Preparation of Ni/Zeolite as esterification catalyst in biodiesel production based on off-grade crude palm oil

Mazlan¹, W A Lestari², A Istiqomah³, D Krisdiyanto¹, E Pramono²*, A W Afrianto¹
¹Department of Chemistry, Faculty of Science and Technology of UIN Sunan Kalijaga Yogyakarta.
²Chemistry Department, Faculty of Mathematic and Natural Sciences, Sebelas Maret University Surakarta, Indonesia.

E-mail: edi.pramono.uns@staff.uns.ac.id

Abstract. This aim of this research is preparation to prepare catalyst of 0% Ni/Zeolite, 5% Ni/Zeolite, and 10% Ni/Zeolite. Catalyst of Ni/Zeolite was prepared by impregnation method. Biodiesel production was conducted by 2 steps, the first step was esterification using 3 types of catalyst 0% Ni/Zeolite, 5% Ni/Zeolite, and 10% Ni/Zeolite. The second step was transesterification using NaOH catalyst. The catalyst were characterized by FTIR to identify functional group and XRD to identify crystallinity. The acidity of catalyst was determined by ammonia adsorption. The catalyst can reduce FFA content in CPO that influence increasing of yield biodiesel production. The formation of biodiesel was confirmed by the GCMS analysis that identified the methyl ester produced. The highest yield of biodiesel production was obtained using 5% Ni/Zeolite catalyst. Based on physical analysis of biodiesel which includes density, acid number, and water content, biodiesel synthesized from palm oil off grade has qualified the Indonesian National Standard for biodiesel.

1. Introduction
Petroleum fuel based on fossil commodities sustain reduction up to 10% each year, and for the consumption of its fuel increased by 6% [1]. By thus main problem, the presence of petroleum fuel reach the limitation situation. Some researcher try to solve by find some overcome alternative fuels i.e. biodiesel. Biodiesel is an alternative fuel made from renewable natural resources from plants, animals or waste product with several treatments. Palm oil off-grade is one of the basic ingredients which can be used in producing biodiesel. Indonesia is the largest palm fruit producing country in the world [2], but there is some difference category for palm fruit commodities, there is some low-quality palm fruit or also called off grade palm fruit. Off grade Palm is a palm fruit that has a low quality and not fit for the manufacture of cooking oil industries. Off grade Palm oil occurs because of several things such as too fast in harvesting palm fruit, slow in the process of taking oil palm fruit or because it is too long in the mobility of sending fresh fruit to the company, so there are palm fruits that have been rotten before reaching the company. Besides off grade palm oil was also produced from the process of sorting fresh fruit carried out directly by the company and decreasing field data which from the sorting of companies about palm fruit there are 7-10% ware off grade palm fruit [3]. One type of heterogeneous catalyst is a bifunctional catalyst in the form of a catalyst with a metal system. The bifunctional catalyst is chosen because the single metal catalyst does not have high thermal stability and will form a solid metal that can reduce surface area, and facilitate the deactivation of the catalyst.
Therefore, metal catalysts need to be dispersed into bifunctional catalysts that are porous, heat-stable and chemical, large surface area, and mechanically strong [7]. Bifunctional catalysts consist of acid and metal sites. Acid site i.e. zeolites and bentonites, while metal sites in transition metals i.e. Nickel, Molybdenum, Cobalt, and can be a metal combination [8].

Zeolites can be modified by the activation process, both physical activation and chemical activation. The zeolite activation process using hydrochloric acid can remove impurities which cover the zeolite pores and can increase the ratio of Si to Al atoms [12]. Addition of Ni content to the zeolite catalyst can increase the acidity of natural zeolite [13, 14]. In addition, an increase of Ni metal content on Ni/Zeolite catalysts with nickel variations of 0, 5, and 10%, shows enhancement in the acidity value of Ni/Zeolite catalysts [15]. Zeolite as a carrier has a role to place the active catalyst metal. Metal is added into zeolite will cause a relatively large surface area, so the reaction will take place more quickly [9]. Metals can be dispersed evenly throughout the pore system to produce an active metal surface [10]. In this way, the catalyst produced is more efficient with several advantages such as large specific surface area, high thermal stability, longer service life, and results in more effective catalysts. There are two things that can cause nickel metal to be impregnated into zeolite. The first is the difference in chemical potential between nickel metal (Ni²⁺) and aluminium in zeolites which have an excess of 1 electron free pair because they receive 4 electrons in the zeolite framework [11].

