Catalytic Cracking of Crude Biodiesel into Biohydrocarbon Using Natural Zeolite Impregnated Nickel Oxide Catalyst

Isalmi Aziz a,*, Edra Aditya Filipilia Ardine b, Nanda Saridewi b, Lisa Adhani c

a Department of Chemistry, Faculty of Sciences and Technology, Syarif Hidayatullah State Islamic University, South Tangerang, Indonesia
b Department of Chemistry Education, Faculty of Education and Teacher Training, Syarif Hidayatullah State Islamic University, South Tangerang, Indonesia
c Department of Chemical Engineering, Faculty of Engineering, Universitas Bhayangkara Jakarta Raya, South Jakarta, Indonesia

*Corresponding author: isalmikimia@uinjkt.ac.id

https://doi.org/10.14710/jksa.24.7.222-227

Abstract

Crude biodiesel is biodiesel that still contains impurities. A catalytic can improve the quality of biohydrocarbons (biogasoline, biokerosene, and green diesel). The catalyst used is nickel oxide impregnated natural zeolite (NiO/Zeolite). The use of nickel can increase the activity of the catalyst because it has an empty d orbital and a smaller molecular size. This study aims to determine the best catalyst that can exhibit the greatest selectivity toward biohydrocarbons. Natural zeolite was activated and impregnated by varying the concentration of NiO (1, 3, and 5% w/w). The characteristics of the catalyst were determined by the crystallinity (X-Ray Diffraction), surface area (Surface Area Analyzer), and functional group (Fourier Transform Infrared). The catalyst and crude biodiesel were put in an autoclave reactor and operated at a temperature of 375°C and 3 hours. The obtained product was tested with Gas Chromatography-Mass Spectroscopy. The results of the XRD analysis showed the presence of NiO at 2θ 37.23; 43.15; and 62.65°. Nickel oxide on the catalyst was detected at a wavenumber of 671 cm⁻¹. The highest surface area was obtained at a NiO/Zeolite 1% of 49.4 m²/g. 1% NiO/Zeolite catalysts gave the best results on catalytic cracking of crude biodiesel with a reaction conversion of 60.79% and selectivity of 9.73%; 29.64% and 9.18% for biogasoline, biokerosene, and green diesel, respectively.

1. Introduction

Crude biodiesel is produced from the oil transesterification with alcohol which is not being purified. The component of the crude biodiesel can contain byproducts, the excess of the reactant, and the catalyst [1]. The conversion of the crude biodiesel generated biohydrocarbon. Biohydrocarbon is one of the biofuels which contains only hydrogen and carbon. Biohydrocarbon consists of biogasoline, biokerosene, and green diesel. The conversion of crude biodiesel into biohydrocarbon can be conducted by utilizing catalytic cracking. Catalytic cracking is more effective than other processes such as thermal cracking and hydrocracking because the catalytic cracking can be conducted at a lower temperature and exhibits a cleaner process to generate the product [2].

The catalytic cracking will need a catalyst. Many catalysts have been used for catalytic cracking; one of them is zeolite [3]. Zeolite is a porous material that has a large surface area [4]. This property will help in catalytic cracking because more frequent contact will likely undergo between reactant and catalyst. Zeolite also has high stability, is inexpensive and abundant, noncorrosive, nonhazardous, and is environmentally friendly. Both natural and synthetic zeolite exhibited Bronsted and Lewis acidity, which is essential for the cracking process. Natural zeolite produces lower costs since the price is lower. Firdaus and Prameswari [5] reported the usage of natural zeolite as the catalyst in 2,2,4-Trimethyl-2,3-dihydro-1H-1,5-benzoazepine. Glycerol esterification also can undergo with the support of natural zeolite as the catalyst [6]. The catalyst can be
impregnated by using transition metals such as Co, Mo, Ni, Cu, Zn, Fe, and Cr [7, 8, 9, 10] to increase the catalytic activity. Aziz et al. [1] upgraded the crude biodiesel by using H–Zeolite and generated 6.26% and 17.6% of gasoline and kerosene, respectively. Juwono et al. [11] achieved 91.93% of hydrocarbons ranging from C7 to C20 by using Pd/Al–MCM–41 as the catalyst for hydrocracking of the fatty acid methyl ester (biodiesel). Norvia et al. [12] used natural zeolite as the catalyst for biodiesel synthesis from waste cooking oil which generated 63.21% methyl ester.

