THE NiO AND MoO$_3$ ENRICHED ZSM-5 AS CATALYST FOR THE HYDROCRACKING OF COCONUT OIL INTO BIO-JET FRACTION

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ABSTRACT
ZSM-5 was enriched with NiO (nickel oxide) or MoO$_3$ (molybdenum oxide) and used as a catalyst to increase selectivity towards the bio-jet fuel fraction from the hydrocracking of coconut oil. NiO and MoO$_3$ were incorporated into ZSM-5 through wet impregnation at various concentrations of 0.5–5% (wt.). The catalyst material characteristics were analyzed using XRD (X-ray Diffraction), TEM (Transmission Electron Microscope), and nitrogen gas adsorption instruments. The catalyst activity was observed through a hydrocracking reaction at a temperature of 475 °C for 3 hours, using coconut oil as feed and the catalyst concentration was 2 (wt.%). The results showed that NiO and MoO$_3$ were distributed successfully into ZSM-5. Catalyst's catalytic activity was strongly influenced by the amount of NiO and MoO$_3$ embedded into ZSM-5. The Ni-1, Ni-5, Mo-1, Mo-3, Mo-4, and Mo-5 catalysts increased the selectivity towards the bio-jet fraction by 55%, 34%, 49%, 37%, 36%, and 62%, respectively when compared to ZSM-5.

Keywords: Bio-jet, Coconut Oil, NiO, MoO$_3$, ZSM-5

INTRODUCTION
All industrial sectors demand the use of energy. Prospects for global primary energy demand are estimated at 1.1% between 2015-2040 and reach 17,487 Mtoe in 2040. Asia is the second-highest demand for primary energy consumption.$^1$ Rapid industrial growth demands a large supply of energy, consequential of the increase in global energy demand, including the transportation sector. Along with the necessity for time efficiency and lifestyle, air transportation has become the consumer’s choice. In 2018, approximately 114 MTOE (Million tons of oil equivalent) of energy was used in the transportation, industrial, household, commercial, and other sectors, with a percentage of 40%, 36%, 16%, and 2%, respectively.$^2$ In the past decade, from 2009 to 2018, crude oil production has decreased by 63 million barrels. The decline in output was caused by the diminishing old oil production wells and the limited number of new oil wells. The decrease in the production of non-renewable energy, namely crude oil, in addition to the commitment of the government to reduce gas emissions has prompted the role of novel and renewable energy to maintain resilience and energy independence.

Indonesia has good potential in providing novel and renewable energy sources of energy. The use of palm oil as a renewable energy source continues to be encouraged through the mandatory biodiesel program.$^3$ Palm oil derivatives are also expected to be used as a fuel blend for aircraft or bio-jets. Several studies have revealed the potential use of palm oil as a bio-jet fuel.$^4,5$ Generally, bio-jet fuel is obtained from fatty acid processing, in which the product has a high cetane number and good lubricity. However, said product still has the disadvantages of low volatility, high viscosity, and is a potential cause of corrosion.$^6$ Therefore, further research is needed to optimize this biofuel production.

Several studies have reported bio-jet synthesis using palm oil. The hydrocracking of palm oil was conducted using a nickel-silver (Ni-Ag) supported on a silica-alumina-phosphate (SAPO-11) catalyst. Banjang et al.$^7$ used Rh/HZSM-5 as a catalyst in which a 30% heptane addition in the feed gave a palm oil conversion of above 90% at 300 °C.$^7$ Jeong et al.$^7$ conducted a study to convert commercial palm oil using 1 wt.% Pt/Al$_2$O$_3$
and 10 wt.% Ni₃P/SiO₂ catalysts and achieved an excellent cracking performance.⁸ Sousa et al. showed promising cracking performance using H-beta zeolite.⁹ Kim et al. conducted a catalytic hydro-conversion of triglycerides (palm oil) using a catalyst (Pt/zeolite). After the final distillation, bio-jet fuel was obtained from palm oil at 55% by weight.¹⁰ Ozkan et al. utilizing used cooking oil to produce biodiesel using calcium catalyst from marine animal shells. The fat content from fatty acid methyl ester (FAME) measured was more than 99%, which indicated that pure biodiesel was obtained.¹¹ The use of nickel oxide, which is supported in ZSM-5, has also been shown to improve the performance of the ZSM-5 catalyst in the transesterification reaction of rubber seed oil.¹²,¹³

