Synthesis H-Zeolite catalyst by impregnation KI/KIO₃ and performance test catalyst for biodiesel production

W. Widayat¹2*, Adit Rizky Wicaksono¹, Lukman Hakim Firdaus¹ and Ndaru Okvitarini¹
¹Department of Chemical Engineering, Faculty of Engineering, Diponegoro University, Jl Prof H. Soedharto SH Tembalang, Semarang 50239, Indonesia
²Material Technology Laboratory Center of Research and Service, Diponegoro University, Jl Prof H. Soedharto SH Tembalang, Semarang 50239, Indonesia
*E-mail: yayat_99@yahoo.com

Abstract. The objective of this research is to produce H-catalyst catalyst that was impregnated with KI/KIO₃. The catalyst was analyzed about surface area, X-Ray Diffraction (XRD) and performance test of catalyst for biodiesel production. An H-Zeolite catalyst was synthesized from natural zeolite with chemical treatment process, impregnation KI/KIO₃ and physical treatment. The results shows that the surface area of the catalyst by 27.236 m²/g at a concentration of 5% KI. XRD analysis shows peak 2-θ at 23.627° indicating that KI was impregnated on H-zeolite catalyst. The catalyst was tested in production of biodiesel using palm oil with conventional methods for 3 hour at temperature of 70-80 °C. The result for conversion Fatty Acid Methyl Ester (FAME) reached maximum value on 87.91% under production process using catalyst 5% KIO₃-H zeolite.

1. Introduction
Fatty Acid Methyl Ester (FAME) is an alternative energy used replacing diesel oil. Commonly, this compound calling as biodiesel. FAME can used as a mixture or pure. In application, biodiesel has composition 10-100% [1]. Some of the advantages of biodiesel is able to lower the greenhouse effect, biodegradable, non-toxic, and specifically reduce levels of CO 65%, CO₂ 78%, SO₂ 90% and unburned carbon 50% when compared to fossil fuels [2]. Biodiesel is a renewable fuel substitution are biodegradable, environmentally friendly, energy efficient, and can meet the needs of energy security without compromising operational engine performance [3].

Commonly, biodiesel produced by using homogeneous catalyst like as sulfuric acid, sodium hydroxide (NaOH) and potassium hydroxide (KOH). Biodiesel production process can be done by using a homogeneous acid catalyst process [4, 5], an acid and base catalyst process [6], supercritical process [7], enzymatic process [8], heterogeneous acid catalyst [9] and sonochemical [1,10]. The combination heterogeneous catalyst and enzymatic process was also done in biodiesel production. It was used Jatropha Curcas seed with lipase [11]. Biodiesel also can be produced by using in situ processing with acid /base catalyst [12, 13]. Biodiesel production is done with the mechanism of the chemical reaction of vegetable oils with methanol to produce Fatty Acid Methyl Ester (FAME) and glycerol as a byproduct [1, 14]. The most commonly used to produce biodiesel is by transesterification of triglycerides from oil-containing material and reacted using the alcohol with the addition of the catalyst. Here is a transesterification reaction mechanism.
The biodiesel production using homogeneous catalyst has disadvantages, such as formation of soaps, biodiesel separation from catalyst very complexly [15, 16]. To overcome the disadvantages, utilization a heterogeneous catalyst in biodiesel production was developed. Heterogeneous catalysts are very easily separated from biodiesel and can be re-used. In addition, biodiesel production by using heterogeneous catalysts did not found soap formation [17].

Heterogeneous catalyst that used in biodiesel production must has acid or base catalyst like as calcium oxide, magnesium oxide, aluminum oxide and zeolite. Some researchers studied biodiesel production by using heterogeneous catalyst. Boz et.al.(2009) used $\gamma$-alumina catalyst that added with potassium fluoride. The results obtained yield of biodiesel 97% [18]. Furuta et.al. (2004) [19] used W/Zr-$\gamma$-Al$_2$O$_3$ and Yan et.al.(2009) [20] used lanthanum impregnated in calcium oxide, CaO. Commonly, the catalyst is manufacturing in industry and expensive. To achieve maximum yield yet, the development of catalyst technology are still required. Indonesia has potential material for developing an catalyst. This material is natural zeolite that is naturally deposited in large enough amount [21]. Natural zeolite itself has a content of Si and Al. Si and Al components can act as a catalyst.

