTS AND DISCUSSION
Characteristics of NiAg/ZH Catalysts

Characterization using XRD is intended to determine the crystallinity of a NiAg/ZH catalyst. In **Figure 1**, you can see the diffractogram pattern of the catalyst after the decilication, activation, and impregnation of metals in the natural zeolite. The crystalline phase of natural zeolite is still preserved. It is evident from the appearance of the peak at 2θ = 9.84°, 11.24°, 22.40°, 28.12°, and 32.01°, a typical peak of clinoptilolite zeolite (JCPDS 00-025-1349; Aziz et al., 2019; Rahmani *et al.,* 2015). Another peak that appears is at 2θ = 44.42°, 52.68°, and 76.26°, which is the peak of the Ni metal. Rashad *et al.* (2021) also confirmed that the Ni metal was detected at peak 44.50°, 51.90°, and 74.60° (JCPD 03-065-0380). While the Ag metal was detected at the peak of 2θ = 38. 21° and 64. 01° (Dong et al., 2021). NiO peaks at 43.0°, 63.0°, 75.0°, and 79.0° (Satriadi *et al.,* 2022) was not detected in catalysts. It indicates that NiO reduction proceeded perfectly. The Difractogram pattern of the NiAg/ZH catalyst suggests that the Ni and Ag metals were successfully impregnated on the surface of the hierarchical natural zeolite support.
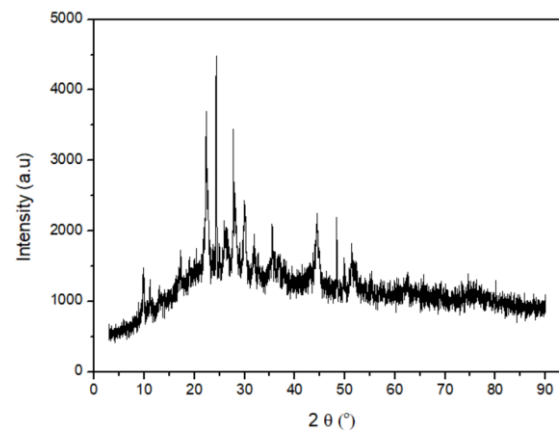

Figure 1. NiAg/ZH catalyst diffractogram pattern

The Brunaeur-Emmet-Teller (BET) analysis on the catalyst showed that the surface area of the catalyst decreased after deciliation,

activation, and impregnation of the metal to 46.7024 m^2/g. Previously, Lampung natural zeolite had a surface area of 51.9 m^2/g (Susanto *et al.,* 2014). This decrease is due to the metal impregnation covering the pores of the catalyst, which is micro-sized so that the surface area is reduced. Aziz *et al.* (2021) also got the surface area of the NiMo/ZH catalyst decreased much larger to 22.91 m^2/g. In this study, the synthesis of hierarchical zeolite was only carried out in 2 stages, namely decilication and activation. At the same time, Aziz *et al.* (2021) used 3 stages (activation, deciliation, and activation) to produce different characteristics. The surface area of NiAg/ZH catalyst micropores is smaller than that of NiMo/ZH catalysts, so the surface is not covered much when metal impregnation is performed. The surface area also decreased (27.26 m^2/g) when Pb metal was impregnated with a natural zeolite (Susanto *et al.,* 2014). Different methods of catalyst synthesis causing a decrease in the resulting surface area are also different.
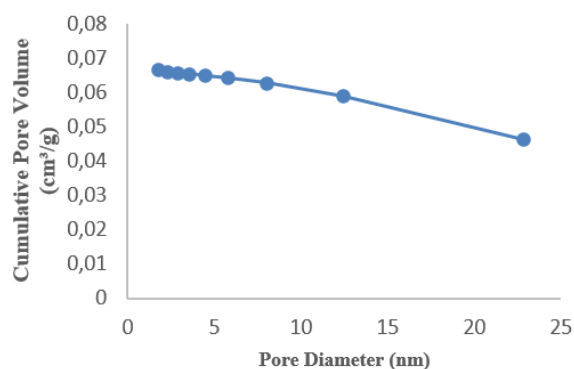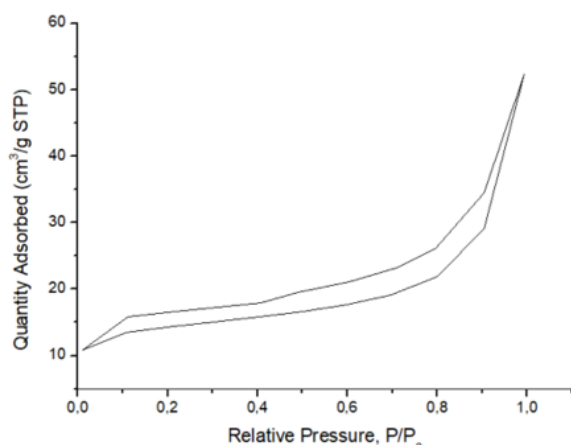
The average pore diameter produced by NiAg/ZH catalysts rises to 6.9632 nm. This increase is due to the deciliation and activation in natural zeolite, causing the follow-up material to be removed so that the pores become open. Bu et al. (2018) state that increasing pore size (pore diameter) in the zeolite skeleton will increase mass transfer and catalytic activity. In **Figure 2a**, you can see the pore size distribution of the NiAg/ZH catalyst. The pore diameter of the catalyst ranges from 1-23 nm. It shows that the hierarchical natural zeolite used as a support is hierarchical because it has a size of 2 pores, namely micro (0-2 nm) and meso (2-150 nm). The presence of meso-sized pores causes the pore volume to increase. As evidenced by the analysis of the Beret Joiner Halenda (BJH), the total pore volume rose to 0.0813 cc/g. This large pore volume is indispensable in catalysis reactions to achieve reaction perfection (Susanto *et al.,* 2014). Apart from pore size distribution data, the formation of mesopores in the catalyst can be seen from the adsorption-desorption isotherm graph, as shown in **Figure 2b**. The NiAg/ZH catalyst adsorption-desorption isotherm type is type IV, with type IV loop hysteresis also indicating the presence of mesopores in the catalyst.