2. Experimental

2.1. Materials
Materials in this research are purchased from Merck and Sigma Aldrich without purification and pretreatment that are chloride acid (HCl, Merck), ethanol (Sigma Aldrich), natrium hydroxide (Sigma Aldrich), methanol (Sigma Aldrich), nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, Sigma Aldrich), silver nitrate (AgNO₃, Sigma Aldrich) and aquadest. Natural zeolites obtained from Wonosari, Gunung Kidul.

2.2. Synthesis of Ni/Zeolite Catalyst
Synthesis of Ni/Zeolite Catalyst conducted by dilute of 50 g Natural Zeolite in 200 mL HCl 2M at 90 °C for 5 hours. The catalyst was dried at 120 °C for 2 hours, and the catalyst calcinated at 500 °C for 3 hours. Nickel was loaded into natural Zeolite by impregnation method with varying nickel concentrations (0%, 5%, and 10% (w/w)). The impregnation process was carried out at 80 °C and stirred for other 3 hours. The Ni/Zeolite catalyst was dried at 120°C for 2 hours. The catalysts calcinated at 500 °C for 5 hours. The catalysts was characterized by Fourier-transform infrared spectroscopy (FTIR) and X-ray powder diffraction (XRD). Acidity of catalyst was obtained by ammonia adsorption.

2.3. Catalytic Activity
Catalytic activity was obtained through esterification reaction of off-grade crude palm oil. Esterification reaction was obtained by added methanol into 20 g of off-grade crude palm oil with ratio oil : methanol (1:12). 2% (w/w) catalysts was added into solution and stirred at 50 °C for 2 hours. Quantitative and qualitative analysis of reaction product was obtained by FTIR and GC-MS.

3. Result and Discussion

3.1. Synthesis of Ni/Zeolite Catalyst
Dilution of natural zeolite with HCl 2M is purposed to separate impurities by the ion exchange method (Figure 1). In addition to dissolving impurities, the activation process with HCl solution aims to replace cations in zeolite interlayer spaces or in zeolite canals with hydrogens (H⁺). The cations can be dissolved by HCl activation such as Ca²⁺, Mg²⁺, Na⁺, Fe²⁺, and Fe³⁺ [16]. HCl activation will increase the surface area and the diameter of zeolite pores due to opened the tip of zeolite layer.
The crystallinity of natural zeolites is influenced by the ratio between Si/Al. If the Si/Al ratio is higher then its crystallinity will be higher [17]. One of the aims of HCl 2M activation is to reduce the Si/Al ratio in zeolite material. In the activation process, the H\(^+\) atoms will attack the oxygen atoms which are bound to Si and Al to produce a silanol group. Based on the value of bonding dissociation energy, the value of Al-O dissociation energy (116 kcal/mol) is smaller than Si-O (190 kcal/mol). When it is activated with 2M HCl, there will be a process of dealumination (Figure 2) on several Al atoms in the zeolite structure.

FTIR analysis is used to analyze functional groups of zeolite samples. Figure 3. shows the functional groups possessed by 4 zeolite samples namely natural zeolite, acid activated zeolite, 5% Ni/Zeolite, and 10% Ni/Zeolite. Based on FTIR data, there are 4 main peaks of zeolites that can identify the vibrations of the functional groups possessed by Zeolites. The peak absorbance at 482.48 cm\(^{-1}\) represents the Si-O-Al functional group and in the peak absorbance at 793.89 cm\(^{-1}\), a peak appears that identifies the bending vibration of Si-O. The peak absorbance at 1043.78 cm\(^{-1}\) represents asymmetry T-O (T= Al or Si), at this peak the wavenumber shifts to a larger one. This indicates that there has been a dealumination process or the process of releasing Al in the zeolite structure to become Al outside the structure. The dealumination process causes decreasing of aluminum in the zeolite structure, decreasing the amount of aluminum causes the distance between Al will be even greater. It causes the vibrations that arise will be greater. In the peak absorbance 1638.00 cm\(^{-1}\), a peak appears which identifies the bending vibrations of O-H from the H\(_2\)O molecule. The peak absorbance at 3428.47 cm\(^{-1}\), a peak appears which identifies the O-H stretching vibrations of the physically bound silanol and H\(_2\)O groups.
Figure 3. FTIR spectra of (a) natural zeolite, (b) 0% Ni/Zeolite, 5% Ni/Zeolite, (d) 10% Ni/Zeolite.