The biofuel production line from biomass is the hydrotreatment of vegetable oils and lipids.¹⁴,¹⁵ Most researchers use vegetable oil raw materials such as palm oil and jatropha curcas to be converted into renewable fuels.¹⁶,¹⁷ The selective hydrocracking process will produce a mixture consisting of a light fraction in the form of naphtha/gasoline, the kerosene/diesel fraction, and the aviation/jet fraction, where each fraction consists of C₆–C₁₂, C₁₀–C₁₅, and C₁₂–C₂₀.¹⁸ The raw material composition, i.e., is acids/triglycerides, significantly determines the distribution of the carbon chain lengths of the hydrocracking product. Hydrocracking, specifically triglycerides, is preferred over transesterification because the product’s properties obtained through special hydrocracking are much better.¹⁹ According to Chatterjee et al., coconut oil contains the most concentrated medium-length chain triglycerides.²⁰ According to Lal et al., coconut oil has lauric acid and myristic acid as its most prominent compounds, making up 49% and 18%, respectively.²¹ Therefore, in this study, coconut oil was chosen as feed/raw material for the hydrocracking process to produce bio-jet fuel.

The use of ZSM-5 in biofuel preparation from biomass has been reported.²²,²³ ZSM-5 is preferred because of its precise pore structure, hydrothermal stability, and adjustable acidity. Many researchers have developed on modifying the ZSM-5 catalyst and showed its possible use in the processing to produce fuels (jet fuel).²⁴–²⁶ Nickel content in Ni/ZSM-5 affects the Lewis/Bronsted acid site of the catalyst and the hydrocarbon products of the hydrocracking process. The Ni-ZSM-5 catalyst showed moderate biofuel yield, high methanation rate, and low solids yield.²⁷ Subsadsana et al. made the ZSM-5 catalyst filled with Ni-Mo-W by wet impregnation method. Ni-Mo-W loading increased the hydrocracking conversion of crude palm oil to liquid biofuel by over 62% and reduced coke formation. Zheng et al. reported the catalytic cracking process of used cooking oil with a combined catalyst of Co-Mo-S/Al₂O₃ and HZSM-5, producing a high liquid product (87.0% by weight). The catalyst allows for up to three reuses without a significant activity reduction. The catalyst provided good performance and high selectivity in hydro-conversion to aviation biofuels (C₉–C₁₅ hydrocarbons).²⁸

The acidity of ZSM-5 can be modified by adding transition metal oxides, thus producing a bi-functional catalyst.²⁹ The role of metals in the ZSM-5 matrix is influenced by the type, concentration, and distribution of metals in the ZSM-5. Nickel metal has good hydrogenation activity, whereas molybdenum reduces catalyst deactivation.³⁰ In general, catalytic performance increases with increasing metal content. We have reported that the distribution of 0.5 (wt.%) of nickel oxide and 1% MoO₃ in ZSM-5 had increased the catalyst’s acidity almost three times higher. In comparison, 4% and 5% molybdenum oxide increased the acidity 11 and 15 times compared to pure ZSM-5. Thus, the catalyst acidity is strongly influenced by the success of nickel and molybdenum oxides loading and their distribution in ZSM-5.³¹,³²

This research describes the ZSM-5 enrichment with nickel and molybdenum functionality to convert coconut oil into bio-jet fraction through a hydrocracking reaction using a semi-batch reactor. This study aimed to study bi-functional catalytic materials at various nickel and molybdenum concentrations to determine their effects, the catalyst's crystal structure, material properties, morphology, and the resulting catalyst's hydrocracking performances.