The acidity value of the NiAg/ZH catalyst, which was analyzed using NH$_3$-TPD, increased to 1.6882 mmol/g. This increase is due to the presence of Ni and Ag metals. Half-filled metal (empty d orbital) can effectively receive electron pairs from adsorbate, thereby increasing acidity, especially Lewis acid (Sriningsih *et al.,* 2014). Profile NH$_3$-TPD NiAg/ZH catalysts (**Figure 3**) show catalysts have two peaks, namely at 264 °C indicating weak acids (<270 °C) and peaks at 504 °C (strong acids, > 350 °C) (Gousi *et al.,* 2017).
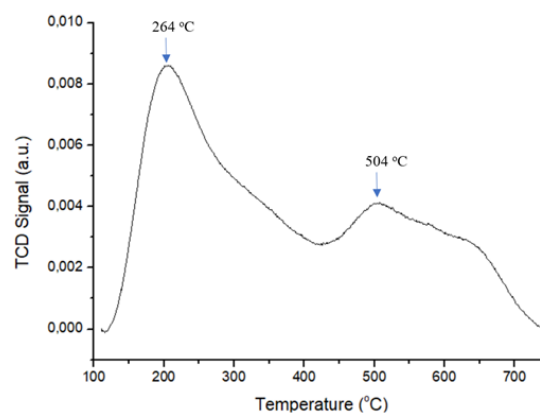

(a)

(b)

Figure 2. Distibution of pore size (a) and desorption adsorption isotherm graph (b) NiAg/ZH catalysts

Figure 3. NH$_3$-TPD profile NiAg/ZH catalyst

Catalytic Deoxygenation of Nyamplung Oil

Catalytic deoxygenation of nyamplung oil is carried out in batches by varying the temperature and reaction time. The temperature was varied from 325, 350, and 375 °C with a constant parameter of 2 h reaction time and a catalyst concentration of 5% w/v. At 325 °C, the selectivity of obtained gasoline (5.93%) and green diesel (13.53%) is still low, and even kerosene is not detected from the GCMS results (**Figure 4**). It shows that at 325 °C, the deoxygenation of nyamplung oil has not been optimal. It was also confirmed by the product's high content of fatty acids (90.48%). When the temperature is raised to 350 °C, the selectivity of the biofuel becomes elevated, mainly the fraction of green diesel (40.97%). The rising temperature causes the kinetic energy of the reactants to get greater so that the interaction with the catalyst is maximized (Li *et al.,* 2014). The selectivity of biofuels drops when the temperature rises to 375 °C. Too high a temperature can increase the cracking reaction, so the selectivity of green diesel drops and turns into light fractions (gases) and residues (Gamal *et al.,* 2020; Cheng *et al.,* 2016).

Febriyanti *et al.* (2020) also vary the temperature from 300-350 oC using the HDO method with a NiMo/γ-Al$_2$O$_3$ catalyst. The yield on diesel fraction rises by 33.8% (300 °C) to 71.78% (350 °C). Budianto *et al.* (2015) convert nyamplung oil using Zn-HZSM-5/alumina catalysts by catalytic cracking process (deoxygenation without hydrogen) semi-batch. At 350 °C, the yield of green diesel produced is about 27.20%. However, when the temperature is raised to 450 °C, the yield rises to 73.86%. Then it goes down again (67.82%) when the temperature is raised to 550 °C. It suggests that differences in catalyst types and process methods greatly affect the conversion of nyamplung oil. For this study, it can be concluded that the optimum temperature for producing green diesel is 350 °C. This temperature is further used in the optimization of reaction time.

