



Preparation and Characterization NiMo/Zeolite Catalyst using Microwave Polyol Process Method for Synthesizing Renewable Diesel from Jathropa Oil

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ABSTRACT

Biofuels have great potential to fulfill the energy needs of Indonesia. The process used is hydrodeoxygenation reaction (HDO) whose products are known as renewable diesel. This study focuses on preparation NiMo/Zeolite catalyst for synthesizing renewable diesel from jatropha oil. Preparation of NiMo/Zeolite catalyst is done by using microwave polyol process method. Microwave polyol method is a modification from incipient wetness method to overcome energy consumption and preparation time problem. Microwave polyol method is done by using a fast and uniform electric radiation from microwave as heating medium to dry catalyst. The catalyst result by using microwave polyol method gives the surface area of 5.45m²/g and has average crystal size of 62.98nm. NiMo/Zeolite catalyst used to synthesize renewable diesel at 375°C, pressure 12 bar, catalyst loading 1% mass of Jathropa Oil and stirrer speed 800 rpm. Based on the characterization results of GC-MS, the catalyst NiMo/Zeolite has conversion of jatropha oil 88,61% with renewable diesel product selectivity and yield are 35.26 and 21.5% respectively. According to result of FTIR and product physical properties, renewable diesel products have similar functional group and have better specifications than commercial diesel with density values: 0.833 gr/cm³, viscosity: 3.02 cst, cetane index: 61.01

Keywords : NiMo/Zeolite, Microwave polyol process, Renewable diesel

1. Introduction

Biofuels has a good potential to fulfill energy needs in Indonesia as well as in the world. Biofuels are able to be alternative energy when the petroleum energy are depleted over time. Biodiesel is one of the biofuels which can be produced from trans esterification of triglyceride by using renewable resources such as jatropha oil. But, the product produced from that reaction still had several problem, such as high content of oxygen. High content of oxygen can lead to the decreasing heating value of fuel and makes the component of the car machine. To overcome this problem, we need to do a modification to reduce the oxygen content on the fuel, which can be done by using hydrodeoxygenation [1] to get a fuel which known as renewable diesel.

Reaction formation of renewable diesel by using hydrodeoxygenation pathway involves a catalyst to decrease the activation energy of the reaction and increase the reaction selectivity. The proven catalyst having high selectivity for hydrodeoxygenation is

NiMo. Boyas [2] in his study are able to synthesize renewable diesel by using NiMo/Al₂O₃ to get n-octadecane with conversion 80%. Similar study is conducted by using NiMoCe/Al₂O₃ are able to convert jatropha oil to be renewable diesel with conversion 88% [3]. It proves the activity of NiMo catalyst for the synthesis of renewable diesel. However, the active phase of the catalyst Ni and Mo itself does not have a large surface so that the reaction would be ineffective and inefficient due to not all of the active area can make contact with the reactants. Therefore, Ni and Mo metal component needs to be distributed on a surface of a solid support which has a large surface area such as zeolites [4]. This is also confirmed by research conducted by Susanto and Wiyo [5] which uses zeolite as Pd catalyst support which successfully providing large surface area and gives conversion up to 91.44%.

NiMo catalyst preparation process generally is still using conventional techniques incipient-wetness method, where in this method takes up to 24 hours preparation and need high consumption of energy [2]. So, modification of the current method is needed to

reduce the time and energy needed to prepare catalyst. In this study, modification is done by using electric radiation of microwave as heating media to dry catalyst. Heating modification using microwave is a simple method, efficient and fast, which only need 3 until 5 minutes for synthesizing catalyst [6]. Moreover, quick time is required to avoid the growth of large metal catalysts, because the size of catalyst is in line with increasing time [7].

This study will synthesize NiMo catalyst synthesis which already proven have a good activity, but use a different way of preparation by using microwave polyol process method and using zeolite as support. pH of the solution, the use of stabilizer compound KBr and activation process will be varied to obtain optimum results that can provide surface area, high activity and selectivity of renewable diesel.