Besides natural zeolite, several other catalysts have been used in the cracking process. Gamma alumina impregnated with NiMo metal was used for hydrocracking of nyamplung oil, resulting in a conversion of 80.82% and a Gasoil selectivity of 81.84% [13]. Activated carbon impregnated with CoMo was used in the catalytic cracking of palm fatty acid distillate to produce a hydrocarbon yield (C1–C12) of 92% [14]. Istadi et al. [15] used HY–Zeolite for palm oil catalytic cracking, resulting in the conversion of 99.11% with a selectivity of gasoline 34.25%, kerosene 31.13%, and diesel 9.34%.

In this research, natural zeolite is impregnated with nickel oxide. Nickel has been chosen since it has the smallest size; hence, the distribution at the surface of the zeolite will be evenly distributed [16]. Nickel impregnation can increase the acidity of the catalyst [17]. Nickel oxide impregnated at natural zeolite has been conducted toward cashew nuts shell liquid hydrocracking. NiO concentration at 1% w/w has been used toward the weight of zeolite [18]. Therefore, this research will vary the NiO concentration at 1%, 3%, and 5% toward the total mass of the catalyst. Also, the activity of NiO/Zeolite has not been observed for crude biodiesel catalytic cracking. In this study, the concentration of NiO was determined to identify the maximum selectivity of the biohydrocarbon fraction (biogasoline, biokerosene, and green diesel).

2. Methodology

2.1. Materials

The experiments were carried out using Pyrex and autoclave with several materials such as Ni(NO3)2·6H2O (Merck, 99.99%), AgNO3 (Merck, 99.99%), NH4Cl (Merck, 99.99%), distilled water, 70% ethanol, natural zeolite (CV. Minatama Lampung) and crude biodiesel. Crude biodiesel was originated from the transesterification reaction of waste cooking oil, methanol, and KOH.

2.2. Synthesis and Characterization of NiO/Zeolite

Natural zeolite, purified using distilled water, was added to the reflux, and NH4Cl (1 M) was added. The reflux was conducted in 3 hours at 90 °C. After reflux, the zeolite was then filtered and washed until the neutral pH was reached. The calcination was then carried out at 450 °C for 3 hours [19]. After that, wet impregnation was conducted using Ni(NO3)2·6H2O. The concentration of impregnated NiO was varied from 1%, 3%, and 5% w/w to the total mass of the catalyst. The mixture was left for 6 hours then further dried in the oven. Impregnated zeolite was then calcined at 500 °C to obtain the NiO/Zeolite [17].

The surface area was determined by using Tristar II Micromeritics Surface Area Analyzer (SAA). The catalysts were loaded into a tube and further degassed with the N2 at 200 KPa for 2 hours at 200 °C. The crystallinity was obtained using Rigaku MiniFlex 600 X–Ray Diffraction (XRD) at 40 kV, 25 mA at 5–90°. The functional groups of the catalyst were analyzed by using the Shimadzu Fourier Transform Infrared (FTIR) spectrometer. The sample was finely grounded with the KBr with the ratio of 1:10 and determined with the wavenumber ranging from 400–4000 cm⁻¹.

