Bio-gasoline production of used cooking palm oil catalyzed by metal supported catalyst Ni/Natural Zeolite (Ni/NZ)

N D Mastutik, Heriyanti, L S Marningsih, and R Basuki*
Chemistry Department, Faculty of Science and Technology, University of Jambi

Abstract. This work aims to synthesized Ni/Natural zeolite (Ni/NZ) catalyst and produces bio-gasoline (main product) and gas (byproduct) from used cooking palm oil by catalytic cracking reaction. Ni/NZ catalyst was prepared by impregnating Ni with various concentrations (0.05; 0.1; and 0.2 M) onto natural zeolite. Ni/NZ catalyst was the characterized by XRD, XRF, and Gas Sorption Analyzer (GSA) to know the specific surface area, pore distribution, and total pore volume. Characterization of product and byproduct conducted by Gas Chromatography (GC), GC- Thermal Conductivity Detector (GC-TCD), and GC- Flame Ionization Detector (GC-FID). From analysis XRD and XRF, showed successfully impregnated Ni onto natural zeolite. The best catalyst was Ni-0.1M/NZ with specific surface area, pore distribution, and total pore volume was 200.327 m²/g, 2.1884 x 10⁻¹ Å, and 2.192 x 10⁻¹ cm³/g, respectively. The product (bio-gasoline) resulted from catalytic cracking reaction was comparable to standard gasoline which had the same retention time of chromatogram at 3.06 min with 95.14 % area. Byproduct of this reaction were 31.94% hydrogen, 13.31% oxygen, 53.94 % nitrogen, 0.18 % CO gas, 0.24 % methane, and 0.39% CO2 gas.

1. Introduction
Because of increased of crude oil price and environmental concern for biodegradable and renewable gasoline, production of gasoline through esterification of biological material (e.g. edible and inedible vegetable oils and animal fats) with alcohol has much attention in recent years as an alternative fuels [1]. Catalytic cracking is one of the methods to break long chain of hydrocarbon to simpler molecule [2]. Because of its advantages, heterogeneous catalyst was often used in this process. It is ease of recovery from the reaction mixture, less requirement of the neutralization agent, less corrosive, leading to safer and more environmentally friendly operation [3]. Optimum result can be achieved by suitability between catalyst and feed. One of the materials, for the heterogeneous catalyst, which have unique structure, is zeolite.

Zeolite is a form of a large family of aluminosilicates which have been studied by mineralogists for more than 200 years [4]. Zeolite is a natural mineral porous alumina silicate (~2 mm) that is composed of tetrahedral alumina (AlO₄⁻) and silica (SiO₄²⁻) which have active site and high thermal stability [5]. The negative charge generate by substitution of Si to Al in the zeolite framework neutralized by bounded weakly cations. There are two types of zeolites, natural zeolite and synthetic zeolite. Natural zeolites contains cations K⁺, Na⁺, Ca²⁺, or Mg²⁺ while synthetic zeolite contains only cations K⁺ or Na⁺. When the cations in the form of proton framework, the Bronsted acid site are form and it is potent to be modified into modified zeolite solid catalyst. Zeolite has a hollow structure that is...
usually filled with water and cations that can be exchanged. It also has specific pore size and nature physico-chemical properties which are very important for adsorbent [6] and catalyst applications [7].

There are many researcher develop zeolite as a support for heterogeneous catalyst by modifying their catalytic active sites which distribute uniformly on most of the solids, their empty spaces structure and canals that are easily reached by reactant molecules. Ni has been reported to enhance the surface acidity of zeolite due to the metal atom deposit on the exterior zeolite surface, each reduced metal atom have electron donor/acceptor properties and could introduced extra proton into the structure [8]. In this work, the preparation and characterization of solid heterogeneous catalyst Ni/NZ was studied. This catalyst was applied to cracking used cooking oil into bio-gasoline. Cooking oil which treated in this work is the most used cooking oil in Indonesia, palm cooking oil. Furthermore, the gas as byproduct was also critically discussed in this paper.