2. Method

The materials used in this study is Jatropha Oil as raw material, natural zeolite from Lampung as catalyst support, precursor $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ as the source of the active nucleus, ethylene glycol and glycerol as a polyols, KBr as stabilizer compound, 3M HCl for zeolite activation, KOH 0.8 M and 0.2 M NaOH solvent on the formation of polynuclear hydroxocomplexes.

Activation process for support - clinoptilolite zeolite from Lampung is washed using demineralized water while stirring for 24 hours. Subsequently zeolite is activated by using 3M HCl while stirring and heated at a temperature of 50°C. Zeolites rinsed until neutral pH and dried at 300°C for 3 hours.

Synthesis Catalyst – 1. NiMo/Zeolite catalyst with NiMo content of 5% was synthesized through microwave polyol method in the EG polyols solution with $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ as a precursor. Precursor is dissolved in 15 mL of distilled water then adding 15 mL of Ethylene Glycol to the solution. 5 gr Zeolite is added to the solution and KOH (0.8M) until pH 8-9, KBr is added to the solution as stabilizer compound and then the solution is dispersed with ultrasonic for 135 minutes. The solution is put in the microwave at 800 W for 3 min and heated at 300°C in furnace for 2 hours.

Synthesis Catalyst – 2. The same method as *Synthesis Catalyst – 1* was used but, the solvent used is Glycerol+EG with ratio 9:1 and without adding KBr and using microwave time 5 min. Table 1 shows the catalyst prepared in this study.

Characterization of catalyst - the resulting catalyst is characterized by several characterization, such as XRD to determine the nature and type of catalyst crystals, BET to determine the surface area, pore size and pore catalyst and SEM-EDAX to determine the morphology and composition of the catalyst.

Table 1. Catalyst Prepared

Catalyst	KBr	Alkaline	Solvent	Heating Time (min)	Activated
NiMo/Z-1	√	√	EG	3	-
NiMo/Z-1A	√	√	EG	3	√
NiMo/Z-1B	√	-	EG	3	-
NiMo/Z-2	-	√	EG+Gly	5	-

Hydrodeoxygenation reaction - The reaction is performed in 330 cc batch reactor integrated with a condenser and furnace. Jatropha Oil is used as feed and NiMo/Zeolite as catalyst with a feed ratio of 100:1 wt, Stirrer speed and pressure during the reaction was kept constant at 800 rpm and 12 bar respectively. Reaction temperature is kept at 375°C and every 15 minutes the gas produced was analyzed by GC-TCD to identify carbon dioxide, carbon monoxide and methane produced by the reaction. The equipment used for reaction can be seen in Figure 1.

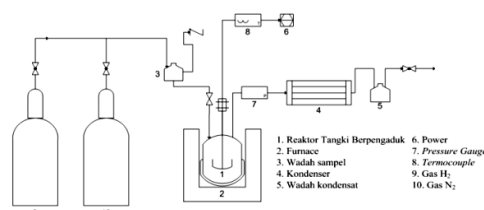


Figure 1. Hydrodeoxygenation Reactor Scheme

Characterization of bottom products - Bottom product was distilled and the resulting distillate is analyzed to determine physical and chemical properties. The characterization was conducted on several tests which are density, viscosity test, cetane index test, FT-IR and component identification by GC-MS.

3. Result and Discussion

3.1 XRD Characterization

The Result of XRD characterization can be seen on the figure 2. Regarding to study conducted by Yaser [8], Diffraction of NiO are detected on $2\theta = 37,3; 43,4; 63; 75,6$ and $79,6$, while regarding to study conducted by Palcheva [9], diffraction of MoO_3 can be detected on $2\theta = 24,2; 27,3; 47,4$ and $57,2$. Based on the test results of XRD, each prepared catalyst was already formed Ni and Mo metal peak on each of the 2 theta. Zeolites which originally had a weak peak, after impregnated the catalyst on the surface has a sharp peak. The intensity of the peak represents the crystallinity, the sharper peak obtained, particles tend to be better crystallinity. Crystallinity NiMo/Zeolite catalyst will affect the catalytic activity. If the high crystallinity, the catalyst also has a high catalytic activity and stable at high temperatures. High crystallinity can also be



regarded that the impregnation process is free from the impurities so that the physical properties of the catalyst NiMo/Z is not compromised.

