Application of modified microwave polyol process method on NiMo/C nanoparticle catalyst preparation for hydrogenated biodiesel production

D F Pratama[1]**, B H Susanto**[1] **and E Ramayeni**[1]

[1]Department of Chemical Engineering, University of Indonesia, Depok 16424, Indonesia
Email: bambanghs@che.ui.ac.id

Abstract. The development of renewable feedstock-based diesel fuel is start to come up as the solution of national energy problem. However, the thermal and oxidative stability of biodiesel is not good enough. As a result, biodiesel can only be added to commercial diesel fuel as a mixture with concentration under 20%. To get better thermal and oxidation stability, partial hydrogenation process is applied to biodiesel caused the increase of monounsaturated FAME structure. Activated carbon supported NiMo nanocrystal catalyst was used in partial hydrogenation reaction to get high activity, conversion, and selectivity. In this research, NiMo/C catalyst was prepared by modified microwave polyol process method, which is provided a rapid heating and cooling process. This method can produce nano-sized NiMo/C catalyst with short time and low energy consumption. NiMo/C catalyst produced in this research has 285.85 m^2/gram surface area and 77.79 nm crystal size, resulting 20.41% conversion and 8.87% selectivity of biodiesel product. Further research should be conducted to obtain optimum condition.

1. Introduction

The depletion of petroleum energy reserves and increasing demand for clean and sustainable energy source has triggered the development of renewable energy source, such as biofuels. Biodiesel is one of the biofuels which can be produced by transesterification of triglyceride from various vegetable oil. But, biodiesel still have several problems. Thermal and oxidative stability of biodiesel is not good enough. As a result, biodiesel can only be added to commercial diesel fuel as a mixture with concentration under 20%.

Oxidative stability of biodiesel fuel depends on the degree of saturation of fatty acids in the starting vegetable oil. The presence of polyunsaturated fatty esters is the cause of oxidative stability with biodiesel [1]. One approach to solve this problem is the hydrogenation of polyunsaturated fatty acid methyl esters (FAME) in biodiesel. Since complete hydrogenation of polyunsaturated FAME to saturated FAME dramatically affects the cold flow properties of biodiesel, partial hydrogenation of polyunsaturated FAME to monounsaturated FAME is a promising solution to improve oxidative stability of biodiesel [2]. The product of this reaction is known as hydrogenated biodiesel.

The catalysts used in partial hydrogenation reaction are supported catalysts based on Ni, Cu, and noble metals. In this study, catalyst used is NiMo/C catalyst. NiMo Catalyst preparation process generally is still using incipient-wetness method, which can takes up to 24 hours preparation time and uses high energy consumption [3]. Using microwave as a heating media instead of conductive heating

in NiMo catalyst preparation is a simple, fast, and efficient method as a modification of current method [4]. Moreover, rapid time is required to avoid the growth of large metal catalyst.

This study will synthesize carbon supported NiMo catalyst by microwave polyol process method with various microwave power and heating time to obtain optimum results that can provide surface area, crystal size, and activity of partial hydrogenation reaction.

2. Experimental section
2.1. Materials
The materials used in this study are granular activated carbon as catalyst support, precursors $(NH_4)_6Mo_7O_{22}.4H_2O$ and $Ni(NO_3).6H_2O$ (Merck) as the source of the active site, ethylene glycol as polyols, sodium hydroxide (Merck) as the source of alkaline, potassium bromide (Merck) as stabilizer compound, and biodiesel from Kemiri Sunan oil (BKS).

2.2. Procedure
2.2.1. Synthesis of catalyst. NiMo/C catalyst with NiMo content of 5% [5] was synthesized through modified microwave polyol process method in the EG polyols solution. Synthesis of catalyst was done through two steps. The first step is impregnation of Mo into activated carbon. Required amounts of precursor $(NH_4)_6Mo_7O_{22}.4H_2O$ was dissolved in distilled water. EG then added into the solution. Activated carbon then added into the solution and KOH was added dropwise until pH 8-10. KBr was added into the solution as stabilizer compound. The solution was stirred on the magnetic stirrer. Next, the solution was dispersed in the sonication bath. The solution then heated in the microwave with certain power and time. that, the solution was filtered, and the solid product then washed with demineralized water and ethanol before heated in the furnace to produce Mo/C. The second is impregnation of Ni into activated carbon. Required amounts of precursor $Ni(NO_3).6H_2O$ $4H_2O$ was dissolved in distilled water. EG then added into the solution. The Mo/C then added into the solution and repeat the exactly same steps as synthesizing Mo/C to produce NiMo/C.

