

Synthesis of renewable diesel through hydrodeoxygenation reaction from nyamplung oil (*Calophyllum Inophyllum* oil) using NiMo/Z and NiMo/C catalysts with rapid heating and cooling method

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Abstract. The synthesis of metal nanocrystal was conducted by modification preparation from simple heating method which heating and cooling process run rapidly. The result of NiMo/Z 575 °C characterizations are 33.73 m²/gram surface area and 31.80 nm crystal size. By used NiMo/C 700 °C catalyst for 30 minutes which had surface area of 263.21 m²/gram, had 31.77 nm crystal size, and good morphology, obtained catalyst with high activity, selectivity, and stability. After catalyst activated, synthesis of renewable diesel performed in hydrogenation reactor at 375 °C, 12 bar, and 800 rpm. The result of conversion was 81.99 %, yield was 68.08%, and selectivity was 84.54 %.

1. Introduction

Due to the depletion of crude reserves, shortage in petroleum supply, and increasing demand for clean hydrocarbon fuels, the production of renewable feedstocks-based fuels from non-edible vegetable oil has emerged to solve at least partially in this problems. As a result, more consumers are now turning to biodiesel fuel instead of petroleum-based diesel for transportation. Unfortunately, biodiesel gave low oxidative stability, higher viscosity, higher cloud point and pour point, higher nitrogen oxides (NO_x) emissions, lower energy density, and higher injector/engine wear [7]. To avoid the disadvantageous physical properties of oxygenated fuels, hydrodeoxygenation of non-edible vegetable oil has been investigated as an alternative pathway of biofuel production.

Hydrodeoxygenation is a series of reactions that convert the molecular structure of triglyceride in non-edible vegetable oil to linear hydrocarbon and it means removal of oxygen from an oxygen-containing compound under hydrogen pressure at high temperatures with the help of heterogeneous catalyst, which product known as renewable diesel [9]. The hydrodeoxygenation process consisted of decarboxylation, decarbonylation, and hydrogenation reaction as can be seen below.



The main drawbacks of this reaction seem to be the large consumption of hydrogen during the process, which increase the production cost [10]. The aim of this experiment is to investigate the effect of temperature and calcination time during the catalyst preparation step on the activity, stability, selectivity, conversion, and yield of triglyceride content in nyamplung oil to renewable diesel product. Mo is found to facilitate the reduction, and promoting C-O activation while inhibiting the C-C breaking [5]. This NiMo/C and NiMo/Z catalysts synthesized through modification of simple heating method which heating and cooling process run rapidly [1]. Several studies using simple heating



method are: Liherlinah et al.[4] synthesizing CuO/ZnO/Alumina catalyststofuel cell applications for 30 minutes; Vioktalamo et al. [8] synthesise Y_2O_3/Gd catalysts todecompose of pollutant for 60 minutes with holding time of 30 minutes, Faisal et al. [11] synthesizing NiMo/Z catalyst for renewable diesel productions, and Fransisca et al.[2] synthesizing NiMo/Ccatalyst for renewable diesel productions. Studies abovewere using the same method but with different treatments. The products was characterized by GC-MS (Agilent) to find functional groups and components of renewable diesel.

2. Methodology

2.1. Materials

This study was conducted in two steps namely the preparation and characterization of nanocrystal NiMo/C and NiMo/Z catalysts and synthesis of renewable diesel in a hydrogenation reactor. The materialswhich needed in this study are:nyamplung oil (UNS Solo), $(NH_4)_6Mo_7O_{24}.4H_2O$ and $Ni(NO_3)_2.6H_2O$ (Merck), activated carbon and zeolite (Merck), HCl (Merck), Aquadest (CV. Dwinika), polyethylene glycol or PEG (Merck) and demineralized water (Bratachem Indonesia).

2.2. Catalyst preparation

Nanocrystal of nickel molybdenum on carbon and zeolite supports was prepared by rapid heating and cooling method adopted from Liherlinah [4] and Vioktalamo [8]. These catalysts were assigned as 5 wt% [6] and required amounts of the precursor salts and polyethylene glycol, i.e., $(NH_4)_6Mo_7O_{24}.4H_2O$, and $Ni(NO_3)_2.6H_2O$ were dissolved in demineralized water. Then, activated carbon or zeolite was added dropwise with constant stirring followed by heating at 100 °C for 40 minutes in that solutions to evaporize water. Polymer solution, as continous media, was used to avoid agglomeration of particle group of catalyst. Therefore the polymer should be remained until the end of the process. Finally the mixture was heated in furnace to evaporize the PEG polymer and to produce the final nanocrystal NiMo/C and NiMo/Z catalysts at 525 °C , 575 °C, 600 °C, 700 °C for 30 minutes and 60 minutes with holding time 30 minutes. After that, these catalysts were rapidly cooled (quenching process) with ice blocks. The catalysts were removed and stored in bottle of sample.