3.2 BET Characterization

Based on Table 2, it shows that the surface area of each catalyst is smaller than the surface area of zeolite before impregnation process. It indicates that the metal impregnation of Ni and Mo in the zeolite support partially closing the zeolite pores which make surface area becomes smaller. Another possibility, NiMo/Z catalyst uniformly dispersed on the outer surface and forming agglomerate that covered most of the supporting surface. It cause a significant decrease in surface area.

BET results obtained also showed that in addition to a significant decline in surface area, catalyst preparation results have large pore diameter, which is in the range of 0.014 until 0.041 cc/g. This large pore zeolite is related to the structure of support itself which indicate that the zeolite is not a flat beam shape, but rather leads to a shape with holes. The pore volume and large pore diameter, indicating that the zeolite structure is very porous and has a large enough pore spaces. Rosdiana [10] in her study explains that the large pore size allow catalyst to have a lot of empty space to the pore which can be used for surface reactions. In addition, the magnitude of pore size of support would allow the particles can interact with the reactants to the catalyst through the pores of the zeolite, so that the reaction can occur not only on the outer surface but also can occur on the inside of the pores of the catalyst.

Based on the results of BET characterization, it appears that the catalyst NiMo/Z-1B has the greatest surface area than the surface area of the catalyst NiMo/Z-1 and NiMo/Z-2. Large surface area of the catalyst is needed to increase the collision between particles so, it would increase the rate of reaction as well as the kinetics reaction. However, sometimes a large surface area catalyst is also avoided because it indicates that the active nucleus that impregnated on the support only slightly attached to the pore of support.

3.3 SEM-EDX Characterization

From Figures 3 and 4 it can be seen that both the magnification of 1000x and 10000x, the four catalysts NiMo/Z prepared have the morphology which tend to be agglomerate. From those figures, it can be seen that either there are small particles or large particle. From those figures also, it can be seen that the catalyst morphology is arranged from flake-shaped box particles which formed an aggregates from small particles. It is proved that the resulting catalyst still do not have a uniform size.

Based on EDAX characterization result, the catalyst NiMo/Z-1 and NiMo/Z-1A showed that the activation process which conducted by using hydrogen gas at 12 bar and Temperature at 375°C for 1hr have already reduce the metal oxide to form metal (table 3). It is shown by the increase in the amount of metal in mass percentage of NiMo from 4.4% to 5.25%, and followed by decreasing in the oxygen content from 43.77% to 39.64%.

Table 2. BET Characterization Result

Catalyst	Surface Area (m ² /g)	Pore Volume (cc/g)	Pore Diameter (A)
Zeolit*	51,9	0,004	10,53
NiMo/Z-1	5,45	0,041	301
NiMo/Z-1B	7,02	0,046	257
NiMo/Z-2	2,6	0,014	209

Table 3 EDAX Characterization Result

Element	% wt			
	NiMo/Z-1	NiMo/Z -1A	NiMo/Z -1B	NiMo/Z -2
O	43,77	39,64	38,09	40,68
Al	12,92	13,90	19,71	19,72
Si	31,30	31,73	26,31	28,89
Mo	3,25	3,90	2,30	0,24
K	7,61	9,44	12,54	10,29
Ni	1,15	1,39	1,05	0,19