2.2.2. Catalyst characterization. The resulting catalyst then characterized with BET (Micrometrics ASAP 2020) to determine the surface area, pore size, and pore volume, SEM-EDX (JED-2300 Analysis Station JEOL) to determine the morphology and composition of the catalyst, and XRD (PANalytical Empyrean) to determine the natural and type of crystals.

2.2.3. Partial hydrogenation reaction. Partial hydrogenation reaction was carried out in a 330 ml stainless steel stirred batch reactor, which integrated with condenser and furnace, at temperature and hydrogen partial pressure of 110 ℃ and 4 bars, respectively. Stirring rate was maintained at 800 rpm. The weight of catalyst used is 1% of feed mass. Biodiesel and NiMo/C catalyst were placed into the reactor. The reaction started by increasing temperature and pressure to the desired point. The reaction occurred in 180 minutes, started when the desired temperature and pressure has achieved.

3. Result and discussion
3.1. BET characterization result
Table 1 shows that the catalyst produced in this study has a small pore diameter and large pore volume. The large pore volume and small pore diameter indicate that the support structure is very porous and has a wide pore space. A catalyst with a large surface area is needed to increase the area of contact of the active nucleus. However, sometimes the overly large surface area is avoided because it is indicated that the active site did not properly impregnated. Small pore diameter also indicated that the active site only attached on the surface, not inside the pore.

Table 1 also shows that with the same heating time, catalyst that is prepared with higher microwave power produced higher surface area. Higher power produces higher microwave intensity, resulting in higher heating rates as well. High heating rates results the ion particles reduced more completely. Meanwhile, with the same microwave power, catalyst that is prepared with less heating time produced
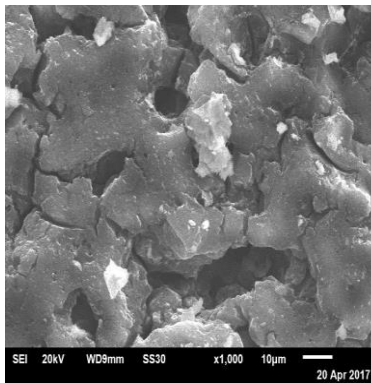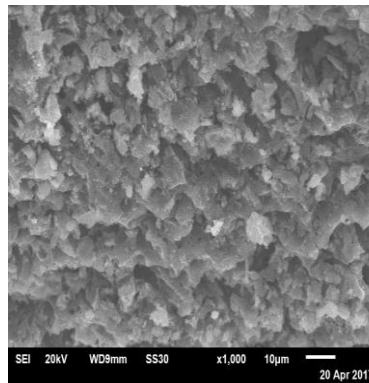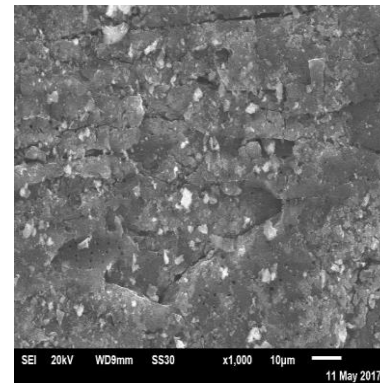
higher surface area. Longer heating process will lead to more agglomeration causing the surface area to decrease. The nucleus of the active site is formed at the beginning of the heating process. Furthermore, the active site nanoparticles grow as temperature increases. As the temperature reaches a higher point, the active site nanoparticles grow larger and begins to form clots. The clump will close the pores of the activated carbon so that the catalyst surface area will be reduced [6]. Catalyst that is prepared with rapid cooling procedure also produced higher surface area.

Table 1. BET characterization result

Catalyst	Microwave Power (Watt)	Heating Time (minutes)	Ultrasonic Dispersion	Rapid Cooling	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter (nm)
NiMo/C-1	550	3	-	√	379.95	0.202	2.132
NiMo/C-2	550	4	-	√	354.63	0.191	2.159
NiMo/C-3	800	3	-	√	411.32	0.224	2.179
NiMo/C-4	800	3	√	-	177.51	0.100	2.263
NiMo/C-5	800	3	√	√	285.85	0.157	2.200

3.2. SEM-EDX characterization result
From figure 1 and 2, it can be seen that the morphology of NiMo/C1 and NiMo/C3 tend to be clumping which is indicated by nonuniform particle size. Whereas, figure 3 shows that NiMo/C5, which is dispersed with ultrasonic wave, has better morphology than the other two which is indicated by more uniform particle size. These results indicated that the usage of ultrasonic wave as a dispersion media can produce better morphology of catalyst because of better dispersion method.