The triglycerides in nyamplung oil contain fatty acids in oleic acid (C$_{18}$H$_{34}$O$_2$) 58.13%; palmitic acid (C$_{16}$H$_{32}$O$_2$) 18.46%; linoleic acid (C$_{18}$H$_{30}$O$_2$) 12.26% and stearic acid (C$_{18}$H$_{36}$O$_2$) 11.14% (Rasyid *et al.,* 2018). Triglycerides are converted to hydrocarbons through catalytic deoxygenation reactions. Based on **Figure 4**, triglycerides undergo a hydrolysis reaction to fatty acids. Furthermore, fatty acids undergo parallel

reactions in decarboxylation and decarbonylation. The decarboxylation reaction produces alkane compounds (n-heptadecene) and CO$_2$ gas. The decarbonylation reaction produces alkenes (heptadecene), CO, and H$_2$O. At 375 °C, no C17 compound was detected (**Figure 5**). It is because the resulting C17 undergoes a cracking reaction into a lighter fraction (C16). Where compound C16 is produced at higher than other temperatures, cracking reactions can occur due to the use of high temperatures (Kaewmeesri *et al.,* 2015). At 350 °C, the resulting C17 and C15 alkane compounds are quite high, which indicates that the decarboxylation reaction takes place to the maximum. Alkene compounds that are decarbonylation products are not detected because the compounds directly undergo a cracking reaction into a lighter fraction. Likewise, at 325 °C, the C15 compound was also not detected, indicating the compound also underwent a cracking reaction resulting in C6 and C12 compounds.
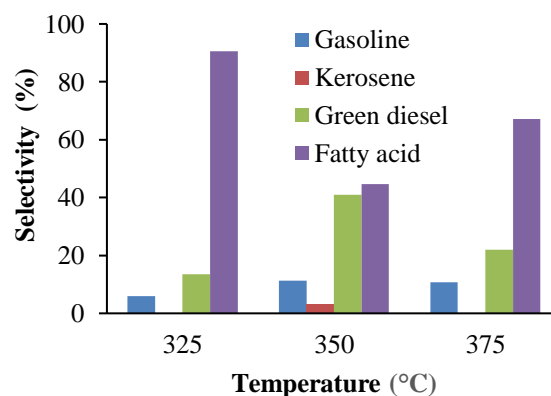

Figure 3. Effect of temperature on the selectivity of catalytic deoxygenation products

The next optimization is the reaction time of 1, 2, and 3 hours with a constant parameter of the temperature of 350 °C and a catalyst concentration of 5%. From **Figure 6**, it can be seen the effect of time on product selectivity. The longer the reaction time, the higher the selectivity of the biofuels produced, especially green diesel. The selectivity of green diesel rose from 35.16% (1hr) to 62.02% (3 hours). The length of the reaction time allows the reactant molecules to react optimally so that the resulting product increases. It is also detected from low selectivity of fatty acids at 3 hours (30.19%), while at 1 and 2 hours, it is still high (60.96 and 44.58%). The high selectivity of fatty acids at 1 hour indicates that the reaction has yet to be maximized. At 1 hour, there is also

no kerosene fraction, and gasoline has a very small selectivity of about 3.88%. It indicates that the cracking reaction proceeds slowly. The dominating product is the green diesel fraction, which means the main reaction is decarboxylation and decarbonylation.

At a reaction time of 3 hours, the results of C17 compounds are all alkene groups. It proves the existence of steric, oleic, and linoleic acid's decarbonylation reactions. The alkane product of C17 was not detected. This compound likely underwent a cracking reaction resulting in a C16 compound whose selectivity

was quite high (**Figure 7**). Interestingly, the product also detected $C_{18}H_{38}$ (alkanes). In theory, this product is produced from the hydrodeoxygenation of stearic acid using hydrogen gas. This product's appearance indicates that hydrogen gas is produced during the reaction, which subsequently reacts with stearic acid producing $C_{18}H_{38}$. But this product has only 1.03% selectivity. In addition, C21 was also detected, indicating a polymerization reaction resulting in a heavy fraction due to the length of the reaction time.
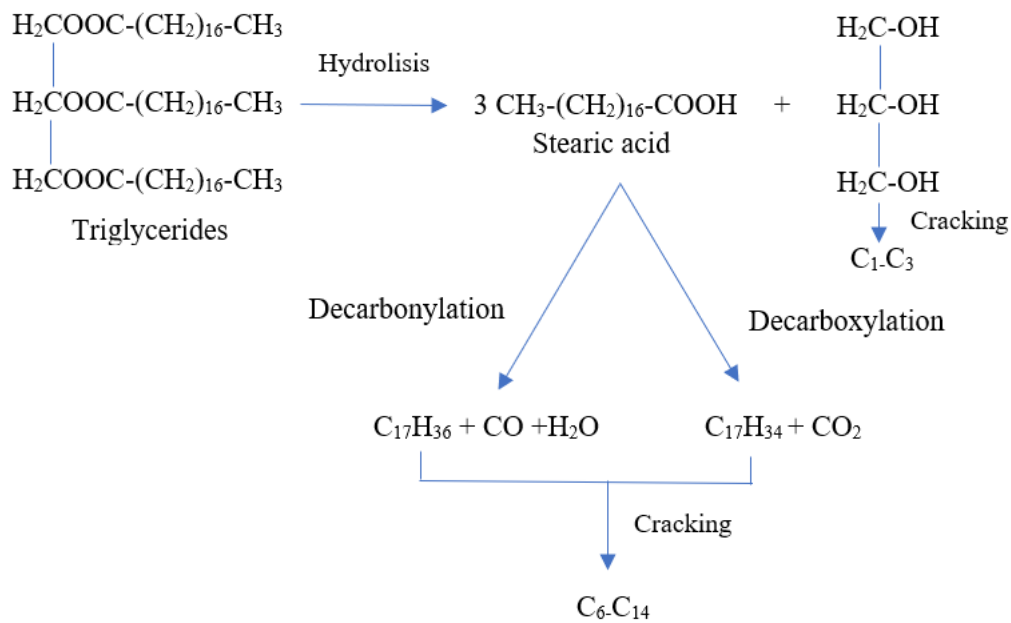

