Synthesis of H/Bentonite and Ni/Al₂O₃-bentonite and its application to produce biogasoline from nyamplung seed (Calophyllum inophillum Linn) oil by catalytic hydrocracking

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ABSTRACT. Hydrocracking process of Nyamplung (Calophyllum inophillum Linn) seed oil to produce biogasoline using H/bentonite and Ni/Al₂O₃-bentonite that pillared by Al₂O₃ as catalyst had been conducted. Bentonite was activated by acidification using HF 1% and H₂SO₄ 0.5 M. Ni metal was impregnated into bentonite with two steps reaction; therewas intercalation with Al₂O₃ kegging ion and Ni metal impregnation using NiCl₂ metal salt. Catalysts were characterized by infrared spectrophotometer (FTIR), X-ray diffraction (XRD), X-ray fluorescence (XRF), BET, TEM and ammonia adsorption. Hydrocracking reaction was variated by Ni/Al₂O₃-bentonite and H/bentonite with ratio catalyst/oil 1:100. Biocrude was prepared by extraction by using ethanol 96%. Hydrocracking oil products were further analyzed by GC-MS. The results show that the acidity of bentonite by activation using HF 1% and H₂SO₄ 0.5 M has been increased from 62.58 to 64.62 mmol/g. Impregnation process also increased the acidity of bentonite from 62.58 to 64.89 mmol/g. Activation using HF 1% and H₂SO₄ 0.5 M, intercalation by Al₂O₃ and impregnation by Ni metal were increasing the crystallinity, surface area, total volume pore and average pore size of bentonite. These techniques were also caused dealumination of bentonite. The hydrocracking process successfully synthesized hydrocarbons with a number of carbon chain between C₅-C₂₀ which include bio-gasoline group compounds. Moreover, catalytic processes by H/bentonite and Ni/Al₂O₃-bentonite also successfully produced 39.83% and 60.37% of biogasoline yields, respectively.

Keyword: activation, bentonite, biogasoline, hydrocracking, "nyamplung", impregnation, intercalation

1. Introduction
In the current of the industrial era, the problem of energy crisis become an issue that very worrying problem. If decreasing fossil fuel reserves and no reduction in consumption of them, it may cause depletion of the primary energy source fossil source. States more than 90% or 10,000 million tons per year of world energy demand supplied from fossil fuels. If exploitation continues with current figures, it is expected that this energy source will be exhausted in the next half-century [1]. The world's fossil fuel energy reserves,
especially petroleum is estimated only 30-50 years later. The most extreme estimates indicate that oil in
Indonesia with the current level of consumption is exhausted within 10-15 years [2].

The problem about the depletion of fossil natural resources to make research on alternative energy
sources have to be done especially for transportation sector that has contributed the high demand for fossil
fuel in Indonesia. Indonesia nowadays is developing renewable energy for based biodiesel it used for B20
blending and applied for diesel engine. In the other side transportation sector also dominated by motor
cycle usage that consumes gasoline. So not only biodiesel we also have to develop biogasoline to substitute
gasoline usage for the transportation sector. Biogasoline is more environmentally friendly, renewable, and
the sustainability of its raw material availability is secure. One of the raw materials that can be used is from
nyamplung oil. Nyamplung oil obtained from seed extraction from nyamplung plant. Excess nyamplung as
raw material is oil from seed has high rendemen, and in its utilization does not compete with the importance
of food. Biogasoline can be obtained by hydrocracking process [3,4,5]. The hydrocracking process consists
of two stages, combining catalytic cracking and hydrogenation, in which aromatic raw materials with heavy
molecules are converted into lighter products in the presence of hydrogen and catalysts. The hydrocracking
process can take place using high pressure, high temperature, catalyst, and hydrogen gas, and one of the
catalysts that can be used in catalytic hydroxide is modified bentonite [6].

This research is expected to provide information about the use of nyamplung seed oil as one of the
alternative energy sources that can produce biogasoline fraction. And know the effect of impregnation and
activation treatment on catalyst characteristics used for hydrocracking process

2. Material and Methods

2.1 Literature reviews

Bentonite is one of the types of excavated materials that its availability in Indonesia is quite abundant.
Bentonite can be intercalated using polarizing agent one of them is Al2O3 which has stable properties so that
the application can be used at high temperature (Taslimah, Ratna, and Azmiawati, 2008). The intercalation
process is carried out to strengthen the interlayer to improve the physical properties of its aluminum silicate
such as crystallinity, basal spacing d001, surface acidity, and thermal stability which is a requirement as a
catalyst, catalyst carrier or as an adsorbent. (Figueras, 1988).

Bentonite is one of clay type that has the main content mineral smectite (montmorillonite) with levels of 85-
95%. According to (Riyanto, 1992) bentonite may be used as a catalyst support, while modified bentonite
may be used as a catalyst. Bentonite is composed of alumina silicate minerals that have a layered crystalline
structure. Bentonite has the ability to expand (swellability) due to interlayer space (interlayer) it has, and
can accommodate the ions molecules dihydrate with a certain size.

Wahyuningsih (2013) conducted a study on bentonite claiming that the polarization process in bentonite
using aluminum oxide (Al2O3) increases the physicochemical properties of bentonite, such as observed basal
spacing of 0.26 nm, specific surface area 103.93 m² / g, and total pore volume 0.06 mL / g but there was a
decrease in the mean of pore jores by 2.23 nm.

