Research article

Conversion of crude palm oil to biofuels via catalytic hydrocracking over NiN-supported natural bentonite

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Abstract: Nickel nitride supported on natural bentonite was prepared and tested for hydrocracking Crude Palm Oil (CPO). The catalyst was prepared using the wet impregnation method and various nickel nitride loading. Subsequently, the nickel nitrate-bentonite was calcined and nitrided under H2 steam. The surface acidity of as-synthesized NiN-bentonite was evaluated using the gravimetric pyridine gas. Meanwhile, the physiochemical features of the catalyst were assessed using XRD, FT-IR and SEM-EDX. The results showed that the NiN species was finely dispersed without affecting the bentonite’s structure. Furthermore, the co-existence of Ni and N species on EDX analysis suggested the NiN was successfully supported onto the bentonite, while the surface acidity features of raw bentonite were increased to 1.713 mmol pyridine/g at 8 mEq/g of nickel nitride loading. The catalytic activity towards the CPO hydrocracking demonstrated that the surface acidity features affect the CPO conversion, with the highest conversion achieved (84.21%) using NiN-bentonite 8 mEq/g loading. At all nickel nitride loading, the NiN-bentonite could generate up to 81.98–83.47% of bio-kerosene fraction, followed by the bio-gasoline ranging from 13.12–13.9%, and fuel oil ranging from 2.89–4.57%.
Keywords: hydrocracking; crude palm oil; nickel nitride; supported natural bentonite; biofuels

1. Introduction

Due to the escalation of industrial activities worldwide, energy needs are increasing every year. This condition is consistent with the significant increase in population and economic development [1]. Fossil fuels have been the main focus in many industrial processes, as well as in automobiles. Globally, the development of cleaner and renewable energy sources is accelerating due to sharp rises in crude oil costs, the depletion of petroleum supplies and the environmental consequences of emissions [2]. Indonesia, in particular, offers enormous potential for clean, renewable energy use. Crude Palm Oil (CPO) is one of the natural resources with a supply that can be used as an alternative energy [3]. In recent years, CPO manufacturing rose to 27.00 million tonnes in 2017 compared with 2001, which is only 0.84 million tonnes. Further, CPO manufacture’s productivity tends to increase yearly by 1.50–10.96%, which suggests its potential as a sustainable feedstock [4].

CPO is made up of triglycerides and fatty acids that can be converted into sustainable fuels by hydrocracking [5]. This reaction uses hydrogen gas and a solid acid catalyst to break long-chain hydrocarbon bonds into short-chain hydrocarbons [6]. The type of solid acid catalyst must be investigated because it has a direct impact on the conversion. Acid catalysts are widely employed in petrochemical reactions and industrial biomass conversion [7,8]. The properties of the catalyst also could be tunable for particular raw material and outcomes. Solid acid, a well-known heterogeneous catalyst, has been extensively explored to generate green and sustainable chemistry due to its high catalytic activity and product selectivity, ease of regeneration and corrosion reduction, and ability to function in continuous reactors [9,10].

Currently, the metal-based catalyst can be utilized for hydrocracking reactions. However, the main disadvantage of metal-based catalysts is that it is more difficult to avoid the formation of agglomerates when it is used as a support catalyst with a wide surface area and proclivity to agglomeration. To compensate for this weakness, a supported catalyst with a wide surface area and an active catalytic site is required [11]. Several supported metal acids, such as Al₂O₃-SiO₂ [12], zeolite [13,14], MCM-41 [15,16], TiO₂-SiO₂ [17] and bentonite [18–20] have been utilized as hydrocracking reaction supported catalysts for producing biofuels. All these support catalysts are impregnated with an active metal, such as Ni-W, Ni, Ni-1,3,5-benzenetricarboxylate (Ni-BTC), NiMo, NiMoS, NiWS and Ni-Cu, for the hydrogenation facility.

In the context of a support catalyst, natural bentonite is very promising, as it reveals superiority because it is abundantly available, can co-exists in Bronsted and Lewis acid sites [21], and the structure, as well as pores, can be straightforwardly modified [22]. Several studies showed that natural bentonite’s catalytic and physicochemical features could be enhanced by adding active species, such as metal-based catalysts, to the bentonite’s surface or matrix catalyst [19,23]. This treatment could promote the acidity and textural features of bentonite, which affects the hydrocracking process [24,25].