2.3. Catalytic Cracking of Crude Biodiesel

Two grams of KOH were dissolved in 50 mL of methanol. Then put in a three-neck flask and add 200 mL of used cooking oil. The mixture was heated to a temperature of 60°C and reacted for 1 hour. The product was put in a separating funnel to form two layers. Crude biodiesel was on the top layer, and crude glycerol was on the bottom layer. 10 gram of crude biodiesel and 0.5 gram of NiO/Zeolite was placed in the reactor. The reactor heater was turned on until 375°C was reached with a stirring rate of 500 rpm. The reaction was carried out for 3 hours [1]. The product obtained from the reaction was removed from the reactor, and the composition was determined using Gas Chromatography–Mass Spectroscopy (GCMS). The sample was injected through the column (DB5–MS UI stationary phase with the specification of 30 m, 0.25 mm, and 0.25 µm with He mobile phase). From the area obtained in the chromatogram, the conversion and the selectivity of the product for each catalyst used in catalytic cracking was calculated using equation (1) and (2) [20].

\[
\text{% Conversion} = \left(\frac{\text{Final Area} - \text{Initial Area}}{\text{Initial Area}}\right) \times 100\% \tag{1}
\]

\[
\text{% Selectivity} = \left(\frac{\text{Product area}}{\text{Total product area}}\right) \times 100\% \tag{2}
\]

3. Results and Discussion

3.1. Catalyst Characterizations

![Figure 1. Diffraction patterns of H–Zeolite and NiO/Zeolite](image)

The diffraction pattern of the activated natural zeolite (H–Zeolite) can be seen in Figure 1. The type of
zeolite used was clinoptilolite that can be observed from the diffraction pattern obtained at 2θ of 9.84, 22.38, 22.72, and 29.94° (JCPDS No. 71-1425) with Miller indices (020), (131), (421), and (331), respectively. This type's natural zeolite diffraction pattern can be found at 2θ of 9.87, 11.18, 21 and 22.25 [22]. From Figure 1, the nickel oxide impregnation did not change the diffraction pattern of the zeolite. The zeolite crystal structure is still able to be sustained. The presence of the nickel oxide at the catalyst can be identified at 2θ of 37.2°, 43.27°, and 62.87° (JCPDS No. 47-1049) with hkl: (111), (200) and (220), respectively. The concentration variation of impregnated nickel led to the different intensities, as can be seen in Table 1. A larger concentration of NiO will lead to higher intensity and higher crystallinity. These will affect the higher catalytic activity.

<p>| Table 1. Peak intensity of NiO at NiO/Zeolite |</p>
<table>
<thead>
<tr>
<th>NiO/Zeolite (1%)</th>
<th>NiO/Zeolite (3%)</th>
<th>NiO/Zeolite (5%)</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>2θ Intensity</td>
<td>2θ Intensity</td>
<td>2θ Intensity</td>
<td></td>
</tr>
<tr>
<td>37.00</td>
<td>59.7</td>
<td>37.32</td>
<td>72.6</td>
</tr>
<tr>
<td>43.29</td>
<td>76.9</td>
<td>43.12</td>
<td>93.4</td>
</tr>
<tr>
<td>62.38</td>
<td>39.4</td>
<td>63.05</td>
<td>47.9</td>
</tr>
</tbody>
</table>

Figure 2. FTIR spectrum of H-Zeolite and NiO/Zeolite 1%, 3%, and 5%

FTIR spectrum from H-Zeolite and NiO/Zeolite can be seen in Figure 2. Catalysts obtained had a double ring at 600–550 cm⁻¹ wavenumbers, which indicated the special feature of the zeolite [23]. At wavenumbers of 900–1000 cm⁻¹, the Si-O asymmetric stretching is present. Bronsted acid sites are present at 1627–1629 cm⁻¹ wavenumbers to all the catalysts, but the presence of Lewis acid sites is only found for H–Zeolite at 1431.18 cm⁻¹. According to Hartanto et al. [24], Lewis acid sites and Bronsted acid sites are present at 1442–1419 cm⁻¹ and 1650–1620 cm⁻¹, respectively. Kadarwati et al. [25] also obtained the Bronsted acid sites and Lewis’s acid sites at 1650–1620 cm⁻¹ and 1401.25 cm⁻¹, respectively, for the natural zeolite used for the bio-oil pyrolysis. Nickel oxide catalyst is found at 671.23 cm⁻¹ wavenumbers, whereas the peak for the H–Zeolite is not present. Rahmani et al. [4] mentioned that the metal impregnation toward zeolite results in a shift of the absorption band, which is not too big.