Figure 1. The morphology of NiMo/C1 catalyst at 1000x magnification

Figure 2. The morphology of NiMo/C3 catalyst at 1000x magnification

Figure 3. The morphology of NiMo/C5 catalyst at 1000x magnification

Table 2. EDX characterization result

Element	Mass percentage (%)		
	NiMo/C1	NiMo/C3	NiMo/C5
C	90.33	91.53	78.88
O	4.13	4.67	6.24
Al	0.46	0.30	2.11
K	2.42	1.02	5.59
Ni	2.66	2.09	2.72
Mo	-	0.63	4.46
Total	100	100	100

The EDX result in table 3 shows that the molybedenum in NiMo/C1 and NiMo/C3 was not well dispersed because the amount of Mo in NiMo/C1 and NiMo/C3 are scrimp and the loading of NiMo are still far from initial loading. Whereas, NiMo/C5 shows more amount of Mo and the loading of NiMo is approaching the initial loading. This result once again indicated that ultrasonic wave can give better dispersion.

3.3. XRD characterization result
Figure 4 and 5 shows the diffractogram of NiMo/C3 and NiMo/C5. It can be seen from the diffractograms that sharp peaks appear on each catalyst. The intensity of peak represents the crystallinity. The sharper peak obtained, means particle tend to have better crystallinity. High crystallinity also will affect to the catalytic activity and stability at high temperature [5]. Sharper peak also indicated larger crystal size. It can be seen from figure 4 and 5 that the diffraction of NiMoO4 appear at $2\theta = 46$, NiO at $2\theta = 63$ and 78.2, and MoO2 at $2\theta = 37.2$.

Table 3 shows the crystal size of NiMo/C3 and NiMo/C5. The crystal size can be obtained using the Scherrer equation. It can be seen that NiMo/C3 has bigger crystal size than NiMo/C5. This is because NiMo/C5 used ultrasonic wave as dispersion media, which can break up clumps and agglomerates so they have a smaller crystal size. From this result, only NiMo/C5 catalyst formed nanocrystalline.
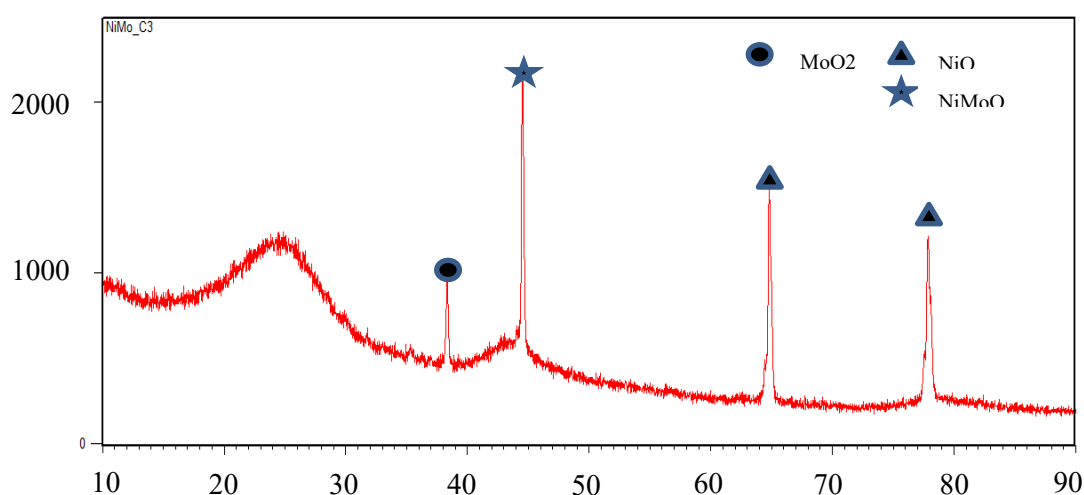