2.3. Catalyst characterization

The catalysts were characterized byXRD (Shimidzu) to determine crystal size and type of crystal catalyst, BET (Micromeritrics ASAP 2020) to determine surface area, pore size and pore volume of catalyst and SEM-EDX (JED-2300 Analysis Station JEOL)to determine the morphology of the catalyst.

2.4. Catalyst activity test

Catalyst activation was carried out at 400 °C with internal temperature being measured by thermocouple. Before catalyst activation, the reactor was purged with nitrogen during experiment (30 minutes) to remove any oxygen content that might have been dissolved and present in nyamplung oil so that activity of catalyst will increase. After that, added hydrogen gas of 10 bar and the temperature was slowly decreased into 100 °C to provide activityperformace during the reaction.

2.5. Hydrodeoxygenation of nyamplung oil

The reaction wasperformed in a 330 mL batch stirred reactor integrated with a condenser and furnace. Extensive stirring of the oil and catalyst in the reactor was achieved using a magnetically driven stirrer with a DC geared motor. Nyamplung oil was used as feed and NiMo/C or NiMo/Z as a catalyst with a feed ratio of 100:1 wt. Nitrogen gas was purged for 30 minutes. Stirrer speed and pressure during the reaction was kept constant at 800 rpm and 12 bar respectively. The reactions were performed at temperature 375°C for 2.5 hours. When the inside temperature of the reactor reached the target value, the hydrogen pressure was adjusted to the desired value. From this time onwards, the reaction time was occured. In this step, the double bonds that were present in the tryglycerides were saturated with hydrogen gas. Every 15 minutes, the resulting gas was analyzed online by GC-TCD to identify the

hydrogen, carbon dioxide, carbon monoxide and methane gasses. The gas products were condensed and collected as condensate. Figure 1 shows a schematic diagram of the apparatus.

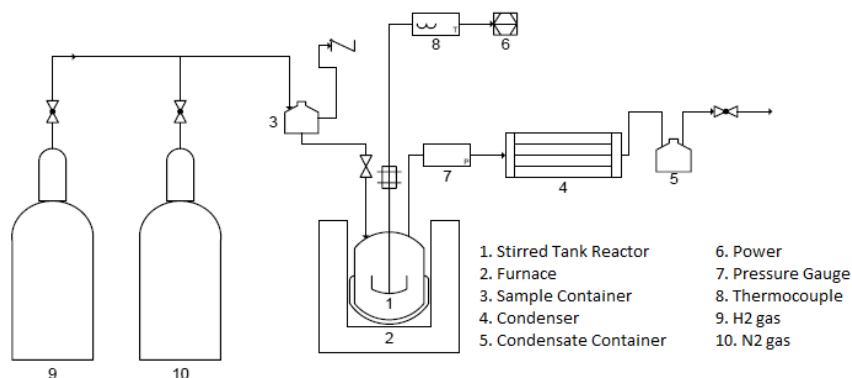


Figure 1. Scheme of Hydrodeoxygenation Reaction

The bottom product was distilled according to the boiling range of petroleum products in three categories i.e. IBP-200 °C, 200-300 °C, and 300-EP. Distillation products were characterized by GCMS to identify fraction component of sample, and also investigate the density, viscosity, and cetane index of the products.

3. Results and Discussion

3.1. Results of catalysts characterization

From BET characterization result, the best catalysts that gives highest surface area are NiMo/C with temperature 700 °C and NiMo/Z with temperature 575 °C for 30 minutes. These catalysts has surface area 263.21 m²/gram and 33.73 m²/gram respectively. Large surface area of the catalyst was needed to increase the collision between particles so it would increase the rate of reaction as well as the kinetics reaction [6]. This NiMo/C and NiMo/Z catalysts were continued confirmed through several tests by SEM-EDX and XRD to see morphology and crystal size of catalyst. Increasing temperature led to more rapid PEG vaporization and sintering of catalyst which occurred during reaction in zeolite but due to activated carbon stable with high temperature, so that increasing of temperature can not effect of catalyst surface area. If temperature increased, surface area of catalyst will reduce due to the collapse of walls inside catalyst pore [9].