Table 2 shows the surface area of the H–Zeolite and NiO/Zeolite. NiO/Zeolite 1% exhibited a high surface area which is 49.410 m² g⁻¹. Higher surface area can increase the catalytic activity because it elevates the contact frequent between the reactant and the catalyst. Increment of NiO concentration exhibited lower surface area, which occurred due to the agglomeration and pore filled by NiO at the catalyst’s surface [26]. Ni impregnation at the HZSM-5 also decreases the catalyst’s surface from 424.6482 to 287.3484 m² g⁻¹ [27].

<table>
<thead>
<tr>
<th>Table 2. The surface area of catalysts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
</tr>
<tr>
<td>-------------------------</td>
</tr>
<tr>
<td>H–Zeolite</td>
</tr>
<tr>
<td>NiO/Zeolite 1%</td>
</tr>
<tr>
<td>NiO/Zeolite 3%</td>
</tr>
<tr>
<td>NiO/Zeolite 5%</td>
</tr>
</tbody>
</table>

3.2. Catalytic Cracking of Crude Biodiesel

Before the catalytic cracking was conducted, the crude biodiesel was analyzed by using GCMS. The chromatogram of the crude biodiesel component can be observed in Figure 3. Methyl linoleate and methyl oleate were the major components in crude biodiesel with the amount of 37.55% and 27.51%, respectively. Aziz et al. [1] also obtained methyl linoleate as the major component of the crude biodiesel with an amount of 39.05%.

Figure 3. GCMS chromatogram of crude biodiesel

Chromatogram of the catalytic cracking product from crude biodiesel using H–Zeolite and NiO/Zeolite as the catalyst can be seen in Figure 4, 5, 6, and 7. Biohydrocarbon generated were classified based on the length of the carbon ranging from C₁₂–C₁₆ (biogasoline), C₁₃–C₁₅ (biokerosene), and C₁₆–C₂₀ (green diesel). There was still an excess of methyl ester, which was not converted, and fatty acid remained. Based on the product constituent obtained from the GCMS, the reaction’s conversion and selectivity can be determined, as seen in Table 3.
Figure 4. Chromatogram of the product of catalytic cracking using H–Zeolite

Figure 5. Chromatogram of the product of catalytic cracking using NiO/Zeolite 1%

Figure 6. Chromatogram of the product of catalytic cracking using NiO/Zeolite 3%

Figure 7. Chromatogram of the product of catalytic cracking using NiO/Zeolite 5%

Table 3. Conversion and selectivity catalytic cracking of crude biodiesel

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity of biohydrocarbon (%)</th>
<th>Total selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Biogasoline</td>
<td>Biokerosene</td>
</tr>
<tr>
<td>H–Zeolite</td>
<td>62.76</td>
<td>6.1</td>
<td>14.81</td>
</tr>
<tr>
<td>NiO/Zeolite 1%</td>
<td>66.79</td>
<td>9.73</td>
<td>29.64</td>
</tr>
<tr>
<td>NiO/Zeolite 3%</td>
<td>46.19</td>
<td>5.19</td>
<td>15.55</td>
</tr>
<tr>
<td>NiO/Zeolite 5%</td>
<td>51.74</td>
<td>6.18</td>
<td>13.5</td>
</tr>
</tbody>
</table>

The highest conversion was obtained by using H–Zeolite with 62.76% conversion. High surface area from the H–Zeolite led to higher conversion. Besides that, H–Zeolite provided Lewis’s acid sites needed for the cracking catalysts, whereas the other catalyst did not provide these catalytic sites. The catalytic sites accelerated the chain cracking of the crude biodiesel, which transformed into biohydrocarbon. Although the conversion achieved by H–Zeolite was higher, the biohydrocarbon selectivity generated from the H–Zeolite was small. The total biohydrocarbon selectivity obtained was 25.18%, consisting of 6.10%, 14.81%, and 4.27% of biogasoline, biokerosene, and green diesel, respectively. Other than biohydrocarbon, H–Zeolite generated higher fatty acids.