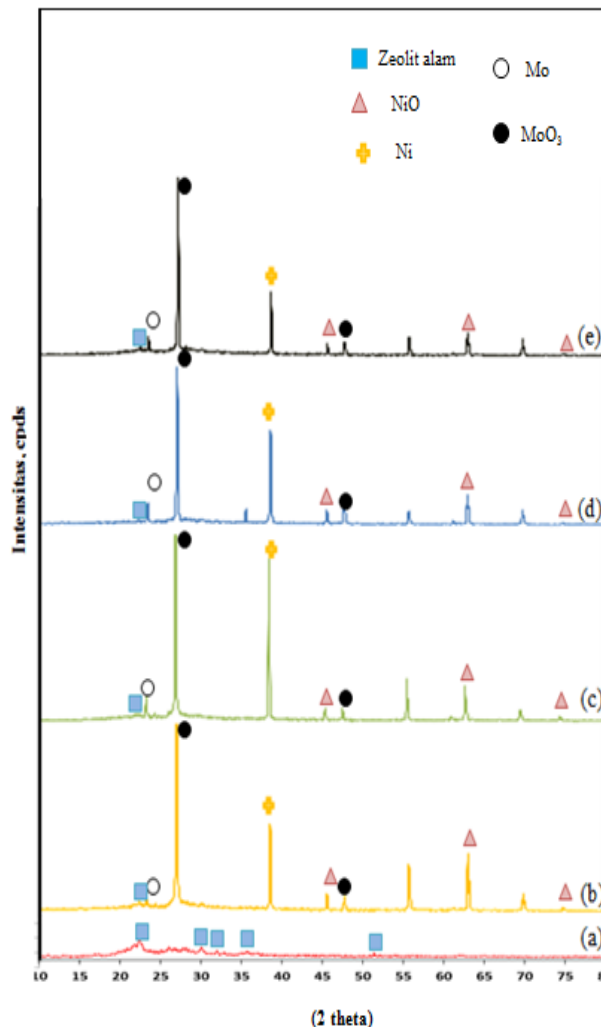


Figure 2. XRD characterization result for (a) Activated Zeolite, (b) NiMo/Z-1, (c) NiMo/Z-1A, (d) NiMo/Z-1B dan (e) NiMo/Z-2

NiMo/Z-2 Catalyst has the smallest Ni and Mo active metal detected by EDX which is not as expected to have 5% loading catalyst. Based on Table 3 it can be seen that the percentage of the total mass of Ni and Mo only 0.43%, while the target loading of NiMo catalyst is 5%. It indicates that there are a lot of losses during catalyst preparation process. NiMo/Z-2 catalysts were prepared by the same method by using the microwave polyol process method. But unlike the other catalysts, the NiMo/Z-2 catalyst uses a different solvent which is a mixture of EG and glycerol at a ratio of 1: 9. Glycerol solvent has a higher viscosity and has a higher boiling point than ethylene glycol (EG). The high viscosity of glycerol gives more resistance to the precursors (Ni and Mo ions) to diffuse to the surface of the catalyst support. It also can makes the possibility that the Ni

and Mo is not attached to the surface of the metal catalyst higher. Moreover, the heating process by using microwave at maximum power 800W makes precursors having a uniform heating and very fast. The possibility of Ni and Mo ions are evaporated with another solution is very high considering that the metals are not attached to the supporting surface. This leads to a fairly high losses and decrease the number of actual catalyst loading.

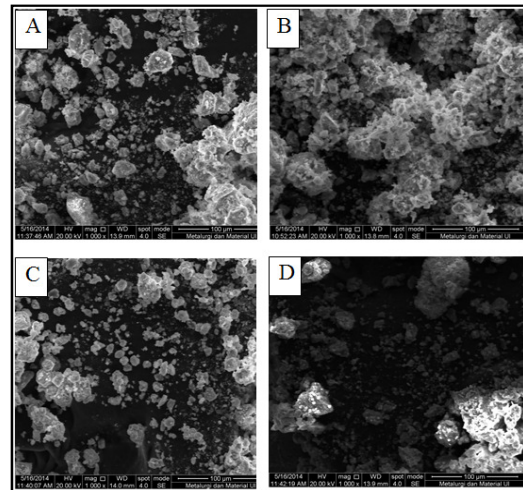
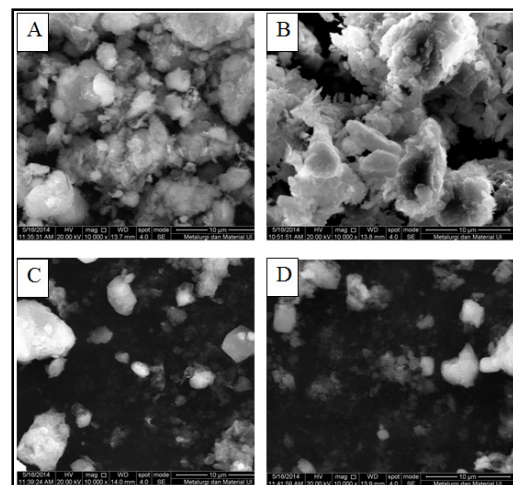