Vibration due to pore opened by a small cavity. It will give a higher absorption pattern than vibrations in a large cavity. All zeolite samples showed the emergence of a peak at wavenumber 385 cm$^{-1}$ that showed the open pore vibrations of natural zeolites. Whereas on 0% Ni/Zeolite, 5% Ni/Zeolite, and 10% Ni/Zeolite successively peaked at 348 cm$^{-1}$; 339 cm$^{-1}$; and 331 cm$^{-1}$. This diversity indicates that the 5% and 10% Ni/zeolite samples have a non-uniform open pore distribution from the natural zeolite and 0% Ni/zeolite. This indicates the presence of Nickel metal affects the open pore of zeolites.

Based on the XRD spectra (Figure 4) shows that the zeolite catalyst used contains mordenite minerals and several clinoptilolite minerals. The peaks show that the presence of mordenite minerals are in 2θ 13.6°; 19.56°; 25.78°; 26.69°; and 27.83°. The peaks showed the presence of clinoptilolite minerals were 9.86° and 22.39°. It has been reported in recent article [7, 17]. These peaks were compared with JCPDS-International Center for Diffraction Data (2001) for mordenite and clinoptilolite minerals.
Based on XRD analysis, spectra of 5% Ni/Zeolite and 10% Ni/Zeolite catalysts showed that it has similar spectra with 0% Ni/Zeolite spectra. The new peaks that appeared after addition of nickel, it showed the presence of nickel metal with 2θ 43.28° and 63.04°. It means that impregnation of nickel to natural zeolite is successfully obtained. It has been reported in some article and compared with JCPDS-International Center for Diffraction Data for nickel metal [16]. Data 2θ of catalysts can be see in Table 1.

**Table 1** The intensity of the 10 largest diffractogram peaks and the crystallinity of acid activated zeolite and balanced by the nickel metal.

| 2θ   | H/Zeolite | Ni/Zeolite (5%) | Ni/Zeolite (10%) |
|------|-----------|-----------------|------------------|
| 9.86 (KL) | 433       | 396             | 515              |
| 13.56 (M)  | 391       | 383             | 478              |
| 19.72 (M)  | 282       | 342             | 396              |
| 22.39 (KL) | 385       | 476             | 520              |
| 25.78 (M)  | 569       | 648             | 699              |
| 26.69 (M)  | 325       | 381             | 1615             |
| 27.83 (M)  | 426       | 555             | 829              |
| Total Intensity | 2811     | 3181            | 5052             |

The catalyst acidity is expressed in milimoles of acidic sites per gram unit of catalyst. The total amount of acid present in the catalyst are both on the external surface and the inner surface of the catalyst. The acidity is determined by the absorption of ammonia gas which is alkaline by zeolites which have an acidic site in its structure. The zeolite acidity can originate from the Lewis acid site, Al and also originate from the Browsted site, H⁺. The measurement of acidity from 4 samples aims to determine the effect of Ni metal on the acidity of the acid zeolite activated.
Figure 5. Solids acidity graph of natural zeolite catalyst

Figure 5 shows the solids acidity graph of natural zeolite, 0% Ni/Zeolite, 5% Ni/Zeolite, 10% Ni/Zeolite are 0.71 g/mmol; 1.21 g/mmol; 1.23 g/mmol; and 1.79 g/mmol. These results indicate the amount of solids acidity increases with activation process using HCl 2M and presence of nickel metal. Addition of HCl solution contributes to switch the active site in the zeolite structure become Bronsted acid sites.

3.2. Catalytic Activity

Characteristics of palm oil showed that the levels of free fatty acid was quite high at 6.2813%. This will affect the results of the reaction in the transesterification process. It will trigger the saponification reaction and complicate the separation process of biodiesel and glycerol due to there are layers that produced from saponification reaction. To overcome this problem, it is necessary to reduce free fatty acid (FFA) content in off-grade crude palm oil.