NiMo/C 700 °C and NiMo/Z °C catalysts also give largest pore volumewhich indicating that the support structure has a large enough pore spaces. In catalysis reaction, large volume is needed to achieve the complete reaction, as the site of the reaction medium and can be regarded as a mini reactor [3]. The reason for low surface area and pore volume for this catalyst could be attributed to the pore blocking by NiMo metal. For sample of NiMo/C and NiMo/Z that was not kept constant, had higher surface area and the sintering that occurred on the catalysts to be weaker than other profil temperature.

The result of XRD characterization can be seen on Figure 2. Carbon and zeolite which originally had a weak peak, after impregnated the catalysts on the surface has a sharp peak. The intensity of the peak represents the crystallinity. The sharper peak obtained, means particles tend to be better crystallinity. High crystallinity also will affect to the catalytic activity and stability at high temperatures.

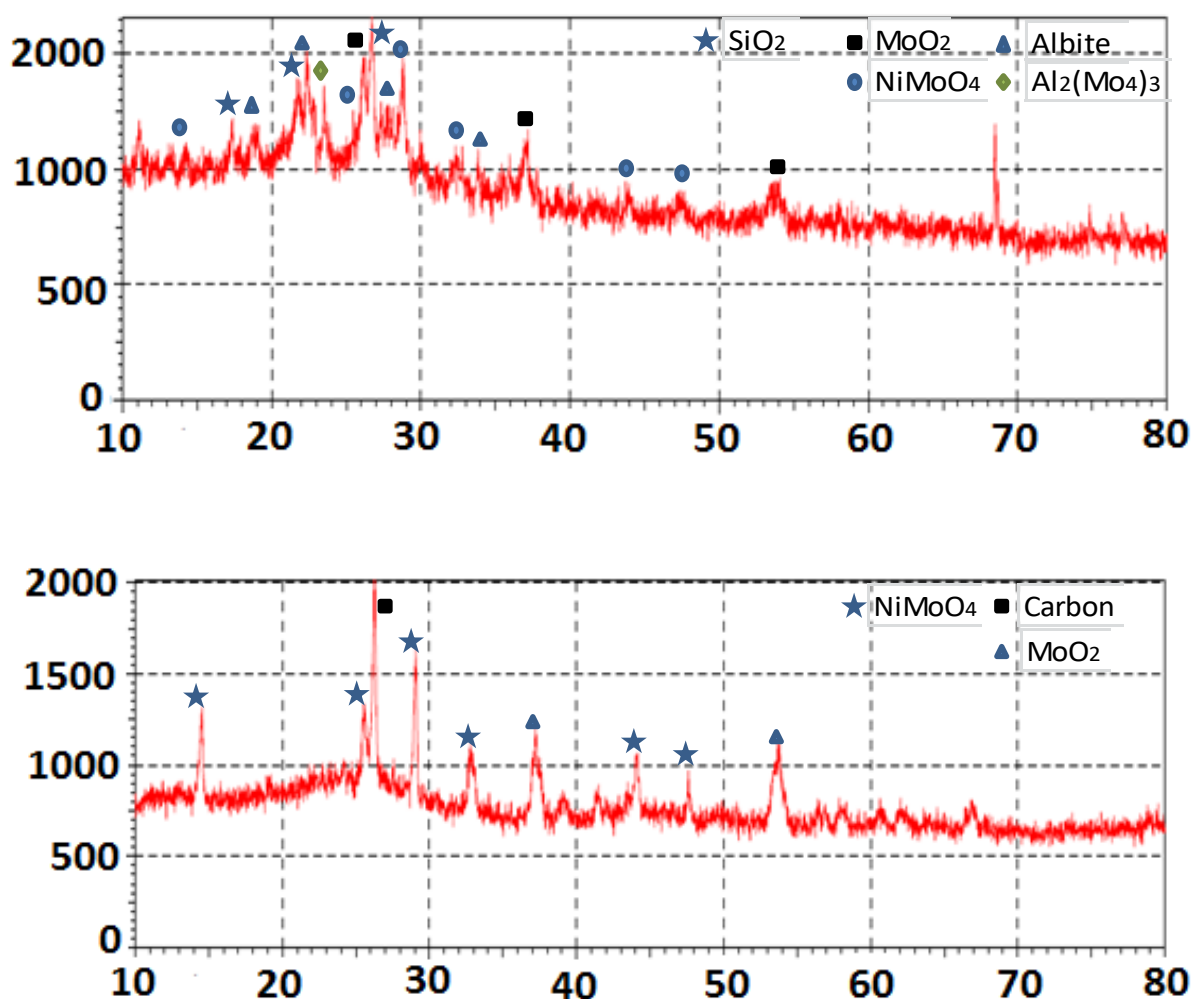


Figure 2. Diffractogram of (a) NiMo/Z and (b) NiMo/C Catalysts

Diffractogram also shows that crystal size of NiMo/C 700 °C which estimated by Scherrer formula is 31.77 nm and for NiMo/Z 575 °C is 31.80 nm. From this result, both of catalyst crystals size which formed were nanocrystalline.