Figure 4. The catalytic deoxygenation reaction path of nyamplung oil through decarboxylation, decarbonylation and cracking
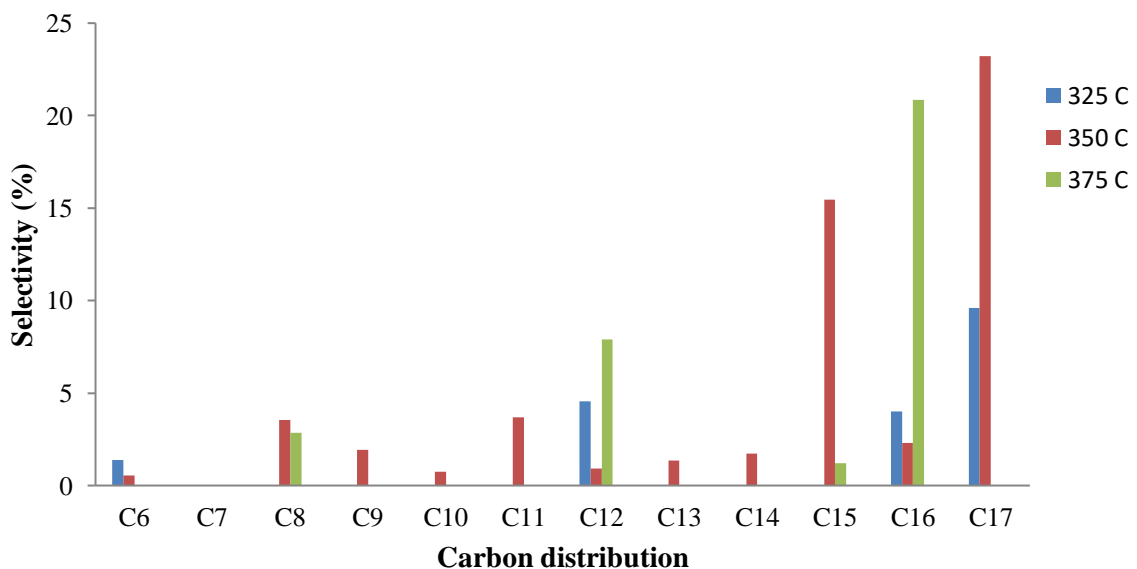