2. Experimental

2.1. Materials
All reagents were analytical grade and used without further purification i.e. NH₄Cl 99.8% (E. Merck), HF 49% (E. Merck), HCl 37% (E. Merck), Ni(NO₃)₂.6H₂O 99% (E. Merck), NH₃ 25% (E. Merck), AgNO₃ 99.8% (E. Merck), methanol (E. Merck), n-hexane (E. Merck), hydrogen, Oxygen, nitrogen gas, and deionized water. Natural zeolite (NZ) was taken from Gunung Kidul, Daerah Istimewa Yogyakarta. Used cooking palm oil was taken from cooking palm oil after minimum 3 times used to frying process.

2.2. Instrumentations
These work used Thermometer, 100 mesh sieve, mortar porcelain, oven, Furnace, calcination and oxidation reactor, desiccator, and other supporting glassware. Characterization of catalyst was performed by gas sorption analyzer (GSA, Quantachrome Nova 4200e), X-ray diffraction (XRD, PANalytical X’Pért™ POWDER), and X-ray fluorescence elemental composition (XRF, Rigaku nexe CG). Characterization of product and byproduct performed by Gas Chromatography (GC, Shimadzu 8A), GC- Thermal Conductivity Detector (GC-TCD, Shimadzu 8A TCD), and GC- Flame Ionization Detector (GC-FID, Shimadzu 8A FID).

2.3. Procedure

Activation natural zeolite
Firstly, Crude NZ was stirred in deionized water for 24 h at RTP. The supernatant was then filtered and dried at 120 °C for 12 h. Activation process performed by Fifty grams of NZ soaked, washed, and dried consecutively by HF 1% for 30 min at RTP, washed, dried at 120 °C for 24 h; then HCl 6 M for 30 min 50 °C, washed until Cl⁻ free, dried at 130 °C for 3 h; last NH₄Cl 1N at 90 °C 3 h a day for a week, dried and sieved 100 mesh size.

Synthesis of Ni/NZ catalyst
Activated NZ was soaked in Ni(NO₃)₂.6H₂O with various concentration, 0.05, 0.1, and 0.2 M to impregnate Ni on NZ. The Ni/NZ sample was then calcinated at 350 °C for 5 h, oxidized with O₂ flow and reduced by micro activity reactor (micromeritics) with H₂ flow at 220 °C for 4 h. Sample cooled at 60 °C for 20 min. Catalyst sample characterized by XRD to know its crystallinity, XRF for elemental composition, and GSA for specific surface area, pore distribution, and total pore volume.

Catalytic cracking reaction of used cooking palm oil
Used cooking palm oil filtered and heated in 3-neck flask at 70 °C and mixed with well-mixture of KOH (1% weight oil), oil and methanol (proportion oil : methanol = 1:9). The mixture stirred at 70 °C for an hour. Glycerol and methyl ester was then separated and analyzed by GC.
Catalytic cracking reaction was carried out in autoclave. The catalyst was reducing first before utilized by heated at 300 °C under H₂ flow for 2 h. An amount 1.5 g catalyst and 150 g oil introduced to
autoclave at 350 °C and 30 bars for 3 h. The product was analyzed by GC-FID and the byproduct (gas) was analyzed by GC-FID.

3. Result and Discussion

3.1. Characterization of Ni/NZ Catalyst

Crude NZ have to be activated because it is still have much metallic ion that will interfere impregnation Ni onto NZ. HF 1% and HCl 6M is added in order to remove Si which outer in framework of zeolite and remove Fe$^{3+}$ and Al$^{3+}$ that will interfere impregnation of Ni onto zeolite. Additionally, it is also increasing Si/Al ratio in framework, acidity, thermal stability, and selectivity of zeolite [9]. NH$_4$Cl is added in order to replace cations in zeolite such as Na$^+$ and Ca$^{2+}$ with NH$_4$$. This step will generate NH$_4$-Zeolite that NH$_4$$^+$ can be remove easily by heated over 33 °C into NH$_3$ to form H-zeolite (H-NZ). Proton, H$^+$ as a Bronsted site will increase the acidity of catalyst and make impregnated Ni distributed uniformly. Concentration of Ni impregnated onto NZ has been varied to optimize amount Ni which the best catalyst to cracking oils. Physical appearance of catalyst can be seen in Figure 1.