Currently, there is much interest in the metal transition nitride due to its attractive physicochemical features, as this catalyst has many potential applications [26–28]. Many metal nitride-based catalysts, such as ScN, VN, TiN, CrN, FeN, CoN and NiN have been extensively explored and used for various purposes [29,30]. Previous studies revealed that the modification of natural bentonite using MoN and ZrN positively affected the hydrocracking activity [3,31]. ZrN/bentonite exhibited high acidity features (1.822 mmol/g) compared with the parent bentonite, with only 0.054 mmol/g.
Notably, the NiN catalyst is fascinating due to its high specific surface area, flexible catalytic features, being relatively inexpensive and abundantly available, once compared with noble metal-based catalysts [32,33]. Accumulation of positive charge on the Ni sites with N substance alloying, the $\Delta G_{H^*}$ in the favored NiN plane decreases significantly to $-0.05$ eV, almost close to the Pt sites [34]. Hence, dispersing the NiN onto the supported catalyst, such as bentonite, would potentially increase the active site catalyst, thereby increasing catalytic performance.

According to the literature review, the NiN catalyst has been utilized for the electrochemical reaction [27,28,33,35,36]. However, their potential application for CPO hydrocracking was limited. In this study, the NiN supported-natural bentonite was prepared, and its catalytic activity towards the hydrocracking of CPO was assessed. This study offers the potential and exploration of natural-based catalysts as inexpensive catalysts. Nickel nitride, as an active species, was studied to evaluate its effect on the natural bentonite catalyst in order to increase its catalytic performance on CPO hydrocracking. This catalyst would provide alternative acidic sites, enhancing the catalytic activity of natural bentonite towards CPO hydrocracking. The effect of NiN loading on the hydrocracking of CPO conversion and their selectivity towards biofuels was evaluated. Furthermore, the physicochemical of natural bentonite and NiN-supported natural bentonite catalyst was assessed using XRD, FTIR, and SEM-EDX, while the surface acidity features were evaluated with the gravimetric method using pyridine gas.

2. Materials and methods

2.1. Synthesis of NiN-Bentonite

The as-saturated Na-bentonite (Na-B) (Bayan, Central java) was first prepared according to that previously reported [21]. The wet impregnation method was employed for the Na-B modification using nickel solution (NiCl$_2$.6H$_2$O, ≥99.0% purity, Merck). Briefly, 5 g of Na-B was dispersed to the 0.1 M of nickel solution, and 1 M of ammonium nitrate solution was gradually added (1 mL/min) (NH$_4$NO$_3$, ≥95.0% purity, Merck), and stirred for 1 h at room temperature (RT). In this process, the volume of nickel solution and ammonium solution varied with different loading, i.e., 2, 4, 6, 8, 10 mEq/g. Afterwards, the solution was stirred for 24 h, and the temperature was increased to 80 °C until it formed a paste. The paste was cleaned with distilled water and dried for 24 h at 105 °C. Subsequently, the dried solid was later calcined at 550 °C for 3 h, and then reduced under an H$_2$ atmosphere at 600 °C for 2 h.

2.2. Characterization of catalysts

The morphology and elemental composition of both the parent Na-B and NiN-B samples were investigated on SEM-EDX JEOL JSM 650. Rigaku Mini Flex 600 and FTIR 8201 resolved the structure and functional groups of catalysts. Based on the previously reported, the pyridine vapour gravimetric method was employed for the catalysts’ surface acidity analysis [21].

2.3. Catalytic activity test

The hydrocracking was conducted in the continuous fixed bed microreactor [37]. The H$_2$ gas was first supplied to the reactor to remove the oxygen gas. A peristaltic pump was used to maintain a CPO feed flow of 11.94 g/min and 12 g of catalyst. The CPO hydrocracking was conducted at 450 °C and
held for 0.12 h with an H$_2$ gas flow of 2 mL/s. Furthermore, the condensable liquid product was vacuum distilled at 200 °C. The residue after vacuum distillation was separated, and the liquid product was analyzed using GC-MS (Thermo Scientific). The total conversion of CPO was determined based on Eq (1) as follows:

\[
\text{Conversion (\%)} = \frac{X_o - X}{X_o} \times 100\%,
\]

where $X_o$ and $X$ are the weight of feed and unreacted feed, respectively.