Figure 5. Distribution of hydrocarbons in catalytic deoxygenation products of oil at temperature variations
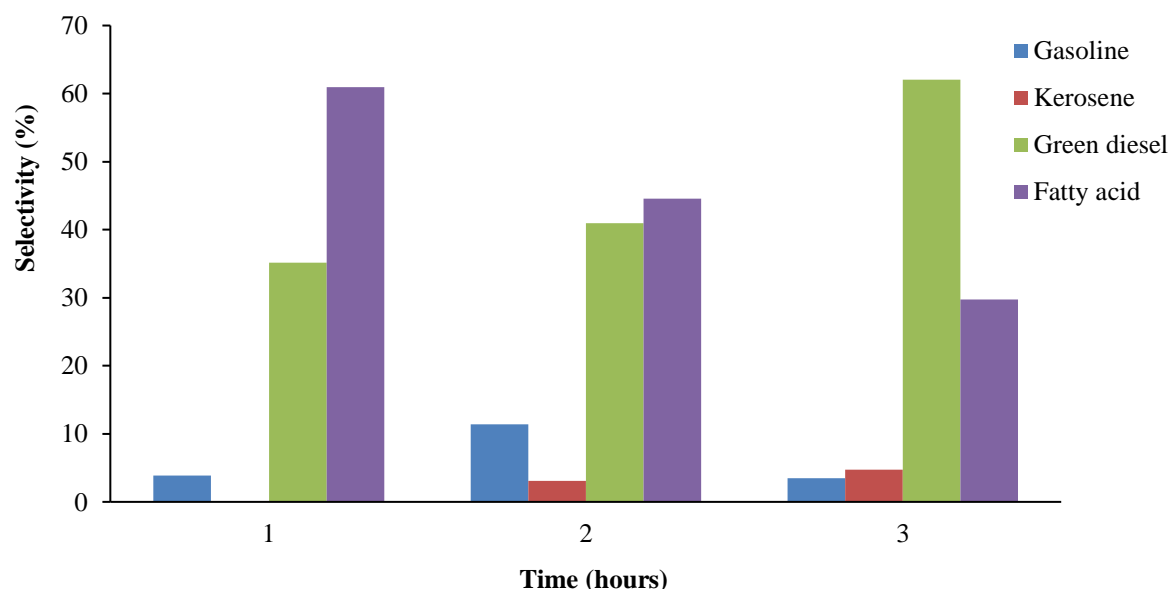
Figure 6. Effect of time on the selectivity of catalytic deoxyenation products nyamplung oil
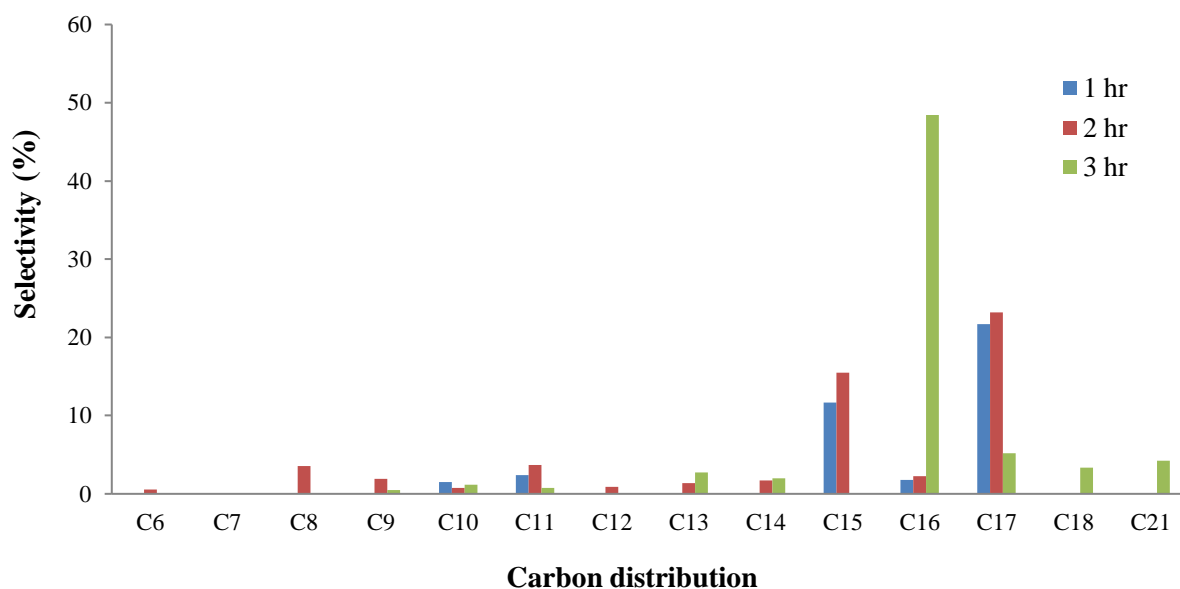

Figure 7. Distribution of hydrocarbons in catalytic deoxygenation products of oil at time variations

Rasyid *et al.* (2018) convert nyamplung oil into biofuels using CoMo/γ-Al₂O₃ catalysts. The yield of gasoline and gasoil (C12-20) is increasing with increasing reaction time and reaching optimum within 2 hours. Trisunaryanti *et al.* (2020), using the hydrocracking method (HDO) with a CoOMoO/γ-Al₂O₃ catalyst (at 550 °C for 2 hours), produced a liquid reaction of 65.56%, gasoline selectivity at 8.61%, and diesel at 5.01%. Prasetyo et al. (2018), using the hydrodeoxygenation method with a NiMo/γ-Al₂O₃ catalyst at a temperature of 400 °C for 3 hours, resulted in a yield of C16-20 of 15.07%.

Compared to the study above, NiAg/ZH catalysts have almost the same activity and are even higher than CoOMoO/γ-Al₂O₃ and NiMo/γ-Al₂O₃. It shows that the use of natural zeolite support and the combination of Ni and Ag metals can produce good catalytic activity.

4. CONCLUSIONS

NiAg-supported hierarchical natural zeolite catalysts (NiAg/ZH) have an acidity value of 1.6882 mmol/g, a surface area of 46.7024 m²/g, a pore volume of 0.0813 cc/g, and an average pore diameter of 6.9632 nm.

This catalyst provides good activity in the nyamplung oil catalytic deoxygenation with optimum activity at 350 °C for 3 hours with a green diesel selectivity of 62.02%. The dominant reactions are decarboxylation and decarbonylation, with side reactions in cracking and polymerization.

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REFERENCES

Adriawan, A. M., Hartanto, R. R., Novizar, A., Aryani, D., Syarifudin, S., & Saputra, M. Y. (2020). Statistik Minyak dan Gas Bumi Oil and Gas Statistics. Direktorat Jenderal minyak dan gas Bumi, Kemeterian Energi dan sumber daya Mineral.