![Physical appearance of catalyst](image)

**Figure 1.** Physical appearance of (a) Crude NZ, (b) H-NZ, (c) Ni 0.05M/NZ, (d) Ni 0.1M/NZ, and (e) Ni 0.2M/NZ

Gas sorption analyzer was conducted to determine the specific surface area, pore distribution, and total pore volume of a material. The specific surface area, pore distribution, and total pore volume of Ni/NZ catalyst according to the BET and BJH method is presented in Table 1.

| Sampel         | Specific surface area (m$^2$/g) | Pore distribution (Å) | Total pore volume (cm$^3$/g) |
|----------------|---------------------------------|-----------------------|------------------------------|
| H-NZ           | 200.841                         | $2.2542 \times 10^{-1}$ | $2.264 \times 10^{-1}$      |
| Ni-0.05M/NZ    | 193.214                         | $2.1185 \times 10^{-1}$ | $2.047 \times 10^{-1}$      |
| Ni-0.1M/NZ     | 200.327                         | $2.1884 \times 10^{-1}$ | $2.192 \times 10^{-1}$      |
| Ni-0.2M/NZ     | 173.402                         | $2.3562 \times 10^{-1}$ | $2.043 \times 10^{-1}$      |

The specific surface area of H-NZ was 200.841 m$^2$/g. The addition of Ni metal decrease its surface area and total pore volume. It means that the impregnated Ni might be covering the pore of the zeolite support and reform active site located in these pore metal sites.

X-ray diffraction pattern commonly used to determine crystallinity, size, and the phase of the zeolite. This method can also detect the effect for the structure of a zeolite as a result of the
modification process such as impregnation or calcination. Characterization of the crystal structure of natural zeolite before and after impregnation with nickel metal using XRD instrumentation has shown in Figure 2. According to the diffraction of catalyst, mordenite phase ($2\theta = 9.84^\circ, 13.48^\circ, 22.34^\circ, 25.74^\circ, 26.66^\circ, 27.68^\circ$) and clinoptilolite phase ($2\theta = 11.2^\circ, 19.72^\circ, 22.42^\circ, 25.82^\circ, 27.92^\circ$) were detected in the structure of natural zeolite based on JCPDS data [10]. The highest peak of catalyst was $2\theta = 22.29^\circ, 25.69^\circ$, and $27.75^\circ$ indicated that the natural zeolite used in this study mainly composed as mordenite with some presence of clinoptilolite phase. There is no change in the value of $2\theta$ after NZ modification indicated that calcination and impregnation did not destroy the crystalline structure of the zeolite [11, 12].

Impregnation of catalyst with Ni metal should be increase the intensity of these peaks. However, it can be assumed that calcination process can remove some impurities in the framework of zeolite and improve the crystallinity of zeolite structure. Ni metal might be dispersing on the structure of Ni/NZ since Ni and NiO phase were not detected in the diffractogram. Ni and NiO should be emerged in $2\theta = 44.508^\circ$ and $43.244^\circ$ [13] but in diffractogram it is not clearly emerged. However, elemental analysis by XRF shows that Ni has high concentration on this catalyst. It can be predicted that Ni metal is not spread uniformly on the surface of zeolite. The amount of elements in Ni/NZ catalyst analyzed by XRF is shown in Table 2.

**Table 2.** The amount of elements in Ni/NZ catalyst analyzed by XRF

| Materials     | Mg (ppm) | Al (ppm) | Si (% mass) | K (ppm) | Na (ppm) | Co (ppm) | Ni (ppm) | Ca (ppm) | Fe (ppm) |
|---------------|----------|----------|-------------|---------|----------|----------|----------|----------|----------|
| Ni-0.05M/NZ   | 17500    | 94200    | 65          | 4590    | 205000   | 60.5     | 8130     | 7720     | 8680     |
| Ni-0.1M/NZ    | 16200    | 83800    | 86.4        | 5180    | 198000   | 72.3     | 7890     | 8740     | 9740     |
| Ni-0.2M/NZ    | 16800    | 90600    | 66.7        | 4780    | 195000   | 52.2     | 4920     | 7480     | 8670     |