3. Results and discussion

3.1. Catalyst characterization

Various techniques were used to characterize the prepared Na-B and NiN-B. Figure 1 depicts the diffractograms of both catalysts. As can be discerned in Figure 1a, the diffraction peaks at 20 of 19.70°, 25.66°, 33.72°, 55.33° and 62.21° were assigned as typical of montmorillonite mineral [38]. These montmorillonite mineral peaks were also consistently observed by another study [39]. According to Huang et al. [40], montmorillonite’s distinctive reflection was indicated by low angle 2 in clay-based materials. Figure 1b shows that this high peak intensity at 5.27° was quite unobservable after being loaded with nickel nitride. This condition occurred, presumably, due to delamination of the silicate layer, which was known as the unique feature in the clay-based material and could lead to the formation of a house of cards structure [41]. Similar findings were also reported by the previous study, which revealed the disappearance of 20 at 5.96° of montmorillonite after being modified by ZrO$_2$ and Ni/Mo-ZrO$_2$ [42].

![Figure 1. Diffractograms of (a) bentonite and (b) nickel nitride-bentonite.](image)

As shown in Figure 1b, a typical montmorillonite phase still existed in the NiN-B, suggesting that NiN did not negatively amend the bentonite structure [43]. Other studies reported [27,30,44] that the nickel nitride phase was difficult to discriminate against the parent Na-B. The NiN phase’s unnoticeable peaks on modified bentonite likely indicated that the NiN was evenly distributed across the surface of the bentonite [45]. Furthermore, there was an intensity change and peak shift on the
NiN-B, probably due to the disproportionate ionic size between natural bentonite and nickel nitride ions. This observation was also reported by Olegario et al. [46] during the modification of Philippine natural zeolite using iron and copper metal oxide.

Figure 2 shows the FTIR spectra of the parent Na-B and NiN-B. The absorption band of Na-B at 3390, 3615, and 1623 cm$^{-1}$ were assigned as the hydroxyl group deformation of water [47]. These peaks on Na-B can also correspond to the stretching vibration of a hydroxyl group from silanol, as well as Al-OH groups [48]. The bands at 984 and 795 cm$^{-1}$ indicated the Si-O-Si and Si-O-Al stretching and deformation bands from the phyllosilicate groups on the bentonite [49]. Other studies also observed these typical absorption bands of bentonite [50].

![FTIR spectra of Na-B and NiN-B](image)

**Figure 2.** FTIR spectra of bentonite and nickel nitride-bentonite.

Due to the overlap between the bentonite’s structural elements, the nickel species absorption bands on the NiN-B were largely unobserved. This condition was also reported coherently during the modification of bentonite using different species Al/Fe and Fe [43,51]. The presence of NiN is likely what caused the phyllosilicate group absorption band on the NiN-B to shift relative to a higher wavelength and gain intensity noticeably similar to other bands. Mishra et al. [52] reported the same phenomenon, revealing that the modification of bentonite with CTAB to organo-bentonite resulted in a shift in absorption towards the higher wavelength. According to Tomul et al. [53], the increase in the intensity of the air bending vibration suggested the rise in air storage capacity and the acidity feature of modified bentonite, due to the generation of a proton by the H$_2$O molecular dissociation in the coordination plane.

Figure 3 shows the SEM micrograph of Na-B and NiN-B. It can be seen that the parent Na-B had a layered surface structure and an asymmetrical irregularly particle shape. This was typical of bentonite surfaces and other as-prepared raw bentonites from previous studies [54–56]. There was no appreciable surface change on the NiN-B compared with the parent Na-B. The Na-B modification using NiN species did not notably influence the bentonite’s morphology, which was consistent with the previous XRD and FTIR results. Vajglová et al. also reported a similar finding [57] by modifying the bentonite using Pt through the impregnation method. Some studies reported that the modified bentonite exhibited a more porous and coarse structure [58,59]. Nevertheless, it was worth noting that some tiny
aggregation species were deposited on the NiN-B, presumably contributing to NiN species’ dispersion towards the bentonite surface. Lin et al. [60] reported that the emergence of particle aggregates on Zr-bentonite, compared with raw bentonite, suggested the success of Zr loaded on the bentonite’s surface.

Figure 3. SEM micrographs of (a) bentonite and (b) nickel nitride-bentonite.

Table 1 and Figure 4 presents the semiquantitative EDX analysis of Na-B and NiN-B. The Na-B consisted of Si, Al, Mg, Na, C and Fe, as well as other impurities, and these components were also reported by other studies [61,62]. Also, the co-existence of nickel (13.19 wt%) and nitrogen (3.23 wt%) in NiN-B confirmed the successful modification of bentonite with NiN species. The Si/Al ratio of the Na-B was relatively unchanged by NiN, suggesting that bentonite’s layer structure was well maintained during modification [53].