Natural zeolite from Indonesia has silica content at minimum 60%. Commonly, it use as an adsorbent in drinking water and wastewater treatment and fertilizer [21]. Zeolite pore surface varies in structure and electric field, it is that causes the zeolite catalyst has different properties [22]. Zeolites have been tested as catalysts for the conversion of oil-rich Free Fatty Acid (FFA) to be converted into (FAME). Marchetti and Erazzu (2008) [23] developed natural zeolites in esterification to minimize the presence of water. Water content can affect in biodiesel production i.e. decreasing conversion of esterification reaction. Therefore, preparation steps includes chemical and physical treatment are needed before using natural zeolite in catalyst application [21].

Chemical treatment is intended to control the activity and selectivity of the zeolite acidity. Comparison between the silica and alumina will leads to property of adsorption activity. Number of Brønsted acid sites of zeolite will grow with increasing aluminum content. Chemical treatment on the zeolite catalyst activation can be done either by acid treatment using HNO$_3$, HCl or H$_2$SO$_4$. Acid treatment is basically to increase the Si/Al ratio. The activity and selectivity of the catalyst is influenced by the characteristics of the catalyst where these characteristics depend on the method of preparation. One method that is often used in the preparation of the catalyst is impregnation method, because in terms of the manufacturing process, it is more practical than other methods of preparation (sol-gel and co-precipitation) [24].

Calcination is the process of heating an object until the temperature is high, but still below the melting point to eliminate compounds that can evaporate. Zeolite activation process through calcination will release water and increase crystallinity. Therefore, calcination of natural zeolite can improve the specific properties of zeolite.

The objective of this research is to study the preparation impregnated H-zeolite catalyst and the characterization and performance of catalysts in biodiesel production.

2. Research Methods

2.1. Materials
The material used here is a natural zeolite from district Wonosari Gunung Kidul. The material size were first reduced and followed by composition, water, and crystallography analysis. Solvent for chemical treatment used here is 4 M hydrogen chloride acid. AgNO$_3$ 0.1 M solution was used as an indicator for washing of catalyst product. Aquadest was used for washing the synthesized material during catalyst preparation. KI and KIO$_3$ used are in analytical grade from MERCK that used as impregnation compounds. Palm oil used as raw material in performance testing of catalyst. Contained
free fatty acid < 0.03%. This schematic view of installed equipment is presented in Figure 1. This equipment also used in biodiesel production. Oven and muffle furnace were used in physical treatment.

2.2. Preparation of H-zeolite Catalyst
The method in preparation of H-zeolite was referred to methods published in our previous papers [21, 25]. The method applied are chemical and physical treatment. Chemical processing was used dealumination process. The dealumination process of acid treatment was carried out with a natural zeolite using 20 ml of hydrogen chloride solution 4 M. The dealumination process was done by reflux at temperature (90 °C). After that, solid was filtered and washed with distilled water repeatedly until chloride was totally removed. The samples were then calcined in inert condition on isothermal temperature at 600 °C until four hours.

2.3. Impregnation of KI and KIO₃
The impregnation method was done by attaching the active compound component on a porous support material. In this research KI and KIO₃ were used as active compounds. The initial step impregnation process carried out by dissolving KI/KIO₃ in 50 mL of distilled water at a concentration of 1-5%. Furthermore, H-zeolite was mixed with a solution of 50 grams of KI/KIO₃ on three neck flask for stirred and heated for 2 hours at 90 °C. The mixture is filtered with suction strainer for further dried sludge screening results. Finally, KI/KIO₃-H-zeolite was obtained after catalyst product was dried in oven at temperature 110 °C.

2.4. Catalyst Characterization
The crystallography of KI/KIO₃-H-zeolite catalyst product were analyzed using XRD photographs a Philips 57.3 mm diameter, camera, with Cu Kα radiation. The analysis process was conducted at Research Center Institute Technology Sepuluh Nopember Surabaya. The surface area analysis was performed by the Brunauer Emmett Teller (BET) analysis using Quantachrome NOVA 1000 High-Speed Gas Sorption Analyser with Po = 711.65 mmHg and nitrogen as carrier gas. The analysis was conducted at Instrumentation Laboratory Department of Chemical Engineering, Institute Technology Sepuluh Nopember Surabaya.

2.5. Catalytic Activity Test.
KI/KIO₃-H-zeolite catalyst was tested for biodiesel production. Biodiesel production process used transesterification reaction by conventional methods. The palm oil must be checked free fatty acid contents < 0.5% [15, 16]. The initial step for the production of biodiesel, all material such as cooking oil, methanol and catalyst are mixed in a three-neck flask. Mole ratio between oil with methanol is 1:6. The mixture was stirred and heated at temperature of 70-80 °C for 3 hours. The product of the transesterification reaction was separated using a decanter to separate biodiesel and glycerol.