Ashokkumar, S., Ganesan, V., Ramaswamy, K. K., & Balasubramanian, V. (2018). Bimetallic Co–Ni/TiO2 catalysts for selective hydrogenation of cinnamaldehyde. *Research on Chemical Intermediates, 44*(11), 6703–6720. https://doi.org/10.1007/s11164-018-3517-7

Atabani, A. E., & César, A. D. S. (2014). Calophyllum inophyllum L. - A prospective non-edible biodiesel feedstock. Study of biodiesel production, properties, fatty acid composition, blending and engine performance. *Renewable and Sustainable Energy Reviews, 37*, 644–655. https://doi.org/10.1016/j.rser.2014.05.037

Aziz, I., Adhani, L., Yolanda, T., & Saridewi, N. (2019). Catalytic cracking of Jatropa curcas oil using natural zeolite of Lampung as a catalyst. *IOP Conference Series: Earth and Environmental Science, 299*(1). https://doi.org/10.1088/1755-1315/299/1/012065

Aziz, I, Adhani, L., Gustama, D., & Renaningsih, T. (2020). Penggunaan katalis hierarchical zeolite pada catalytic cracking minyak jarak pagar. Para Cita Madina.

Aziz, I, Retnaningsih, T., Gustama, D., Saridewi, N., Adhani, L., & Dwiatmoko, A. A. (2021).

Catalytic cracking of jatropha oil into biofuel over hierarchical zeolite supported NiMo catalyst. *4Th International Seminar on Chemistry, 2349*(June), 020004. https://doi.org/10.1063/5.0051737

Baharudin, K. B., Abdullah, N., Taufiq-Yap, Y. H., & Derawi, D. (2020). Renewable diesel via solventless and hydrogen-free catalytic deoxygenation of palm fatty acid distillate. *Journal of Cleaner Production, 274*, 122850. https://doi.org/10.1016/j.jclepro.2020.122850

Bu, L., Nimlos, M. R., Robichaud, D. J., & Kim, S. (2018). Diffusion of aromatic hydrocarbons in hierarchical mesoporous H-ZSM-5 zeolite. *Catalysis Today, 312*, 73–81. https://doi.org/10.1016/j.cattod.2018.02.012

Budianto, A., Sumari, S., & Udyani, K. (2015). Biofuel production from nyamplung oil using catalytic cracking process with Zn-HZSM-5/γ alumina catalyst. ARPN *Journal of Engineering and Applied Sciences, 10*(22), 10317–10323.

Cheng, S., Wei, L., Zhao, X., & Julson, J. (2016). Application, deactivation, and regeneration of heterogeneous catalysts in bio-oil upgrading. *Catalysts, 6*(12). https://doi.org/10.3390/catal6120195

Dong, G., Luo, Z., Cao, Y., Zheng, S., Zhou, J., Li, W., & Zhou, X. (2021). Understanding size-dependent hydrogenation of dimethyl oxalate to methyl glycolate over Ag catalysts. *Journal of Catalysis, 401*, 252–261. https://doi.org/10.1016/j.jcat.2021.07.028

Estephane, J., Aouad, S., Hany, S., El Khoury, B., Gennequin, C., El Zakhem, H., El Nakat, J., Aboukaïs, A., & Abi Aad, E. (2015). CO2 reforming of methane over Ni-Co/ZSM5 catalysts. Aging and carbon deposition study. *International Journal of Hydrogen Energy, 40*(30), 9201–9208. https://doi.org/10.1016/j.ijhydene.2015.05.147

Fauzi, R. A., Tursiloadi, S., Dwiatmoko, A. A., Sukandar, D., Aulia, F., Rinaldi, N., & Sudiyarmanto, S. (2019). Performance of Modified Natural Zeolites by Sodium Hydroxide Treatments in The Esterification of Glycerol and Oleic Acid. *Jurnal Kimia Valensi, 5*(2), 236–241. https://doi.org/10.15408/jkv.v5i2.9976

Febriyanti, E., Roesyadi, A., & Prajitno, D. H.

(2020). Konversi Minyak Biji Nyamplung (Callophyllum Inophyllum Linn) Menjadi Biofuel dengan Katalis Berbasis NiMo / γ-Al₂O₃. *Berkala Saintek, 8*(3), 89–95.

Gamal, M. S., Asikin-Mijan, N., Khalit, W. N. A. W., Arumugam, M., Izham, S. M., & Taufiq-Yap, Y. H. (2020). Effective catalytic deoxygenation of palm fatty acid distillate for green diesel production under hydrogen-free atmosphere over bimetallic catalyst CoMo supported on activated carbon. *Fuel Processing Technology, 208*(July). https://doi.org/10.1016/j.fuproc.2020.106519

Gousi, M., Andriopoulou, C., Bourikas, K., Ladas, S., Sotiriou, M., Kordulis, C., & Lycourghiotis, A. (2017). Green diesel production over nickel-alumina co-precipitated catalysts. *Applied Catalysis A: General, 536*, 45–56. https://doi.org/10.1016/j.apcata.2017.02.010