**EXPERIMENTAL**

**Material**
The commercial ZSM-5 supplied by Zibo Linxi Chemical Co., Ltd. China, distilled water, other chemicals from Merck such as ammonia 30% (solution), (NH₄)₆MoO₂₄.4H₂O powder, NiCl₂.6H₂O, ethanol, and coconut oil purchased commercially from supermarkets.
Catalyst Preparation

Commercial ZSM-5 was activated by heating at 100 °C to remove volatile molecules. Catalyst preparation in this section drew on previous work described elsewhere. The impregnation process used a wet method to distribute nickel and molybdenum metals onto the ZSM-5 matrix. Single impregnation on ZSM-5 with MoO₃ and NiO varied from 0.5%, 1%, 2%, 4%, and 5% by weight of ZSM-5. The 0.5% NiO metal impregnation was carried out by dissolving 0.37 g of NiCl₂.6H₂O in 100 mL double distilled water then adding 15 g of ZSM-5. The mixture was stirred at room temperature for 24 hours, then heated at 90 °C and dried at 110 °C for several hours. The solid was then calcined at a temperature of 550 °C for 6 h under nitrogen gas. The product obtained was 0.5 wt.% NiO/ZSM-5 and coded Ni-1. The same procedure was performed for other variations of NiO concentration with a stoichiometric setting. Likewise, the same method was carried out for the MoO₃/ZSM-5 catalyst with Mo originating from (NH₄)₆Mo₇O₂₄·4H₂O. The codes for all catalyst samples are presented in Table-1.

| Description               | Catalyst Code | Description               | Catalyst Code |
|---------------------------|---------------|---------------------------|---------------|
| 0.5 wt.% NiO/ZSM-5        | Ni-1          | 0.5 wt.% MoO₃/ZSM-5       | Mo-1          |
| 1 wt.% NiO/ZSM-5          | Ni-2          | 1 wt.% MoO₃/ZSM-5         | Mo-2          |
| 2 wt.% NiO/ZSM-5          | Ni-3          | 2 wt.% MoO₃/ZSM-5         | Mo-3          |
| 4 wt.% NiO/ZSM-5          | Ni-4          | 4 wt.% MoO₃/ZSM-5         | Mo-4          |
| 5 wt.% NiO/ZSM-5          | Ni-5          | 5 wt.% MoO₃/ZSM-5         | Mo-5          |

Catalyst Performance and Hydrocracking Product Analysis

The hydrocracking process used a semi-batch reactor. Coconut oil was used as a feed. The catalyst/feed ratio was 2 wt.%, which used 0.2 g of catalyst (Cat. I) for 10 g of coconut oil feed (F). Hydrogen gas flowed into the reactor column to remove oxygen contained in the feed. The running process under atmospheric pressure started by setting the temperature to 475 °C for 3 h with a temperature rise rate of 10 °C/min and a hydrogen flow rate of 10 mL/min. The weight of the liquid product is denoted as L. The residual weight (R) can be determined by weighing the residual feed in the reactor. The weight of coke (C) was determined by subtracting the initial weight (F) from the liquid weight (L), residual weight (R), and cokes weight (C). The hydrocracking product percentage was determined by Eqns.-1 to 4.33

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\% \text{ Liquid (wt.) } = \frac{L}{F} \times 100\% \\
\% \text{ Residue (wt.) } = \frac{R}{F} \times 100\% \\
\% \text{ Coke (wt.) } = \frac{C}{F} \times 100\% \\
\% \text{ Gas (wt.) } = \frac{G}{F} \times 100\% \\
\text{Conversion} \% = \left( \frac{\text{initial weight of the reactant} - \text{final weight of reactant}}{\text{initial weight of reactant}} \right) \times 100\% 
\]

The liquid product components are determined using Gas Chromatography-Mass Spectrophotometry (GC-MS). The peak area on the chromatogram determined the percentage of each component. The specific hydrocarbon was obtained by adding up the total area of the component peaks on the chromatogram within the above range of the chromatogram’s total area for each sample. Fraction percentage was calculated using Eq.-6 and Eq.-7. The chromatogram’s peak area fraction was also used to calculate selectivity using Eq.-8 and 9.