The usage of NiO as the active component increased the catalytic activity, as shown in NiO/Zeolite 1%. Ni metal enhanced the catalytic sites, increasing the acidity that acted in the carbon chain cracking [17]. Also, Ni was distributed at supporting pores and formed the external pores, which gave acid sites for the catalyst’s surface [28]. NiO/Zeolite 1% generated higher total selectivity and conversion of biohydrocarbon than 3% and 5% concentration. The biohydrocarbon total selectivities of 48.55% were obtained through the NiO/Zeolite 1%, consisting of 9.73%, 29.64, and 9.18% biogasoline, biokerosene, and green diesel, respectively. 60.79% of conversion is obtained from the catalysis. The selectivity occurred due to the high surface area exhibited by the catalyst; thus, maximum selectivity was obtained. Moreover, the NiO/Zeolite 1% exhibited a higher surface area than the support (H–Zeolite).

Other than the highest biohydrocarbon total selectivity, the NiO/Zeolite 1% also generated the highest selectivity of biogasoline, biokerosene, and green diesel. This showed that the catalyst was able to break down the crude biodiesel into lighter fractions. The NiO/Zeolite with 3% and 5% composition generated lower biofuel conversion and selectivity than the H–Zeolite. The lower surface area caused this; hence the contact between the reactant and the catalyst was not maximum. NiO/Zeolite 5% generated 51.74% and 26.84% conversion and total selectivity of biohydrocarbon, respectively. This result is better than the NiO/Zeolite 3%, which only generate 46.19% and 23.44% of conversion and total selectivity of biohydrocarbon, respectively. Kadarwati and Wahyuni [29] reported that Ni/Zeolite 2% is the optimum concentration for palm oil hydrocracking with 80.23%, 1.42%, and 18.35% fraction yield C2–C5, C6–C9, and C10–Cn, respectively. Cashew nuts shell liquid hydrocracking
using NiO/Zeolite 1% generated 65.62% conversion with 17.16% gasoline, 12.04% diesel, and 36.44% heavy oil selectivity [18]. This showed that the raw material could affect the optimum Ni concentration.

4. Conclusion

Natural zeolite had a similar type of crystallinity to clinoptilolite. Nickel oxide impregnation was not affecting the diffraction pattern of natural zeolite and a few transformations at the absorption band. The increase of impregnated NiO concentration at the catalyst is not directly proportional to the increase of generated biohydrocarbon conversion and selectivity. NiO/zeolite 1% showed good catalytic activity with the highest conversion of 60.79%, gasoline selectivity 9.73%, kerosene 29.64%, and green diesel 9.18%.

Acknowledgment

The authors thank the Publication and Research Center (Puslitpen), LP2M UIN Syarif Hidayatullah Jakarta, which supported the research funding through Applied Research Cluster and Higher Institution Development (Un.01/KPA/233/2018).

References


[10] Xiaosong Yang, Jing Liu, Kai Fan, Long Rong, Hydrocracking of Jatropha Oil over non–sulfided PTA–NiMo/ZSM–5 Catalyst, Scientific Reports, 7, 1, (2017), 41654 https://doi.org/10.1038/srep41654


[16] Wega Trisunaryanti, Triyono Triyono, Ria Armunanto, Lathifah Puji Hastuti, Desinta Dwi Ristiana, Resi Vita Ginting, Hydrocracking of α–Cellulose Using Co, Ni, and Pd Supported on
https://doi.org/10.14710/jksa.16.1.33–37

https://doi.org/10.20886/jphh.2016.34.3.189–197

https://doi.org/10.1023/A:100632000600


https://doi.org/10.15408/jkv.v3i2.518

http://dx.doi.org/10.17977/um026v1i2017p035


https://doi.org/10.1111/j.tj.v78.8821

https://doi.org/10.14710/jired.2021.35970


https://doi.org/10.9767/bcrec.13.3.1929.456–465

https://doi.org/10.1086/51003–9953(09)60005–0

http://dx.doi.org/10.14710/jired.4.1.32–38