Morphology plays an important role in activity and selectivity of the catalyst. From Figure 3 in SEM result, it can be seen that the magnification of 1000x and 10000x, these catalysts have the morphology which tend to be agglomerate and consist of small particles and large particles.

Based on EDX characterization result, the average yield active core NiMo content in carbon support was 6.76 wt% and 6.72 %wt in zeolite support. This number is almost close to the number of active nuclei was added during preparation which is 5 wt%. Increasing metal loading favors sintering due to weak interaction with supported phase, agglomeration and micropore blocking could also take place [5]. The SEM results can be seen in Figure 3.

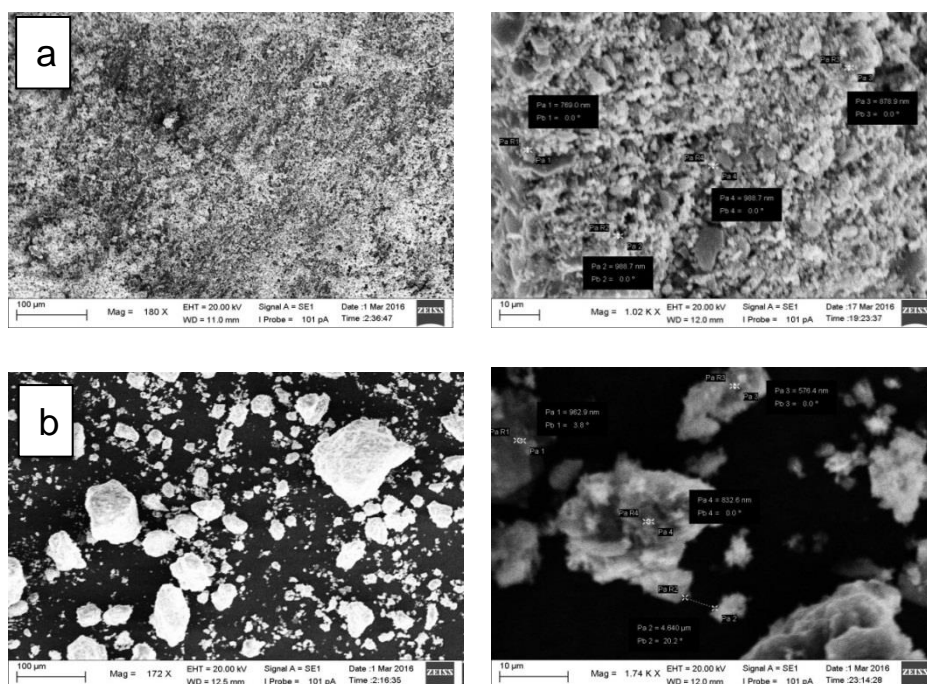


Figure 3. Catalyst Morphology of (a) NiMo/C 700 °C and (b) NiMo/Z 575 °C Catalysts at 1000x and 10000x Magnification

High *loading* which produce on both of catalyst happened due to percent weight of oxide element still high. Oxide element can be removed while catalyst activation next before hydrodeoxygenation reaction with hydrogen gas.

3.2. Results of catalysts characterization

Reactions of hydrodeoxygenation were carried out after the catalyst activation completed and the reactor temperature reaches 100°C. Hydrodeoxygenation of nyamplung oil was performed with four sample catalysts which had lowest crystal size, highest surface area, and good morphology namely NiMo/C, NiMo/C activated, NiMo/Z, and NiMo/Z activated. After HDO reaction, the products still in mixture and had to be purified through distillation process. Distillation products at temperature 300-EP were carried out to determine the physical and chemical properties of renewable diesel product.

3.2.1. Results of Activation Catalyst Test on Hydrodeoxygenation Reaction. GCMS shows that the distillation bottom products consist of hydrocarbon fractions (C₅-C₂₃) and oxygenates such as acetone, alcohol, aldehyde, carboxylic acid, etc. The percentage of oxygenate contained in the products less than 15% as can be seen on Table 2.