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\% C_4 - C_9 \text{ (GC area) } = \frac{\text{GC area of } C_4-C_9}{\text{Total of GC area}} \times 100\% \\
\% C_{10} - C_{15} \text{ (GC area) } = \frac{\text{GC area of } C_{10}-C_{15}}{\text{Total of GC area}} \times 100\% \\
\% \text{ selectivity } C_4 - C_9 \text{ (wt.) } = \frac{\text{GC area of } C_4-C_9}{\text{Total of GC area}} \times \text{Liquid (wt. %)} \\
\% \text{ Selectivity } C_{10} - C_{15} \text{ (wt.) } = \frac{\text{GC area of } C_{10}-C_{15}}{\text{Total of GC area}} \times \text{Liquid (wt. %)}
\]
Detection Method
The elemental composition in the catalyst was determined using the WDXRF (Wavelength Dispersive X-ray Fluorescence) Rigaku supermini200. The X-ray diffraction patterns were gained from Rigaku using Cu Kα radiation Cu-Kα1= 1.54059 Å, Cu-Kα2= 1.54441 Å). The generator of the X-ray was operated at 30 kV and 30 mA. The TEM images were obtained on an electron microscope JEOL JEM-1400. The adsorption-desorption of N2 for the catalysts was measured using a Gas Sorption Analyzer (GSA) (Quantachrome NovaWin). The liquid products were analyzed using Gas Chromatography-Mass Spectrophotometry (GCMS-QP2010S SHIMADZU).

RESULTS AND DISCUSSION
Catalyst Elemental Composition
The Si/Al ratio of the catalyst tends to increase after being impregnated by metal oxides. Meanwhile, the NiO content in the catalyst increased along with the increase in the concentration of nickel precursor added. However, in Ni-2, the nickel oxide content in ZSM-5 was less than Ni-1, conceivably because not many nickel precursors managed to enter the pores of ZSM-5 or exchange the counterbalancing cations. The high concentration of nickel precursors does not guarantee that the nickel content in ZSM-5 will be increased as well, as is the case with Pandiangan et al. The same trend can be seen in the MoO3/ZSM-5 catalyst. The Mo-3 and Mo-4 catalysts were similar to Ni-2 because the Mo oxide content in ZSM-5 was less than Mo-2.

Catalyst Crystal Structure
The XRD characterization was done on ZSM-5, modified ZSM-5, and their impregnated catalyst products to determine the crystal phase formed by the impregnation process of nickel and molybdenum metals to ZSM-5. The crystal phase can be either NiO or MoO3. Fig.-1 (a) and (b) show the diffractograms of the ZSM-5 catalyst and its impregnated counterparts NiO/ZSM-5 and MoO3/ZSM-5. All synthesized samples showed X-ray diffraction patterns corresponding to the single-crystal phase product with the MFI structure at 2θ = 23.3°, 24° and 24.3° (JCPDS 00-044-0002), which had not been affected by the addition metal by wet impregnation. All catalyst diffractograms contain specific peaks of the ZSM-5 matrix. This revealed that after impregnation with NiO and MoO3 and calcination at 550 °C for five hours, the ZSM-5 molecular sieve still retained its structure and crystallinity. However, some samples showed a slight shift in the 2θ angle, a decrease in peak, and a change in peak intensity. Mo-1/ZSM-5, Mo-2/ZSM-5, and Ni-4/ZSM-5 did not experience a shift in the 2θ angle compared to ZSM-5. These catalysts, too, did not experience peak widening, though a slight increase in intensity compared to ZSM-5 can be observed. The crystallinity of ZSM-5 before and after the impregnation was the same. This may be due to the even metal dispersion on the ZSM-5 surface and thus had not decreased the degree of crystallinity. Additionally, the NiO and MoO3 metals were relatively small compared to the weight of ZSM-5.