Biodiesel product was analyzed by using Gas Chromatography (GC). The analysis process was conducted at Chemical Analysis Laboratory Polytechnic Malang using HP 5890, with OV-07 column and FID (Flame Ionization Detector). The operation used nitrogen as gas carrier with flow rate 28 ml/minute, temperature 125-275 °C and detector temperature 275 °C. The initial temperature was kept constantly for 3 minute, then increased at a rate of 15°/minute until final temperature reached to 275 °C. The compounds will be analyzed free fatty acid ester with internal standard methods [1, 13]. The data was used for calculation biodiesel conversion with this equation (1)

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X = \frac{\text{Triglyceride reacted}}{\text{Triglyceride initial}} \times 100\%
\]

3. Results and Discussion

3.1. Characterization Catalyst

The results of BET analysis using H-zeolite catalyst with KI concentration of 5 wt% presented in Figure 2. Figure 2 shows the relationship relative pressure with volume at standard conditions (STP). Volume of nitrogen gas adsorbed by H-zeolite catalyst was measured as 28.013 cc. From figure 2, the specific surface area of KI/ H-zeolite catalyst was obtained 27.236 m²/g. Total surface area is more smaller than H-zeolite that produced Widayat et.al, 2010 [26]. The data is then compared in several studies conducted by using other types of catalyst as shown in Table 1.

![Figure 2. Volume gas versus relative pressure (P/Po).](image)

In the previous studies, natural zeolite catalyst has a surface area of 172.92 m²/gram [25]. H-zeolite that syntheses from natural zeolite from Gunung Kidul district obtained surface area of 199.76 m²/gram. KI compound that impregnated in H-zeolite caused the increasing the basicity of H-zeolite catalyst and affected to the activity and active surface area of the catalyst [9]. In this research, KI compound caused decreasing on specific surface area of H-zeolite because after impregnation process H-zeolite was dried at temperature 115 °C without further calcination. Commonly, natural zeolite has
a surface area of about 20 m²/gram. The dealumination and calcination processing affected to change the surface area and pore volume. Dealumination process caused an increasing in ratio of Si/Al and dissolution of CaO impurity. The increasing ratio SiO₂ to Al₂O₃ leads to change the framework of the zeolite as a result of dissolution in acid solution or reaction and calcination process. The changes in the zeolite framework will lead to change the pores of the zeolite resulting the changes on its surface area and pore volume. Acid treatment will increase the surface area [21, 25].

| Catalyst                  | Surface Area (m²/g) | Reference |
|---------------------------|---------------------|-----------|
| Natural zeolite           | 172.929             | [25]      |
| Sodium Silicate (Na₂O.nSiO₂) | 5.91               | [26]      |
| Calcium Aluminate         | 21.29               | [27]      |
| Ca/Al/Fe₂O₃               | 25.89               | [28]      |
| KI-H-zeolite              | 27.236              | This research |
| H-zeolite                 | 199.760             | This research |

H-zeolite and KI-H-zeolite catalyst also was analyzed by using XRD. The diffractogram was presented in Figure 3. This figure shows H-zeolite and KI-H zeolite catalyst has the same XRD patterns. Impregnation process affected in some 2θ, indicating that KI compound impregnated in H-zeolite. After impregnation process, KI-H-zeolite was dried in oven and was not followed by calcination. The influence of impregnation of KI in the process of a solid catalyst detected on 2θ with a peak value of 22-24 [29].

The others research conducted by Xie and Li (2006) [9] about heterogeneous catalyst impregnated by KI for biodiesel production from soybean oil reported that KI compounds was shown in 2θ between 22-24. Peak at 2θ 23.62 of KI-H-zeolite has higher intensity than H-zeolite. KI-H-zeolite has dominant peak and the highest intensity at 2θ is 25.62. This 2θ is a SiO₂ compound as the main component of natural zeolite from Gunung Kidul. Therefore, in peak at 23.62 referred to KI that impregnated in H-zeolite catalyst.