Hafriz, R. S. R. M., Salmiaton, A., Yunus, R., & Taufiq-Yap, Y. H. (2018). Green Biofuel Production via Catalytic Pyrolysis of Waste Cooking Oil using Malaysian Dolomite Catalyst. *Bulletin of Chemical Reaction Engineering & Catalysis, 13*(3), 489–501. https://doi.org/10.9767/bcrec.13.3.1956.489-501

Hongloi, N., Prapainainar, P., & Prapainainar, C. (2021). Review of green diesel production from fatty acid deoxygenation over Ni-based catalysts. M*olecular Catalysis*, January, 111696. https://doi.org/10.1016/j.mcat.2021.111696

Hosseinzadeh-Bandbafha, H., Tabatabaei, M., Aghbashlo, M., Khanali, M., & Demirbas, A. (2018). A comprehensive review on the environmental impacts of diesel/biodiesel additives. *Energy Conversion and Management, 174*(June), 579–614. https://doi.org/10.1016/j.enconman.2018.08.050

Istadi, I., Riyanto, T., Buchori, L., Anggoro, D. D., Gilbert, G., Meiranti, K. A., & Khofiyanida, E. (2020). Enhancing Brønsted and Lewis Acid Sites of the Utilized Spent RFCC Catalyst Waste for the Continuous Cracking Process of Palm Oil to Biofuels. *Industrial and Engineering Chemistry Research, 59*(20), 9459–9468. https://doi.org/10.1021/acs.iecr.0c01061

Kadja, Grandprix T.M, Rilyanti, Mita, Mukti, Rino R., Marsih, I Nyoman, I. (2013). Strategi Sintesis Zeolit Hirarkis : Kajian Metode Cetak Lunak dan Cetak Keras Synthesis Strategy of Hierachical Zeolites : Soft-and Hard-templating method. *Jurnal Matematika & Sains, 18*(3), 103–114.

Kaewmeesri, R., Srifa, A., Itthibenchapong, V., & Faungnawakij, K. (2015). Deoxygenation of waste chicken fats to green diesel over Ni/Al₂O₃: Effect of water and free fatty acid content. *Energy and Fuels, 29*(2), 833–840. https://doi.org/10.1021/ef5023362

Kamaruzaman, M. F., Taufiq-Yap, Y. H., & Derawi, D. (2020). Green diesel production from palm fatty acid distillate over SBA-15-supported nickel, cobalt, and nickel/cobalt catalysts. *Biomass and Bioenergy, 134*(January), 105476. https://doi.org/10.1016/j.biombioe.2020.105476

Karavalakis, G., Jiang, Y., Yang, J., Durbin, T., Nuottimäki, J., & Lehto, K. (2016). Emissions and Fuel Economy Evaluation from Two Current Technology Heavy-Duty Trucks Operated on HVO and FAME Blends. *SAE International Journal of Fuels and Lubricants, 9*(1), 177–190. https://doi.org/10.4271/2016-01-0876

Kordulis, C., Bourikas, K., Gousi, M., Kordouli, E., & Lycourghiotis, A. (2016). Development of nickel based catalysts for the transformation of natural triglycerides and related compounds into green diesel: A critical review. *Applied Catalysis B: Environmental, 181*, 156–196. https://doi.org/10.1016/j.apcatb.2015.07.042

Leksono, B., Eritrina, W., & Hasnah, T. M. (2012). Budidaya Tanaman Nyamplung (Callophyllum inophyllum L.) untuk Bioenergi dan Prospek Pemanfaatan Lainnya. November, 7–20.

Li, L., Quan, K., Xu, J., Liu, F., Liu, S., Yu, S., Xie, C., Zhang, B., & Ge, X. (2014). Liquid hydrocarbon fuels from catalytic cracking of rubber seed oil using USY as catalyst. *Fuel, 123*, 189–193. https://doi.org/10.1016/j.fuel.2014.01.049

Murnieks, R., Apseniece, L., Kampars, V., Shustere, Z., & Malins, K. (2016). Investigation of Deoxygenation of Rapeseed Oil over Raney Nickel and Ni/SiO₂−Al₂O₃ Catalysts. *Arabian Journal for Science and Engineering, 41*(6), 2193–2198.

https://doi.org/10.1007/s13369-015-1932-2

Prasetyo, J., Adiarso, A., Murti, S. D. S., Senda, S. P., Rfdh, S. M., Prada, Y. E., & Oktariani, E. (2018). A Preliminary study of deoxygenation of *Calophyllum inophyllum* L. oil for green diesel production. *IOP Conference Series: Materials Science and Engineering,* *334*(1). https://doi.org/10.1088/1757-899X/334/1/012005

Rahmani, F., Haghighi, M., & Amini, M. (2015). The beneficial utilization of natural zeolite in preparation of Cr/clinoptilolite nanocatalyst used in CO_2-oxidative dehydrogenation of ethane to ethylene. *Journal of Industrial and Engineering Chemistry, 31*, 142–155. https://doi.org/10.1016/j.jiec.2015.06.018