Based on the esterification production analysis, FFA content in products are 0.2510%; 0.9705%; 1.4557%; and 0.7278% for H₂SO₄, 0% Ni/Zeolite, 5% Ni/Zeolite, and 10% Ni/Zeolite, respectively (Figure 6). It has decreased FFA content in crude palm oil (CPO) with FFA content is 4.02%. Characteristic of CPO can be seen in table 2.

| Table 2. Characteristic of Off Grade Palm Oil |
|-----------------|-----------|----------|
| Characteristic   | Unit      | Value    |
| Color            | -         | Reddish yellow |
| Acid Number      | NaOH/g    | 6.2813   |
| Free Fatty Acid  | %         | 3.8400   |
| Levels           | %         | 0.0801   |
| Water Levels     | %         |          |
| Density          | kg/L      | 0.8678   |

The best catalyst for esterification reaction was 10% Ni/zeolite (10%) catalyst with % FFA is 0.7278%. H₂SO₄ catalyst is used as a comparison with prepared catalyst. FFA concentration of palm oil with zeolite catalyst are still lower than H₂SO₄ catalyst, but due to insignificant differences and the FFA concentration produced in the esterification reaction is lower than 2%. It can be conclude that Ni/Zeolite catalyst can be used as an alternate to replace H₂SO₄ catalyst in the esterification.
Esterification using zeolite have conducted through two steps. The first reaction with 0% Ni/Zeolite catalyst and the second reaction with 5% Ni/Zeolite and 10% Ni/Zeolite catalyst. Both reaction are reversible reaction. In this mechanism, the carbocation is formed first due to the binding (H+) of 0% Ni/Zeolite to the oxygen atom in the free fatty acid carbonyl group. 0% Ni/Zeolite has H+ levels greater than natural Zeolite, due to the activation process using HCl 2M. The binding of oxygen atoms by H+ is a nucleophilic substitution reaction that occurs due to the role of Bronsted acid on the 0% Ni/Zeolite.

Figure 6. Free fatty acid levels graph of esterified palm oil.

Figure 7. Esterification Mechanism with 0% Ni/Zeolite Catalyst.
Then the process of carbocation attack occurs which is unstable by the electron pair of oxygen atoms in methanol. The last step is the release of H$_2$O followed by the process of re-forming the catalyst 0% Ni/Zeolite and the formation of methyl esters as a product. The mechanism applies equally when using a 5% Ni/Zeolite catalyst and 10% Ni/Zeolite catalyst. The mechanism of reaction can be seen in Figure 7.

**Figure 8.** Yield of biodiesel product using variation catalysts.

Figure 8 shows the yield of biodiesel is influenced by the type of catalyst used in the esterification. The type of catalyst used in the esterification were the catalyst without the nickel metal in the form of 0% Ni/Zeolite and with a metal in such as 5% Ni/Zeolite and 10% Ni/Zeolite. Yield of biodiesel production can be seen in Table 3.

Biodiesel product is characterized by FTIR to determine the functional group. Figure 9 shows that the FT-IR analysis of palm oil biodiesel. The spectra show 8 major peaks that appear. The biodiesel reaction is successfully occur with confirmation of peak at wavelength 1743 cm$^{-1}$. It is vibration of C=O stretching and the existence of peak at wavelength 1168 cm$^{-1}$ that are vibration of C-O stretching. This is what indicates the existence of a methyl ester group. Biodiesel product peaks can be seen in Table 4.

**Table 3** The yield of off grade palm oil biodiesel with variations of catalysts type in the esterification reaction

| Sample | Catalyst Type | Yield (%) |
|--------|---------------|-----------|
| B01    | H/Zeolite     | 55.60     |
| B02    | 5% Ni/Zeolite | 70.23     |
| B03    | 10% Ni/Zeolite| 67.77     |
**Figure 9.** Infrared Spectrum of a. Off Grade Oil Palm b. Biodiesel.