3.2. Qualitative Analysis
The results of biodiesel products presented in Figure 4. Figure 4(a) is a chromatograph biodiesel standard on retention time at 7.76 to 15.73. Figure 4(b) is a chromatograph for biodiesel that produced by using conventional method for 2 hours at temperature 50 °C. In this research, FAME had a retention time of 7.90 to 12. Intensity in Figure 4(b) is less intense than intensity of figure 4(a). When compared to standard in Widayat et.al., (2013b), the expected results of biodiesel analysis with GC: 8.77 minutes was methyl stearic (C\textsubscript{18:0}); 9.23 minutes was methyl oleic (C\textsubscript{18:1}); 10,28 minutes was methyl linoleic (C\textsubscript{18:2}); and 11.99 minutes was methyl arachidic (C\textsubscript{20:0}). Figure 4(b) has retention time for FAME in 7.90; 8.69; 10.12; 11.36 and 12.20. For the same retention time in Figure 4(b) with Widayat et al (2013b), shown the biodiesel product contain methyl stearate (RT 8.69), 10.12 minutes was methyl linolenic(C\textsubscript{18:3}), 11.36 minutes was methyl nonadecanoic (C\textsubscript{19:0}) and 12.20 minutes was methyl eicosanoic (C\textsubscript{20:1}). Although the entire peak was not obvious, but this shows that the FAME was indeed formed in biodiesel sample and triglyceride was not detected again.

3.3. Catalytic Testing for Biodiesel Production

The results of catalyst testing for biodiesel production was presented in figure 5. Figure 5 shown a comparison of catalyst testing for biodiesel production with potassium hydroxide (KOH), natural zeolite, KI-H-zeolite and KIO\textsubscript{3}-H-zeolite. Biodiesel production with KOH catalyst obtained conversion of 84.16% and H-
zeolite as catalyst obtained 56.08%. Biodiesel production with KIO₃ –H zeolite as catalyst obtain the higher 87.91% at catalyst concentration 5%. The results of biodiesel production with KOH catalyst is greater than H-zeolite catalyst with impregnation KI and KIO₃. However, in the case of catalyst separation is easier to use heterogeneous catalyst such H-zeolite. H-zeolite catalysts without impregnation has lower biodiesel conversion than the KI-H-zeolite and KIO₃–H-zeolite. This is because the K⁺ ion in KI fill vacant sites in the zeolite pores and further can accelerate dispersion and decomposition of KI from the basic sites on the activation process [9].

![Figure 5. Effect of catalyst concentration on biodiesel conversion.](image)

| Parameter   | Product | Overall | SNI 04-7182-2006 |
|-------------|---------|---------|------------------|
| Density     | KI 0.878| KIO₃ 0.879| 0.866 – 0.9 g/ml |
|             |         |         | 0.85 – 0.89 g/ml |
| Viscosity   | 2.79    | 2.72    | 2.32 – 10.92 Cst |
|             |         |         | 2.3 – 6 Cst      |
| Acid Number | 0.25    | 0.36    | 0.19 – 0.42mg-KOH/gr |
|             |         |         | Max 0.8 mg-KOH/gr |

The biodiesel products have density between 0.866-0.9 g/ml. Density of biodiesel products parameter included in the standard density of biodiesel according to SNI04-7182-2006 ie0.85-0.89g/ml. The concentration of KI/KIO₃ in H-zeolite affected the activity in methyl ester reaction. So, KI/KIO₃ concentration affected in quality of biodiesel on parameter includes density, viscosity and acid number. These results are in good agreement with the results reported by Cao et al. (2008) [30].

The result of biodiesel viscosity is out of the range of biodiesel viscosity based on SNI 04-7182-2006. Biodiesel production using KI/KIO₃ and H-zeolite catalyst in small concentration caused lower methyl ester production. This caused viscosity biodiesel higher than biodiesel standard. The acid number of biodiesel is important parameter. Acid number can show possibility of oxidation process to form short-chain acids as a result of the decomposition of peroxide and hydroperoxide compounds. In real application, the accumulation of acid in biodiesel can cause a condition that can damage the engine. Overall, characters such as acid number, density and viscosity of the biodiesel produced using synthesized catalyst of KI/KIO₃-H-zeolite meet the requirements of parameter value of SNI 04-7182-2006.

4. Conclusions
KI/KIO₃-H-zeolite catalyst was synthesized by chemical, physical treatment and impregnation processing. KI–H-zeolite catalyst has surface area of 27.236 m²/gram. XRD analysis reveals the evidence of the successful KI impregnation in H-zeolite. The obtained parameters of the produced biodiesel meet the parameter of biodiesel standard SNI 04-7182-2006. The chromatograph shows Fatty Acid Methyl Ester (FAME) production in low concentration (below 10%). The biodiesel conversion obtained by KI/ KIO₃-H-zeolite as catalyst reached 87.91%.
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