Rashad, A. M., El Sharkawy, H. M., Ebiad, M. A., El sayed, H. A., Tantawy, A. H., Hebash, K. A., El sabagh, S. M., & Taman, A. R. (2021). Recent trends for clean fuel production by deoxygenation of pure palmitic acid using Ni/C catalyst. *Egyptian Journal of Chemistry, 64*(2), 883–892. https://doi.org/10.21608/EJCHEM.2020.408 45.2829

Rasyid, R.-, Aditya S. W, R., Dian.L, D., Mahfud, M., & Roesyadi, A. (2015). Efektifitas katalis Co/Mo pada hydrocracking minyak nyamplung. *Reaktor, 15*(4). https://doi.org/10.14710/reaktor.15.4.268-273

Rasyid, R., Malik, R., Kusuma, H. S., Roesyadi, A., & Mahfud, M. (2018). Triglycerides hydrocracking reaction of nyamplung oil with non-sulfided CoMo/γ-Al_2O_3 Catalysts. *Bulletin of Chemical Reaction Engineering & Catalysis, 13*(2), 196–203. https://doi.org/10.9767/bcrec.13.2.734.196-203

Satriadi, H., Pratiwi, I. Y., Khuriyah, M., Widayat, Hadiyanto, & Prameswari, J. (2022). Geothermal solid waste derived Ni/Zeolite catalyst for waste cooking oil processing. *Chemosphere, 286*(P1), 131618. https://doi.org/10.1016/j.chemosphere.2021. 131618

Sriningsih, W., Saerodji, M. G., Trisunaryanti, W., Triyono, Armunanto, R., & Falah, I. I. (2014). Fuel Production from LDPE Plastic Waste over Natural Zeolite Supported Ni, Ni-Mo, Co and Co-Mo Metals. *Procedia Environmental Sciences, 20*, 215–224.

https://doi.org/10.1016/j.proenv.2014.03.028

Susanto, B. H., Nasikin, M., Sukirno, & Wiyo, A. (2014). Synthesis of Renewable Diesel through Hydrodeoxygenation Using Pd/zeolite Catalysts. *Procedia Chemistry, 9*, 139–150. https://doi.org/10.1016/j.proche.2014.05.017

Trisunaryanti, W., Triyono, T., Ghoni, M. A., Fatmawati, D. A., Mahayuwati, P. N., & Suarsih, E. (2020). Hydrocracking of calophyllum inophyllum oil employing Co and/or Mo supported on γ-Al_2O_3 for biofuel production. *Bulletin of Chemical Reaction Engineering & Catalysis, 15*(3), 743–751. https://doi.org/10.9767/BCREC.15.3.8592.7 43-751

Tsuji, M., Miyamae, N., Lim, S., Kimura, K., Zhang, X., Hikino, S., & Nishio, M. (2006). Au@Ag Core−Shell Nanoparticles Prepared by the Microwave−Polyol Method.pdf. *Crystal Growth & Design, 6*(8), 1801–1807.

Wan Khalit, W. N. A., Asikin-Mijan, N., Marliza, T. S., Safa-Gamal, M., Shamsuddin, M. R., Azreena, I. N., Saiman, M. I., & Taufiq-Yap, Y. H. (2022). One-pot decarboxylation and decarbonylation reaction of waste cooking oil over activated carbon supported nickel-zinc catalyst into diesel-like fuels. *Journal of Analytical and Applied Pyrolysis, 164*(February), 105505. https://doi.org/10.1016/j.jaap.2022.105505

Xiao, W., Wang, F., & Xiao, G. (2015). Performance of hierarchical HZSM-5 zeolites prepared by NaOH treatments in the aromatization of glycerol. *Royal Society of Chemistry, 78*, 63697–63704. https://doi.org/https://doi.org/10.1039/C5RA 07593A

Zhang, Y., Duan, L., & Esmaeili, H. (2022). A review on biodiesel production using various heterogeneous nanocatalysts: Operation mechanisms and performances. *Biomass and Bioenergy, 158*(September 2021), 106356. https://doi.org/10.1016/j.biombioe.2022.106 356

Zheng, Z., Wang, J., Wei, Y., Liu, X., Yu, F., & Ji, J. (2019). Effect of La-Fe/Si-MCM-41 catalysts and CaO additive on catalytic cracking of soybean oil for biofuel with low aromatics. *Journal of Analytical and Applied Pyrolysis, 143*(18), 104693. https://doi.org/10.1016/j.jaap.2019.104693

Zikri, A., Puspita, I., Erlinawati, Sutini PLAgus, M., Elbi Zalita, P., & Andre, K. (2021). Production of Green Diesel From Crude Palm Oil (CPO) Through Hydrotreating Process by Using Zeolite Catalyst. *Proceedings of the 4th Forum in Research, Science, and Technology (FIRST-T1-T2-2020), 7*, 67–74. https://doi.org/10.2991/ahe.k.210205.013

Zikri, A., Puspita, I., Erlinawati, Sutini PLAgus, M., Elbi Zalita, P., & Andre, K. (2021). Production of Green Diesel From Crude Palm Oil (CPO) Through Hydrotreating Process by