**Figure 2.** X-ray diffraction pattern of the crystal structure of natural zeolite before and after impregnation with nickel with Cu-Kα radiation
3.2. Catalytic Cracking Reaction Product and Byproduct

Catalytic cracking reaction occurred in autoclave reactor at 350 °C, 70 bar for 2h. The final result of this reaction was the filtered and analyzed by GC-FID (Figure 3). When this product (bio-gasoline) was compared with commercial gasoline, they had similarity of the main components. The standard commercial gasoline had retention time 2-9 s with maximum area at 3.05 s (95.69%), another fraction (small fraction, 4.31%) spread less than 1% area at 2-9 s. There is similarity of retention time at 3.06 s of H-NZ (94.95%), Ni-0.05M/NZ (95.74%), Ni-0.1M/NZ (95.14%), and Ni-0.2M/NZ (94.99). Another fraction (another fraction, less than 3% area) of product of these catalysts spread at retention time 18-25 s. The byproduct of this reaction was gases, which analyzed by GC-TCD (Table 3). This reaction has potential to produce H₂ gas for fuel cell. The H₂ gas was increased in line with increase of concentration Ni on catalyst.

| Materials   | H₂ (%) | O₂ (%) | N₂ (%) | CO (%) | CH₄ (%) | CO₂ (%) |
|-------------|--------|--------|--------|--------|---------|---------|
| Ni-0.05M/NZ | 2      | 17     | 77     | 0.5    | 0.6     | 0.9     |
| Ni-0.1M/NZ  | 31     | 13     | 53     | 0.18   | 0.24    | 0.39    |
| Ni-0.2M/NZ  | 65     | 7.2    | 27     | -      | -       | -       |
Figure 3. Chromatogram by GC-TID of (a) standard commercial gasoline, (b) bio-gasoline catalyzed by H-NZ, (c) bio-gasoline catalyzed by Ni-0.05M/NZ, (d) bio-gasoline catalyzed by Ni-0.1M/NZ, and (e) bio-gasoline catalyzed by Ni-0.2M/NZ.

4. Conclusion
Impregnation Ni onto NZ did not damage the crystallinity of NZ, even though Ni has spread uniformly on surface of NZ. The Ni/NZ catalyst plays important role in catalytic cracking of used cooking palm oil. Impregnated Ni onto NZ increased the percentage of main component of gasoline. Byproduct of this reaction was H₂ (potential for fuel cell) which increase in line with increasing amount of Ni on NZ.

Acknowledgement
We thank to LPPM University of Jambi through DIPA fiscal year 2017 no. SPDIPA-042.01.2.400950/2017, research contract no. 283/UN21.7/PP/2017 for financial support of this work.

5. References
[1] Lin H C and Tan C S 2014 *Journal of the Taiwan Institute of Chemical Engineers* **45** 495
[2] Zhao X et al 2015 *New Biotechnology* **32** 300
[3] Diamantopoulos N et al 2015 *Journal of Thermodynamics & Catalysis* **6** 143
[4] Castaldi P et al 2008 *Journal of Hazardous Materials* **156** 428
[5] Smart L and Moore E 1993 *Solid State Chemistry 1st Edition* (London: Chapman and Hall University and Professional Division)
[6] Wibowo E et al 2017 *Procedia Engineering* **170** 8
[7] Ahmed T et al 2018 *Fuel* **211** 566
[8] Djaz B et al 1985 *Zeolite: synthesis, structure, technology and applications* (New York: Elsevier) pp 667-674
[9] Shirazi L et al 2008 *Crystal Research and Technology* **43** 1300
[10] Tursiloadi S et al 2015 *Procedia Chemistry* **16** 563
[11] Srebowata A et al 2014 *Catalysis Communications* **57** 107
[12] Reddy G R and Balasubramanian S 2016 *Microporous and Mesoporous Materials* **231** 207
[13] Li T at al 2016 *International Journal of Hydrogen Energy* **41** 21883