Figure 4. EDX spectra of (a) bentonite and (b) nickel nitride-bentonite.
Table 1. EDX results of bentonite and nickel-nitride bentonite.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic (wt%)</th>
<th>Na-B</th>
<th>NiN-B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>25.13</td>
<td>18.39</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>8.11</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0</td>
<td>13.19</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>0</td>
<td>3.23</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>1.81</td>
<td>1.57</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>2.01</td>
<td>1.01</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>0.29</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>39.24</td>
<td>35.5</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>3.12</td>
<td>2.07</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>16.18</td>
<td>15.09</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>1.3</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>1.2</td>
<td>1.13</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>0.38</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>1.23</td>
<td>1.22</td>
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</table>

Figure 5 shows the surface acidity features of Na-B and NiN-B with different loading. The Na-B had a relatively low surface acidity of 0.086 mmol pyridine/g compared with NiN-B 2 mEq/g of 0.721 mmol pyridine/g. This indicated that the NiN species positively affected the surface acidity of the parent natural bentonite by providing both new Lewis and Bronsted acidic sites, raising the surface acidity of Na-B. Furthermore, the interaction of nickel with nitrogen in metal-nitride compounds facilitates a more significant enlargement in electron density [63], which directly affects the surface acidity of the catalyst. The previous study also reported that the total acidity of raw bentonite could be increased by using MoP species [21].

![Figure 5. The surface acidity of bentonite and nickel nitride-bentonite.](image-url)
Moreover, as the nickel nitride loading increased, the surface acidity of the NiN-B catalyst also increased. The previous study also consistently noticed this metal-nitride acidity features trend [31]. As shown in Figure 5, the highest surface acidity was accomplished by loading 8 mEq/g nickel nitride with a surface acidity of 1.713 mmol pyridine/g. However, a low nickel loading (10 mEq/g) reduced the surface acidity of the catalysts to 1.685 mmol pyridine/g. This condition was most likely caused by catalyst agglomeration, which reduced adsorption efficiency towards the pyridine probe and, thus, surface acidity. The decrease of acidity features at 10 mEq/g metal loading was also observed on the ZrN-bentonite [3].

3.2. Catalytic activity test

The hydrocracking was performed using the continuous fixed bed microreactor over the NiN-B catalyst with different nickel nitride loading. The measurements were recorded in triplicates, and the results were shown as a mean value. Figure 6 shows conversion results using bentonite and NiN-B catalysts. The parent bentonite catalyst exhibited low conversion compared with the NiN-B catalyst, which is suggested to be due to low acidic sites. The NiN-B with 2 mEq/g nickel nitride loading generated up to 65.4% CPO conversion and increased the nickel nitride loading gradually this process. According to Figure 6, the highest conversion was generated by 8 mEq/g nickel nitride loading of 84.21%, while an insignificant decrease was observed on 10 mEq/g nickel nitride loading. This result confirms that the NiN species could enhance the bentonite catalyst performance toward high CPO conversion.

![Figure 6. Effect of nickel nitride-bentonite catalyst with different loading on CPO conversion.](image)

It has been reported that the vegetable oil conversion through the hydrocracking reaction is inherently affected by the catalyst’s acidity [31]. These Lewis and Bronsted acid sites are crucial in the hydrogenation process, including the production of reactive carbocations [64]. Furthermore, the higher nickel nitride loading provided a more acidic environment on the catalyst’s surface throughout the synergetic effect between nitride groups and metal. This condition effectively promoted the CPO conversion [65]. As can be seen from Figure 6, higher nickel nitride loading provided highly acidic sites, which promoted a high catalytic process. Similarly, the previous study showed that ZrN-bentonite
could exhibit a conversion of up to 87.93% at 8 mEq/g metal loading, while the ZrP-bentonite achieved 86.04% at 10 mEq/g metal loading, which indicated that the catalyst acidity highly affected the CPO conversion [3]. Another study also reported a positive correlation between the catalyst acidity and the catalytic performance in the hydrocracking process [66]. According to a previous study, CoMo-supported alumina catalyst exhibited a conversion of 64.21% during a 2 h hydrocracking at 400 °C [67], while NiW-supported HZSM-5 generated 48.16% at 350 °C for 1 h reaction [68]. The CPO that has not yet undergone prosperous cracking is denoted as residue. According to the results of the CPO hydrocracking, the parent catalyst exhibited high residue, whereas the nickel nitride-bentonite showed low residue, and tended to decrease for prolonged high nickel nitride loading, which was proportional with high conversion. The low residue result suggested that the catalyst was effective for CPO hydrocracking [69].