Table 1. Comparison Physical Properties of Renewable diesel with Other Products

Sample	Density (gram/mL)	Viscosity (cst)	Cetane Index
NiMo/C	0.86	1.37	54
NiMo/C activated	0.78	1.16	81.83
NiMo/Z	0.87	1.39	53.96
NiMo/Z activated	0.86	1.35	55.30
Nyamplung Oil	0.94	90.88	-
Biodiesel	0.85	2.30	51
Diesel	0.82	1.90	40
SNI	0.85 - 0.89	2 s/d 6	Min. 51

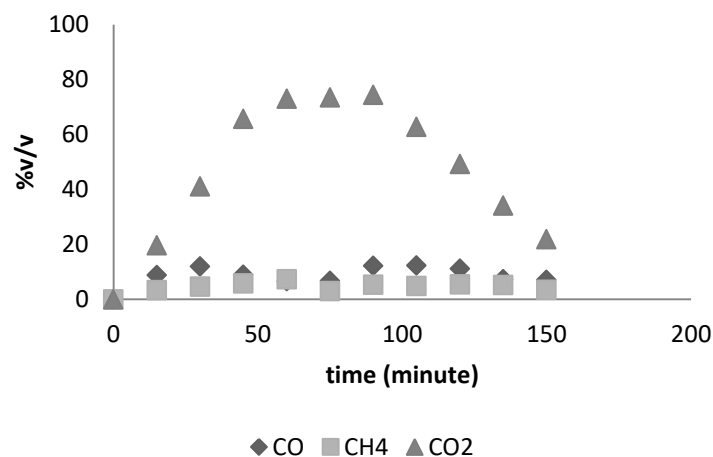
Table 2. Selectivity and Yield of Distillation Product (300-EP)

Sample	Product	% Selectivity	% Yield	% Conversion	% Oxygenate
NiMo/C activated	Biogasoline	12.32	9.92	81.99	10.29
	Biokerosene	2.35	1.89		
	Renewable diesel	84.54	68.08		
	Lubricant	0.79	0.64		
NiMo/Z activated	Biogasoline	10.17	8.11	80.95	10.71
	Biokerosene	4.43	3.53		
	Renewable diesel	74.54	59.46		
	Lubricant	10.86	8.66		

NiMo/C activated was a sample that produced the smallest percentage of oxygenate (10.29%). Based on this result, it can be seen that NiMo/C activated catalyst was the suitable catalyst to produce renewable diesel with the largest hydrocarbon content.

From Table 2 it can also be seen that the largest conversion of reactants occurred at NiMo/C activated catalyst with 81.99%. Similar with conversion, NiMo/C activated also has the largest selectivity and yield of C₁₂-C₁₈ fraction (diesel fraction) which are 84.54 % and 68.08 %. To evaluate the effectiveness and selectivities of NiMo/C activated catalyst in desired hydrodeoxygenation pathway, so analysis of gas products with GC-TCD were important as seen at Figure 4.

From Figure 4, NiMo/C activated catalyst was selective to decarboxylation reaction as equation in (1). This reaction can break oxygen bond so that alkane bond can be produced which indicates CO₂ gas was high approximately 80%. This NiMo/C activated catalyst also can minimize the production of methane and CO gases, so that alkene bond which undesirable product was not formed. Therefore, can be concluded that NiMo/C activated catalyst which has highest loading, highest surface area, and lowest crystal size, can convert nyamplung oil to renewable diesel with yield was 68.08%, conversion was 81.99%, and selectivity was 84.54%.

**Figure 4.** Gas Products Result of NiMo/C Activated Catalyst

4. Conclusion

In this study, NiMo/C and NiMo/Z catalysts were prepared by rapid heating and cooling method with polymer solution as a growth inhibitor. Characterization of catalysts have shown that NiMo/C catalyst has lowest crystal size of 31.77 nm and surface area of 263.21 m²/g which prepared at 700 °C when the heating temperature was not kept constant. The experimental conditions were 375 °C for average reaction temperature and 150 minutes for residence time. These conditions with NiMo/C activated led to dominant yield of 68.08% of diesel fraction (C₁₃-C₁₈), conversion was 81.99%, and selectivity was

84.54%. It means the oxygenation removal pathway of nyamplung oil through NiMo/C activated catalyst was successfully converted into the renewable diesel which the specification met the petroleum diesel standard.

Acknowledgments

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