Figure-1 (a) shows the presence of nickel oxide observed at 2θ = 37.4°, 43.3°, and 63° (JCPDS 01-073-1519), in which the peaks correspond to the crystal lattices, (111), (200), and (220), respectively. This implies that Ni-based active ingredients exist in a NiO cubic structure. The XRD pattern for the ZSM-5 sample with Ni ≤3 wt.% did not show the NiO phase diffraction peaks indicating that the NiO particles were very scattered, and the particle size was too small to be detected. The NiO diffraction peak at 2θ=43.3°, which corresponds to the new NiO phase's crystal field (200), was detected in the samples' diffraction patterns at Ni content higher than 3 wt.%. This peak intensity was higher with increasing nickel concentration, even though the peak was relatively broad and low in intensity. This finding indicates that the NiO structure had low crystallinity in the ZSM-5 matrix.

Figure-1(b) shows the XRD pattern of the MoO3/ZSM-5 catalyst. Like the nickel-bearing catalysts, all samples showed diffraction peaks of the MFI structure. After Mo loading, the MFI structure of the ZSM-5 matrix was retained. The Mo impregnated product diffractogram presented new 2θ peaks at = 27.24°, 33.9°, 39.08°, and 49.32° (JCPDS File No. 04-012-8070), in which their intensities were more substantial with increasing MoO3 concentration. However, these diffraction peaks did not appear in the 3 wt.% MoO3 catalyst indicating that MoO3 was highly dispersed. Mo and Ni’s excellent dispersion proves that ZSM-5 is good support for uniform metal loading. The diffraction peaks of MoO3 at 2θ = 27.3°, with the
characteristic lattice of (021), appeared sharply on Mo-3, Mo-4, and Mo-5 catalysts. This indicated that MoO$_3$ had high crystallinity in ZSM-5. Calculations based on the Scherrer equation showed that the MoO$_3$ crystal size was more than 15 nm larger than the ZSM-5 channel diameter (~0.55 nm), meaning that some of the crystals may be on the catalyst surface. Furthermore, the absence of other peaks on the diffractograms, apart from ZSM-5 and MoO$_3$, indicated no new crystal species produced during the catalyst synthesis process.

**Microstructure of the Catalyst**

Catalyst microstructure was observed using transmission electron microscopy (TEM). For all samples using Scanning Electron Microscope (SEM) has been previously reported. In this report, TEM observations were only carried out on samples of ZSM-5, Ni-5, and Mo-5 as the latter two contained a high concentration of nickel oxide and molybdenum oxide (5 wt.%).

Fig.-2 (a) shows a mesoporous ZSM-5 image with spherical morphology with a particle size of 100-200 nm diameter. The results indicate that the synthesis process began with nucleation and crystal growth. No other particles had filled the pores. Fig.-2 (b) represents the Ni-5 sample microstructure, in which 5 wt.% Nickel oxide was assigned to ZSM-5. Small particles in the matrix were considered to be nickel oxide particles. The nickel particles were evenly distributed within the ZSM-5, consistent with the X-ray diffraction pattern. There appeared to be an increase in the particle size of ZSM-5 with the addition of nickel. This is probably due to the nickel metal entering the pore of ZSM-5, which affected the size of ZSM-5. Meanwhile, Fig.-2 (c) represents the structure of Mo-5, i.e., 5 wt.% molybdenum oxides dispersed onto ZSM-5.

Darker parts of the matrix can be estimated to be the molybdenum oxide dispersed in mesoporous ZSM-5. The presence of molybdenum oxide particles was not as obvious as the tiny nickel oxide particles. The particle size of molybdenum oxide might have been slightly more significant than the pore of ZSM-5. A higher metal concentration impregnated may cause potential blockage to the pore and narrow the pore diameter. Said findings were in accordance with the pore and surface parameter measurement results from nitrogen adsorption.

**Nitrogen Adsorption Analysis**

Figure-3 shows that the adsorption and desorption isotherms of the commercial ZSM-5 and Mo and Ni metals impregnated catalyst was of type IV isotherm with H4 hysteresis loops in the wide range of
0.3<P/P_0<0.99. The nitrogen gas desorption patterns differed from their adsorption patterns in all samples, indicating that micropore and mesoporous (2-50 nm) structures coexist in the catalyst. The presence of this mesoporous skeleton prompted a high specific surface area. The resulting mesopores were conical and closed cylinders with a tapered tip in shapes.\textsuperscript{36,37} Even though the samples had the same pore type, the catalysts’ ability to adsorb nitrogen differed for each sample. Concerning this, the Mo-3 sample obtained the highest N\textsubscript{2} absorbances.