**Table 4** Biodiesel functional group from off grade palm oil

| Wavenumber (cm⁻¹) | Functional group                                      |
|-------------------|------------------------------------------------------|
| 3464              | -OH stretching vibration (H₂O)                      |
| 3001              | C=C bending vibration (aliphatic)                    |
| 2919              | CH stretching vibration (aliphatic) CH₃, CH₂          |
| 2855              | CH stretching vibration (aliphatic)                  |
| 1743              | C=O stretching vibration (ester)                     |
| 1458              | C-H scissor vibration and bending vibration for methyl|
| 1168              | C-O stretching vibration (ester)                     |
| 725               | C-H vibration (aliphatic group)                      |

Qualitative and quantitative analysis is used in determining the amount and type of methyl esters contained in off-grade palm oil biodiesel. The peaks on the GC chromatogram shows the number of methyl esters contained in biodiesel. Each chromatogram peak separated with different retention times. This difference is influenced by the number of carbon chains in each type of methyl ester, where the methyl ester which has the shortest carbon chain will come out first.
Methyl palmitate comes first than methyl oleate and methyl stearate at the appearance. The esterification reaction is purposed to separate product and catalyst easily. Ni/Zeolite catalyst showed high conversion from CPO to Biodiesel product and it can reduce FFA content of CPO. It can be conclude that Ni/Zeolite catalyst can be used as an alternative catalyst to replace H₂SO₄ catalyst in the esterification step.

**Table 5. Retention time and area of the five chromatogram peaks of off grade palm oil biodiesel**

| Peaks | H/Zeolite catalyst | 5% Ni/Zeolite catalyst | 10% Ni/Zeolite catalyst |
|-------|---------------------|------------------------|------------------------|
|       | Retention time (Mins) | Total area (%) | Retention time (Mins) | Total area (%) | Retention time (Mins) | Total area (%) |
| 1     | 33.029              | 0.976                 | 33.616                 | 0.530                 | 33.028                 | 0.880                 |
| 2     | 37.896              | 37.568                | 38.086                 | 38.870                | 37.855                 | 37.172                |
| 3     | -                   | -                     | 41.417                 | 9.540                 | -                      | -                     |
| 4     | 41.608              | 54.458                | 41.616                 | 45.800                | 41.649                 | 54.789                |
| 5     | 41.999              | 4.707                 | 42.016                 | 5.270                 | 41.978                 | 5.008                 |
| Total | 97.707              | 100.000               | 97.849                 |                       |                        |                       |

The GC chromatogram showed the existence of five peaks were then analyzed using mass spectrophotometry (MS). Based on MS analysis, it is found that the five peaks that appear that have different areas, ranging from the highest to the lowest area respectively are methyl oleate (45.80%); methyl palmitate (38.87%); methyl linoleate (9.54%); methyl stearate (5.27%); and methyl myristate (0.53%) (Table 5). The appearance of methyl palmitate comes first than methyl oleate and methyl stearate because methyl palmitate has the shortest carbon chain than methyl oleate and methyl stearate. Methyl oleate and methyl stearate have carbon chains with the same length, but because methyl oleate has a lower molecular weight than methyl stearate, it will come out first and have a lower retention time than methyl stearate. The total area of the total methyl ester (biodiesel) chromatogram with 0% Ni/Zeolite, 5% Ni/Zeolite, and 10% Ni/Zeolite catalysts in the mixed esterification are 97.707%; 100%; and 97.849%. The greatest yield of methyl ester (biodiesel) is obtained using a 5% Ni/Zeolite catalyst that is equal to 100% which is strengthened through the yield of biodiesel obtained from off grade palm oil using a 5% Ni/Zeolite catalyst greater than the 0% Ni/Zeolite and 10% Ni/Zeolite catalysts.

Biodiesel obtained from off grade palm oil is analyzed to find out the characteristics of the biodiesel. The results of the analysis compared with the standards in SNI 04-7182-2006. Biodiesel analysis is performed on density of temperatures, acid numbers, and water levels (Table 6).