Figure 7 shows biofuel fractions resulting from the NiN-B with the different nickel nitride loading. Employing various nickel nitride loading resulted in no significant difference in the biofuel fractions. This suggested that the acidity concentration likely had no strong correlation with the quantity of each biofuel fraction [70]. Instead, hydrocracking parameters, such as temperature, might likely affect biofuel distribution. It can be seen that, among the nickel nitride loading, the bio-kerosene had a higher fraction (81.98–83.47%), followed by the bio-gasoline (13.12–13.9%) and fuel oil (2.89–4.57%).

In this reaction, the fatty acid glycerol ester linkages disintegrate into free fatty acids. The hydrogenation reaction is involved in the creation of bio-kerosine. Concurrently, the decarboxylation reaction begins with the active catalyst site contacting fatty acids through the oxygen atom adsorption on the carboxyl groups of fatty acids. The bio-kerosene fraction is produced in large amounts under these conditions [3]. Meanwhile, the bio-gasoline portion was made by additional hydrocracking of the bio-kerosene. Heavy fractions, such as fuel oil, were generated from insufficient cracking or coupling reactions. The previous study reported that ZrN-bentonite could achieve a bio-kerosene fraction of ca. 72–75% and bio-gasoline fraction of ca. 21–22%, while ZrP-bentonite could generate the bio-kerosene and bio-gasoline fractions of ca. 74–83% and ca. 6.8-14%, respectively [3]. Furthermore, MoN-bentonite 8 mEq/g metal loading could exhibit a bio-gasoline fraction of up to 28.7% [31].
on the hydrocracking investigation, the NiN-B catalyst showed an acceptable performance towards biofuel production through the CPO hydrocracking compared with other supported bentonite catalysts. The proposed mechanism of CPO hydrocracking using nickel nitride-bentonite is presented in Figure 8. The CPO hydrocracking process can occur as a result of a parallel reaction between the decarboxylation reaction and the carbon-carbon bond-breaking reaction of unsaturated fatty acids. This parallel reaction allows the formation of carbon dioxide gas products and gasoline fraction oil. This reaction, likewise, begins with the adsorption of unsaturated fatty acids as a provider of electrons to the catalyst surface as an electron acceptor. The weak bonds formed between fatty acids that have phi electrons ($\pi$) and, subsequently, the catalyst, led the carbon-carbon bonds of unsaturated fatty acids to become weak and eventually break. Further hydrogenation reactions generated gases, such as propane, biofuel fractions and water.

![Diagram of the proposed mechanism of CPO hydrocracking using nickel nitride-bentonite.]

**Figure 8.** The proposed mechanism of CPO hydrocracking using nickel nitride-bentonite.

4. Conclusions

A series of NiN-bentonite with varying nickel nitride loading was prepared, and their catalytic activity towards the CPO hydrocracking was evaluated. By using the wet impregnation method and nickel solution, as well as ammonium solution as the nickel and nitrogen precursors, respectively, the natural bentonite was modified with NiN species. Also, the as-prepared catalyst was calcined and reduced under an H$_2$ atmosphere. According to the catalyst’s characterizations, the NiN species was sufficiently supported on the surface of the bentonite. Moreover, the surface acidity of the parent natural bentonite was enhanced, with the highest acidity of up to 1.713 mmol pyridine/g achieved by the 8 mEq/g of nickel nitride loading. The hydrocracking catalytic test revealed that the NiN-bentonite with 8 mEq/g exhibited up to 84.21% CPO conversion, with a bio-gasoline fraction of 13.12%, bio-kerosene of 83.12 and a fuel oil of 3.76%. This catalyst provides a potential application for CPO hydrocracking with adequate performance.
Acknowledgments

The financial support by The LPPM Universitas Sriwijaya under Hibah Kompetitif scheme research grant 2022 No. 0109/UN9.3.1/SK/2022 is gratefully acknowledged. The authors also acknowledge the National Research and Innovation Agency (BRIN) for providing access to instrumental analysis.

Conflict of interest

We declare no conflicts of interest.

References


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