The pore parameters of all the prepared catalysts are shown in Fig.-4 (a). All catalysts, both ZSM-5 and those enriched with NiO and MoO\textsubscript{3}, have surface areas of 220-416 m\textsuperscript{2}/g, providing abundant active sites for adsorption. The surface area, pore radius, and pore volume were higher for nickel and molybdenum impregnated catalysts than untreated ZSM-5. This emphasizes the capabilities of the ZSM-5 to provide a medium for the dispersion of molybdenum and nickel. Additionally, it was found that the surface area and pore volume tended to behave similarly. This indicates that there was no pore-blocking due to the metal oxide impregnation. In molybdenum, the parameter of pore properties tended to decrease with the increase in the amount of molybdenum except for Mo-3. Meanwhile, the surface and pore properties had shown consistency for nickel up to 4%, indicating that nickel impregnation had not affected the surface and pores. This result is in line with TEM data, which showed that the nickel particle size is much smaller than ZSM-5 and thus was able to be evenly dispersed. The impregnation of 5\% molybdenum and 5\% nickel resulted in a lower pore radius, indicating a pore narrowing caused by metal oxides. The decrease in surface and pore parameters with the increasing amount of molybdenum impregnated is understood because molybdenum oxide’s particle size may be slightly smaller than the particle size and pore diameter of ZSM-5. Higher molybdenum oxide on the surface and internal pore would decrease surface area, pore diameter, and pore volume.

The pore size distributions for ZSM-5 and its nickel and molybdenum oxides impregnated counterparts are shown in Fig.-4 (b). The catalysts’ diameters ranged from 3 to 18 Å, which indicated that micro-sized pores dominated the pores. A mesoporous structure is evidenced by hysteresis in the adsorption-desorption isotherm. Molybdenum-bearing ZSM-5 catalyst showed a pore size distribution at a smaller pore width. Meanwhile, the nickel-bearing ZSM-5 had provided a larger pore width. Fig.-4 (b) reinforces the data obtained from the TEM results, which show that the larger molybdenum particle size had more effect on the pore width.

**Coconut Oil Composition**

Coconut oil contains saturated fatty acids such as caproic acid (C6) 0.26\%, caprylic acid (C8) 4.96\%, capric acid (C10) 4.26\%, lauric acid (C12) 66.94\%, myristic acid (C14) 21.08\%, palmitic acid (C16) 1.83\%, tetracosanoic acid (C24) 0.46\%, and 2,7-Octadien-1-ol, acetate 0.22\%.
Hydrocracking Products

Hydrocracking products in liquid, gas, and coke forms for various catalysts can be seen in Fig.-5. ZSM-5 catalyst produced 26.77, 14.96, and 0.33 wt.% of liquid, gas, and coke, respectively. Thermal cracking produces a gaseous fraction product because the formation of radicals caused by high temperature relatively high occurs, resulting in short-chain hydrocarbons ($C_1$ – $C_4$) compounds such as methane – butane. Catalyst can increase the rate of hydrocracking reaction to produce the liquid fraction. Catalytic cracking occurs through carbocations with the minimum number of C atoms, resulting in the hydrocarbon liquid fraction products being more dominant.

In the present study, the catalysts containing NiO generally experienced an increase in gas products, whereby Ni-1, Ni-2, Ni-3, Ni-4, and Ni-5 produced 20.77, 25.80, 23.34, 27.60, and 16.42 wt.%, respectively. However, liquid products had tended to decrease. The increase in the liquid product was only obtained for Ni-1 and Ni-5 catalysts at 28.24 and 35.00 wt.%. In contrast, the catalyst containing MoO$_3$ had significantly increased liquid product at 33.02, 24.71, 45.09, 30.53, and 35.48 wt.% for Mo-1, Mo-2, Mo-3, Mo-4, and Mo-5, respectively. The resulting gas product was also more than ZSM-5 with less residue. Overall, the MoO$_3$ impregnated catalyst was more selective in producing organic liquid and gas products than the catalyst impregnated with NiO. Both NiO and MoO$_3$ catalysts produced very little coke, all of which were less than 2%, although on average, MoO$_3$ produced slightly more coke than NiO catalyst.