Figure 3. SEM Characterization Result 1000x Magnitude for (a) NiMo/Z-1, (b) NiMo/Z-1A, (c) NiMo/Z-1B, (d) NiMo/Z-2



Gambar 4. SEM Characterization Result 10000x Magnitude for (a) NiMo/Z-1, (b) NiMo/Z-1A, (c) NiMo/Z-1B, (d) NiMo/Z-2

Catalyst Activity Test

NiMo/Z catalyst used is the best catalyst with actual loading close to target 5% wt and has the smallest crystal size of the catalyst. Based on characterization result, NiMo/Z-1 have better characteristic such as crystallinity, have the best actual loading. So, NiMo/Z-1 is selected to be used to test the activity for synthesizing renewable diesel, even though the surface area of the catalyst NiMo/Z-1 is slightly lower than the catalyst NiMo/Z-1B.

3.4.1 Stability and Activity Test

Based on the analysis of gas samples by using GC-TCD, which can be seen at Figure 5, it show that hydrogen as a reactant decreased quite rapidly at the beginning and relatively constant at the end. In addition, it appears that CO₂ and CO gases continue to rise over time.

The gas formation indicates that there has been a carboxylation reaction which produces CO₂ and carbonylation reactions which produce CO gas. In addition, the formation of CO and CO₂ gases continue to rise to 46% which indicates that the catalyst has a high catalytic activity.

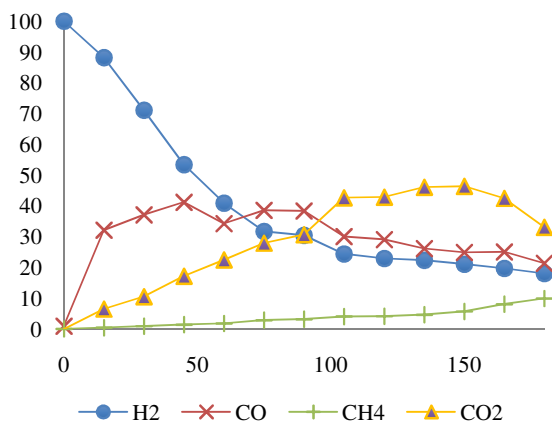


Figure 5. Gas Profile During Reaction

In Figure 5 also illustrates that there is no significant reduction in the formation of CO and CO₂ gas. This decrease indicates that the possible reduction of these gases have been caused by fewer reactants can react and also due to the deactivation of the catalyst. Deactivation of the catalyst is probably due to the collapse of the supporting structure of natural zeolite. The structure of natural zeolite preparation results have low Si/Al ratio which only 2:42. This low ratio affects to the catalyst which is not stable at high temperatures. So that after some time the structure will be damaged

or collapsed. However, the data of GC-TCD showed insignificant reduction, so it can be concluded that in a lab scale which has been demonstrated, the catalyst has good stability in the reaction for 3 hours

Table 4. Conversion, Selectivity and Yield Renewable Diesel

Sample	Conversion(%)	Renewable Diesel Selectivity (%)	Yield (%)
RD-NiMo/Z-1	88,615	35,260	21,515

From Table 4 it can be seen that the conversion of reactants into products at 375°C and 12 bar using a NiMo/Z-1 catalyst reaches 88.615% conversion. Based on this data, the catalyst NiMo/Z-1 is proved have a high activity is able to transform of jathropa oil into the final product. The product that produced is under product containing renewable diesel. Table 4 also shows the second level of selectivity of the catalyst. Catalyst selectivity NiMo/Z-1 to produce renewable diesel is 35,260% and the yield of catalyst NiMo/Z-1 has reached yield 21,515%.