**Table 6. Comparison of Physical Characteristics of Biodiesel [4]**

| SNI Characteristic of Biodiesel | Standard Biodiesel | Palm Oil Biodiesel |
|----------------------------------|--------------------|--------------------|
| Density of temperature (kg/m³)   | 850-890            | 856                 |
| Acid number (mg-kOH/g)           | Max. 0.8           | 0.69               |
| Water levels (%-Vol)             | Max. 0.05          | Trace (0.05)        |

Acid number affects the combustion process, if the acid number gets higher, it can deposition the combustion system. The high of acid number for this fuel can be used as a solvent that can improve the quality of the fuel system [18]. Based on Table 6 shows the biodiesel acid number from palm oil grading 0.69 mg-kOH / g. Biodiesel water content based on SNI 04-7182-2006 is a maximum of 0.05%. This is because rising water levels can cause corrosion to the engine and the formation of paraffin crystals at cold temperatures which can clog the flow of fuel. Based on the research results, the water levels of off grade palm oil biodiesel is 0.05 and easily changes depending on the storage process. Table 6 shows that the density, amount of acid, and water levels of biodiesel made from grade palm oil is accordance with the Indonesian National Standard for biodiesel.

**4. Conclusion**

Biodiesel is the renewable fuel that can replace petroleum fuel. Biodiesel production is conducted through two steps are esterification and transesterification reaction. Esterification reaction is purposed to decrease FFA concentration to increase yield of biodiesel product. The benefit of using heterogeneous catalyst is to separate product and catalyst easily. Ni/Zeolite catalyst showed high conversion from CPO to Biodiesel product and it can reduce FFA content of CPO. It can be conclude that Ni/Zeolite catalyst can be used as an alternative catalyst to replace H₂SO₄ catalyst in the esterification step.
Acknowledgement
The authors wish to thank the chemical laboratory and the Faculty of Science and Technology, Sunan Kalijaga State Islamic University of Yogyakarta for supporting this research.

References
[1] Kuncahyo P, Fathallah A Z M, Semin 2013 Pom. Eng. J. 2 62-66
[2] Puji S 2015 Study of the Effect of Diethyl Ether Counseling on Biodiesel Synthesis with Heterogeneous CaO Catalysts from Palm Oil Mill Liquid Waste Oil (Yogyakarta: UIN Sunan Kalijaga)
[3] Aziz I, Nurhayati S, Rahman A 2012 Val. J. 2 511-515
[4] Hadi W A 2009 J. of Reg. Research 8 2
[5] Musta R 2010 J. of Flux Phys. 7 149-159
[6] Trisunaryanti W 2015 Catalyst Material and Character (Yogyakarta: Gadja Mada University Press)
[7] Trisunaryanti T, Triwahyuni E, Sudiono S 2005 Indo. J. Chem. 5 48-53
[8] Yoosespha W, Helwani Z, Saputra E 2016 J. of FTEKNIK 3 2
[9] Farida I 2018 Modification of Natural Zeolite with Zirconium Oxydechloride PSTA BATAN Products and its Catalytic Test for the synthesis of glycerol-derived compounds (Yogyakarta: UIN Sunan Kalijaga)
[10] Hartono R, Wijanarko A, Hermansyah H 2002 Conf. Ser: Mat. Sci. Eng. 345 1-4
[11] Istadi 2011 Catalyst Technology for Energy Conversion (Yogyakarta: Graha Science)
[12] Fatimah N F, Utami B 2017 J. C-T. 1 35-39
[13] Nurhayati N D, Wigiani A 2014 Synthesis of Ni-Cr/Zeolite Catalysts with Separate Impregnation Methods (Surakarta: National Seminar on Chemistry and Chemistry Education VI)
[14] Bijang M C, Aryanto Y, Trisunaryanti W 2002 J. of Tech. 15 57-69
[15] Ramdhani G D, Fatimah N F, Sarjono A W, Setyoko H, Nurhayati N D 2017 J. of Chem. and Chem Ed. 1 72-79
[16] Irvantino B 2013 Preparation of Natural Ni / Zeolite Catalysts With Senokimia Method For Catalytic Cracking Polypropylene and Polyethylene (Semarang: Semarang State University)
[17] Wijaya K, Hadi K, Herlina I, Kurnia T A 2016 Nano Material (Application in making biofuels) (Yogyakarta: UGM Press)
[18] Furqon M H, Prasetya A, Wilopo W 2013 J.of Sys Eng, 1 1