The liquid product contains bio-gasoline fraction, bio-jet, and others. All catalysts produced $C_7$, $C_8$, and $C_9$ hydrocarbons, while, specifically, Ni-3, Ni-4, Ni-5, Mo-3, Mo-4, and Mo-5 catalysts had produced $C_4$ hydrocarbons. Many factors affect a catalyst's performance, including porosity, surface area, and acidity. The surface area plays a role in bringing the feed closer to the active site. Meanwhile, the catalyst pores play a role in filtering compounds that can pass through them. Acidity indicates the availability of active catalytic sites in the cracking feed. Sriatun et al. have reported that nickel oxide and molybdenum oxide increased the acidity of the catalyst. These metal oxides act as Lewis acids. Hydrocracking is one of the chemical reactions that favor Lewis acid sites. The presence of nickel oxide or molybdenum oxide in ZSM-5 would dissociate hydrogen. The nickel oxide can reduce carbon deposition or carbon residue formation. The Lewis acid site of nickel oxide enhances the adsorption of the feed on the catalyst. Consequently, the hydrocracking process can undergo optimally.

Meanwhile, the bio-jet fraction consists of n-paraffin/saturated hydrocarbons ($C_{10} - C_{15}$), olefins/unsaturated hydrocarbons, slightly branched paraffin, cyclo-paraffins, and aromatics. The main constituents of the bio-jet fraction are undecane, dodecane, and tetradecane. ZSM-5 catalyst enriched with NiO or MoO$_3$ produced lower pentadecane hydrocarbon content than ZSM-5.

Other groups of liquid products consist of non-biofuel components. The highest content of caprylic acid ($C_{10}$) indicates that the fatty acids from the feed had yet been cracked into hydrocarbons. However, the percentage of carboxylic acids/fatty acids found in this study was <35%. This value is lower than the research results by Mutaqii et al., which was at 86.63%. However, ketones, aldehydes, alcohols, and others were also found in addition to previously said compounds as side-products of the hydrocracking reaction.
All ZSM-5, NiO/ZSM-5, and MoO₃/ZSM-5 catalysts were active in the coconut oil conversion, as shown in Fig.-6.

![Composition chart](image)

Fig.-5: Composition (wt. %) of Hydrocracking Product using ZSM-5, (a) NiO/ZSM-5 Catalysts, and (b) MoO₃/ZSM-5 Catalysts

![Conversion chart](image)

Fig.-6: Total Conversions with the Use of ZSM-5, NiO/ZSM-5, and MoO₃/ZSM-5 Catalysts

The order of conversion rates was MoO₃/ZSM-5 > NiO/ZSM-5 > ZSM-5. These results provide information that metal oxides have a positive function in improving hydrocracking performance. It can be concluded that MoO₃ has a better effect than NiO, with average conversion values of 54.61% and 45.79%, respectively. The total conversions for Mo-1, Mo-2, Mo-3, Mo-4, and Mo-5 were 53.17, 42.29, 64.86, 56.08, and 56.66 wt.%, respectively. Whereas for Ni, they were 50.00, 39.92, 46.58, 39.52, and 52.95 wt.%

The difference of outcomes for the nickel oxide and molybdenum oxide impregnation in producing hydrocracking components is probably due to the metals involved. Ni has an atomic number of 28 with an electron configuration of [Ar] 3d⁸ 4s¹, while Mo has an atomic number of 42 with an electron configuration of [Kr] 4d⁵ 5s¹. Molybdenum has a relatively larger size than nickel because it is in the second row of the transition group and has more unpaired electrons than Ni. This results in molybdenum having stronger Lewis acid nature. According to the results of previous studies, the acidity of catalysts containing MoO₃ tends to be more significant. Although the MoO₃/ZSM-5 catalyst has a smaller pore diameter than NiO/ZSM-5, the higher conversion results indicate that the acidity plays a bigger role than the pore size of the catalyst. This process still produced a relatively large residue of 58%, 54%, and 45% for ZSM-5, NiO/ZSM-5, and MoO₃/ZSM-5 catalysts. This unsatisfactory residue percentage may be due to the coconut oil’s low heating temperature and difficulty maintaining the hydrogen flow.
Selectivity of Bio-jet Fraction