3.4.2 Physical Properties Renewable Diesel

3.4.2.1 Density

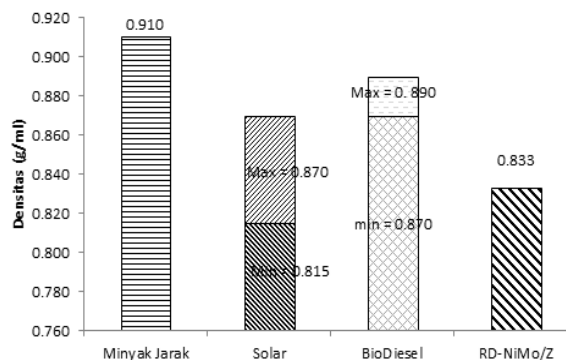


Figure 6. Product Density Results and Comparison with Jatropha Oil and Commercial Diesel

Figure 6 show that the density of the product renewable diesel produced from catalyst NiMo/Z-1 by using microwave polyol process able to decrease the density of the jathropa oil. In addition, it also can be seen that the renewable diesel density from reaction by using catalyst NiMo/Z-1 is lower then biodiesel density and in the acceptable range of commercial diesel density. This results indicate that the hydrodeoxygenation reaction from jathropa oil has

successfully produced renewable diesel with a better density. The decreasing value in density from raw material into renewable diesel product caused by carbon chains cracking of jathropa oil which will decrease the molecular weight of renewable diesel product. Molecular weight of component will affect the value of the density of the component.

3.4.2.2 Viscosity

Figure 7 shows the results of the viscosity test results from renewable diesel product by using NiMo/Z-1 as catalyst. It can be seen in Figure 7 that there is significant decrease in the viscosity of jathropa oil as the raw material to the product of the hydrodeoxygenation reaction using NiMo/Z-1.

Products which obtained from the reaction using catalyst NiMo/Z-1 has viscosity of 3.02 cst which 40 cst lower than raw material viscosity (92.8% lowering). Moreover, the viscosity of the product is still in the range of commercial solar viscosity which refers to ASTM D975 (1.9 to 4.1 cst), but slightly below the standard limit viscosity of Biodiesel.

The Decreased viscosity is caused by the termination of jathropa oil carboxylate bond which contain a carbonyl group (CO) and hydroxyl (-OH). -OH group on the carboxylic bond can form hydrogen bonds with the carbonyl group (CO) resulting in stronger bonds between molecules and increase the viscosity. Therefore, when hydrodeoxygenation is taken, there will be a cracking process which terminate the carboxylate group and decrease the viscosity.

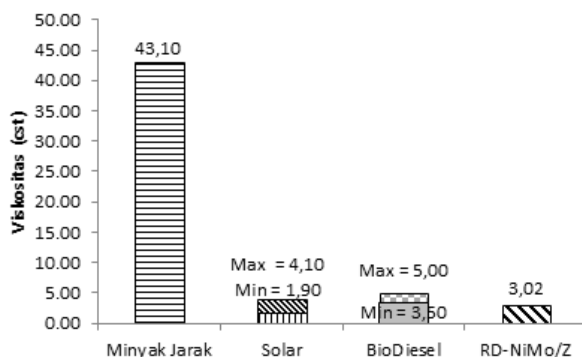


Figure 7. Product Viscosity Result and the comparison to Jathropa Oil and Commercial Diesel

In general, diesel fuel must have a low viscosity to make sure diesel can flow when the starting the engine cold take place. But sometimes too small viscosity is avoided, because the too small viscosity can cause power losses at high temperature in the engine.