Figure 4. Diffractogram of NiMo/C3

Table 3. Crystal size

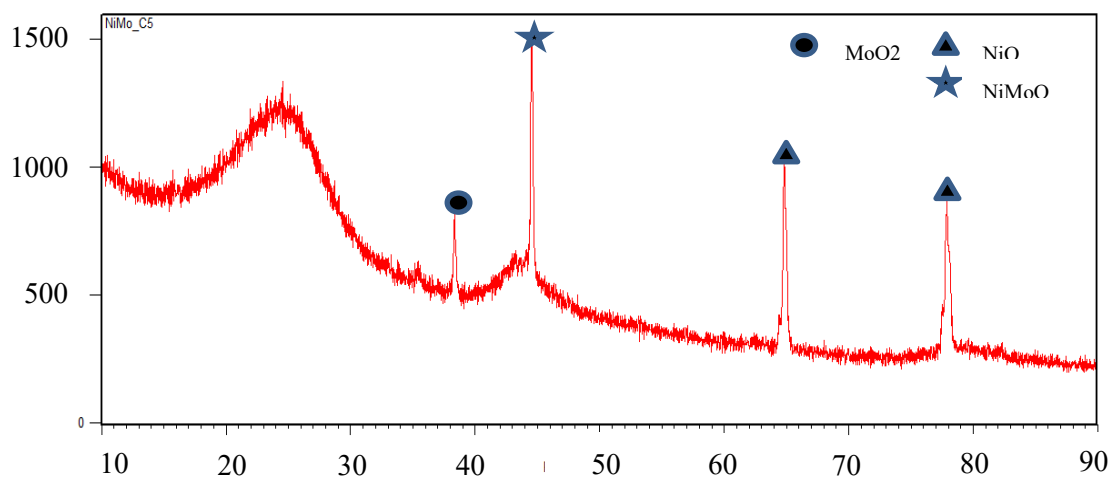| Catalyst	Crystal size (nm)			
	NiO	MoO$_2$	NiMoO$_4$	Average
NiMo/C3	121.866	180.304	64.981	122.857
NiMo/C5	68.105	105.128	69.800	77.785

Figure 5. Diffractogram of NiMo/C5

3.4. *Partial hydrogenation reaction result*

Partial hydrogenation reaction was performed to break the double bond on *Biodiesel Kemiri sunan* (BKS). The activity of NiMo/C5 catalyst in this study was determined by how much double bonds were broke during the partial hydrogenation reaction.

Table 4 shows the data obtained from GC-MS. it can be seen that after the partial hydrogenation process, changes occur when the decreased of Methyl 9,11,13 Octadecatrienoate (18:3) and Methyl Linoleate (18:2) components, as well as the increased of the Methyl Oleate component (18:1) as the desired component of the H-FAME product. This result shows that the NiMo/C5 catalyst used in the partial hydrogenation reaction has been able to break the double bonds C18:3 and C18:2 present in biodiesel. On the other hand, a very small increase of Methyl Oleate (18:1) indicates that although NiMo/ C5 catalysts have been able to break the double bonds in a partial hydrogenation reaction, the NiMo/C5 catalyst still cannot aim the reaction into the desired product, which is *Methyl Oleate* (18:1).

Figure 6 shows that partial hydrogenation reaction still results low conversion, yield, and selectivity. This is maybe because the BKS as the raw material contains high amount of C18:3, which causes the difficulties produce C18:1 because the hydrogenation occurred step by step, from C18:3 to C18:2 then from C18:2 to C18:1. Another reason is the amount of catalyst used in this reaction is too small so that the reaction did not run optimally.

Table 4. Component identification for BKS and H-FAME

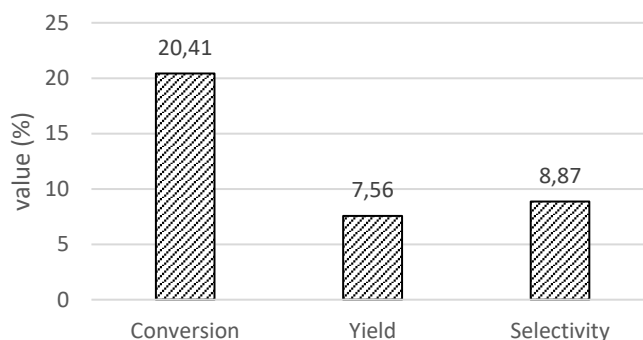| Component	Mass percentage (%)	
	BKS (%)	H-FAME (%)
Methyl Stearate (18:0)	8.60	8.99
Methyl Oleate (18:1)	5.63	6.81
Methyl Linoleate (18:2)	24.20	20.30
Methyl 9,11,13 Octadecatrienoate (18:3)	42.97	40.74

Figure 6. Conversion, yield, and selectivity

4. Conclusion

In this study, NiMo/C catalyst were prepared by modified microwave polyol process. The best catalyst produced in this study was NiMo/C5, which was prepared with 800W microwave power for 3 minutes with ultrasonic dispersion and rapid cooling process. Characterization result have shown that NiMo/C5 has 285.85 m^2/g surface area and 77.79 nm crystal size. The NiMo/C5 catalyst was used in partial hydrogenation reaction of *Biodiesel Kemiri Sunan* at 120 ^{o}C and, 4 bar for 180 minutes with 1% catalyst weight, resulting 20.41% conversion and 8.87% selectivity. This result indicated that the catalyst has low activity for partial hydrogenation reaction of *Biodiesel Kemiri Sunan* with those operating condition. Research should be done further using the national standard biodiesel to determine the optimum amount of catalyst used.

5. Acknowledgement

6. References

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