The organic liquid component (OLC) is the main product targeted in this hydrocracking reaction as it contains the bio-jet fraction. The OLC compositions are presented in Fig.-7.

![Fig.-7: Fraction Composition of OLC (Liquid Product) produce from the Use of ZSM-5, (a) NiO/ZSM-5 Catalysts, and (b) MoO$_3$/ZSM-5 Catalysts](image)

The most dominant OLC components were undecane ($C_{11}$), dodecane ($C_{12}$), and tetradecane ($C_{14}$) compounds. The product targeted in this study is the bio-jet fraction, a fraction containing $C_{10}$–$C_{15}$. However, this product generally exists as a mixture with other components such as the $C_4$-$C_9$ or naphtha/gasoline fraction and other products (alcohol, ketones, and carboxylic acids). The components of OLC based on GC-MS are presented in Fig.-7. The tendency of the catalyst’s higher ability to produce a light fraction of $C_4$-$C_9$ (fraction of naphtha/gasoline) was observed in the catalysts containing NiO. The catalysts containing both MoO$_3$ and NiO had produced a bio-jet fraction of $C_{10}$-$C_{15}$, generally higher in amount than ZSM-5 without metal oxides. The higher production of the desired product is closely related to the acidity present in each catalyst. In general, MoO$_3$ was able to significantly increase the selectivity towards products of the bio-jet fraction along with the increasing concentration of the metal oxide embedded/impregnated in ZSM-5, as shown in Fig.-8.

![Fig.-8: Bio-jet Fraction Selectivity of ZSM-5, NiO/ZSM-5, and MoO$_3$/ZSM-5 Catalysts](image)

However, MoO$_3$ ability to produce a bio-jet fraction was low. Treatment with NiO at low concentrations can increase the amount of bio-jet obtained. However, the trend observed was inversely proportional to the amount of concentration used. Suppose the OLC’s overall results are reviewed, more hydrocarbon products $<C_{10}$, even butane ($C_4$), were obtained. In terms of the composition of the hydrocracking products, there was an increase in the percentage of gas fractions with an increase in NiO presence, meaning that NiO addition is selective or promotes the production of the light fraction ($C_4$-$C_9$). In this case, it can be concluded that ZSM-5 impregnated with MoO$_3$ metal oxide is more selective towards bio-jet fraction products than...
NiO. The bio-jet fraction is part of the hydrocarbons in the C\textsubscript{10}-C\textsubscript{15} chain group, both straight and branched-chain alkanes, where the straight chains are decane, undecane, dodecane, tridecane, tetradecane, and pentadecane. Based on the table, bio-jet selectivity increased with nickel oxide.

**CONCLUSION**

Enrichment with nickel oxide (NiO) and molybdenum oxide (MoO\textsubscript{3}) has been successfully carried out on ZSM-5 support material ZSM-5. NiO and MoO\textsubscript{3} impregnation in the concentration range of 0.5-5wt.\% did not affect the crystal structure of ZSM-5 but had increased its ability to adsorb nitrogen gas. This subsequently increased the selectivity in producing hydrocracking products. ZSM-5 impregnated with NiO had increased light fractions (C\textsubscript{4}-C\textsubscript{9}) or bio-gasoline production. However, selectivity towards bio-jet fraction arose only in Ni-1 and Ni-5. ZSM-5 impregnated with MoO\textsubscript{3} was more selective towards bio-jet fraction products than NiO. Catalytic activity was strongly influenced by the amount of NiO and MoO\textsubscript{3} embedded in ZSM-5.

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