3.4.2.3 Cetane Number

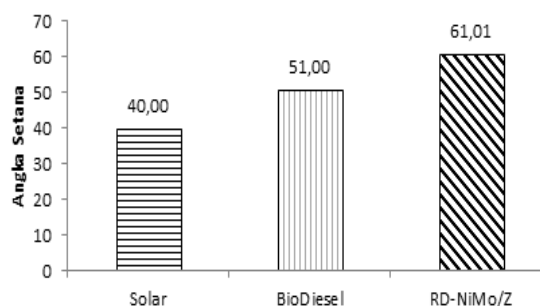


Figure 8. Cetane Number of Renewable Diesel Product and the Comparison with Bio Diesel and Commercial Diesel

Cetane index characterization results in Figure 8 shows that the cetane index of the renewable diesel products produced by HDO reaction using catalysts NiMo/Z-1 has meet the minimum value of cetane index allowed by ASTM-D975. Cetane index RD-NiMo/Z-1 products has 61.01 value better than cetane index of commercial diesel and biodiesel. It proves that the NiMo/Z-1 has a high activity and able to make decarboxylation reaction, decarbonilation, cracking and hydrodeoxygenation become more effective, so as a result, renewable diesel has better specifications than commercial diesel

3.4.3 IR Spectra

In figure 9 it can be seen that the jathropa oil, commercial solar and renewable diesel products resulted by catalyst NiMo/Z-1 has an absorption at a wavelength of 2940 cm^{-1} which indicates the presence of C-H bonds and C-C. In addition to straight chain, all three of these compounds have the same absorption at wave number $1650\text{-}1450\text{ cm}^{-1}$. This compound is caused by stretching vibration of C-C which indicates the presence of aromatic rings. Moreover from that figure, it can be seen that the C=O carbonyl group who have an absorption at $1700\text{-}1750$ has decreased sharply compared with jathropa oil which indicate the content of carbonyl compounds decreased. In the jathropa oil IR spectra, it is found a C-O group at wave number 1150 cm^{-1} and C=O group at wave number 1710 cm^{-1} . It is confirmed that the composition of jathropa oil is in esters form. While the diesel IR spectra from RD-NiMo/Z-1, was not found any compounds of C-O which indicates the reaction products and diesel fuel doesn't have ester group. Ester group has successfully cracked either through carboxylation reactions and carbonylation.

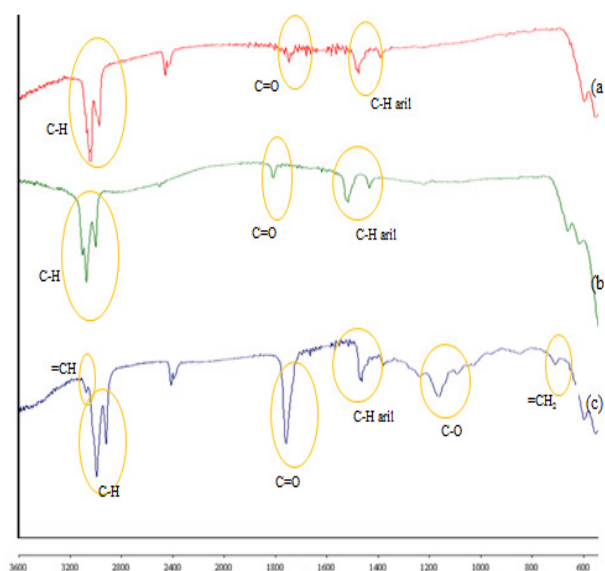


Figure 9. FTIR Result for Sample (a) Rd-NiMo/Z-1, (b) Commercial Diesel, (c) Jathropa Oil

4. Conclusion

The conclusion that can be drawn from this study are:

1. The best catalyst prepared by using microwave polyol process method is NiMo/Z-1 catalyst that prepared using treatment 1, with the addition of KBr compounds and alkali atmosphere (pH=8,3)
2. Catalyst NiMo/Z-1 resulting from treatment 1 has high crystallization with 62,98 nm crystal size, and has surface area, pore size and pore volume 5,45 m²/g, 301 Å and 0,041 cc/g respectively.
3. Activity catalyst test by using hidrodeoxygenation reaction showed that the catalyst NiMo/Z-1 from treatment 1 at condition 375^oC and 12 bar is able to produce renewable diesel product with conversion 88,615%, fraction selectivity renewable diesel and yield fractions 35,260 and 21,515% (wt) respectively.
4. Renewable diesel reaction results using catalytic NiMo/Z-1 has better specifications than commercial diesel with the density 0,833 g/cm³, viscosity 3,02 cst, cetane index 61,01.

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