In the research of Youg-Gou and Ko (2000), the manufacture of alkylated bentonite alumina was carried
out by using a polyoxocation (Al13O4 (OH)24(H2O)12) 7+ derived from NaOH and AlCl3 solution with a molar
ratio of Al / OH = 2. After the calcination of the oxidized aluminoxide the aluminum becomes Al2O3.

The study of Nickel metal expansion in alkyl-pillar bentonite for use as a catalyst in hydrocracking of
petroleum fraction has been done by Darmawan (2004). The study suggests that the acidity of bentonite is
enhanced by the inclusion of transition metals that have an unfilled d orbital.
Table 1. Component of fatty acid constituent of nyamplung seed oil

| Fatty acid component | (%)  |
|----------------------|------|
| Palmitic Acid C\textsubscript{16:0} | 12.01 |
| Stearic Acid C\textsubscript{18:0} | 12.95 |
| Oleic Acid C\textsubscript{18:1} | 34.09 |
| Linoleic Acid C\textsubscript{18:2} | 38.29 |
| Linolenic Acid C\textsubscript{18:3} | 0.3  |

From the table 1 the highest oil contain of nyamplung seed oil is oleic acid and linoleic acid. Overall nyamplung seed oil consist of the fatty acid chain C\textsubscript{16-18}.

2.2 Pre-treatment of bentonite
Two kilograms of natural bentonite was soaked in aquadest while stirring with a magnetic stirrer for 24h, then centrifuged to separate the soft and coarse parts both heated to 80-110°C.

2.3 Activation by HF 1%
The soft bentonite was dissolved in 1% HF solution at a 1: 2 ratio and stirred with a stirrer for 20min; then the suspension was centrifuged with a 2000 rpm rotational speed for 20 min. The precipitate is separated and neutralized using aquadest to ph 5-6 then dried.

2.4 Bentonite activation by H\textsubscript{2}SO\textsubscript{4}
50 g of HF-bentonite was dissolved in 200 ml of 0.5 M H\textsubscript{2}SO\textsubscript{4} solution. The solution was stirred for 1 hour. The precipitate is separated and neutralized using aquadest to ph 5-6 then dried and filtered 250 mesh.

2.5 Development of pillaring agent and intercalation of keggin ion Al\textsubscript{3+} to bentonite
The solution of the pillaring agent was prepared by reacting a 0.4 M AlCl\textsubscript{3}.H\textsubscript{2}O solution with 0.88M NaOH solution in stirrer for 24 h to homogeneity and then suspension of 4g H-bentonite in 200 ml of distilled water and stirred for 20 min. The centrifuges at 2,000rpm for 15 minutes and the precipitate is taken. The precipitate is washed with distilled water until there is no Cl ion. The Cl-Cl content is checked using AgNO\textsubscript{3} solution.

2.6 Ni metal impregnation process
2,0244g of NiCl\textsubscript{2}·6H\textsubscript{2}O dissolve in 100ml aquadest, then pillared bentonite with 250 mesh size added and stirred using reflux system for 4 hours using 80-90°C of temperature. Then the bentonite is separated and dried using 500°C of temperature with the N\textsubscript{2} gas flow 20ml/min for 4hours. Then continued by reduction process using H\textsubscript{2} gas flow 20ml/min at temperature 400°C for 4 hours.

2.7 Catalyst acidity test
The catalyst acidity test was performed by NH\textsubscript{3} gas adsorption method.

2.8 Nyamplung seed oil hydrocracking using H/bentonite and Ni/Al\textsubscript{2}O\textsubscript{3} Bentonite
The hydrocracking process conduct by catalyst variation using H-bentonite and Ni/Al\textsubscript{2}O\textsubscript{3}-bentonite on the oil hydrocracking of nyamplung seed oil. Hydrocracking was used reactor heat 500 ° C for 2 hours with 20 ml/min of H\textsubscript{2} gas flow. The hydrocracking product was analyzed using GC-MS.
3. Results and Discussion

3.1 Acidity test of the catalyst

One of the parameters that affecting the catalitic ability of the catalyst is acidity. Acidity test was performed to determine the acidity change of the catalyst from each treatment. Acidity test was conducted by using NH$_3$ adsorption. The principle of this acidity test is to calculate the change of catalyst weight after NH$_4^+$ ion is given then cation exchange between H$^+$ ion and NH$_4^+$.

Table 2. Result of catalyst acidity measurement

| Catayst               | Acidity (mol/gram) |
|-----------------------|--------------------|
| Initial Bentonite     | 62.58              |
| H/bentonite           | 64.62              |
| Ni/ Al$_2$O$_3$-bentonite | 64.89          |

Result of acidity test showed in table 2 that the acidity of bentonite be after treatment is increasing. That is mean that activation of bentonite using acid has been conduct. Then impregnation Ni metal into bentonite also increase the acidity, that it also increase the catalytic ability of bentonite.

3.2 Characterization of catalyst with infrared spectrophotometer (FTIR)

The absorption peak at 1635.64 cm$^{-1}$ is the indication of an O-H bending vibration of water molecules. Figure 1 shows the presence of water molecules contained in bentonite minerals.

![Infrared spectra](image)

Figure 1. Infrared spectra (a) H/bentonite dan (b) Ni/ Al$_2$O$_3$-bentonite

462.92 cm$^{-1}$ adsorption at H / bentonite and 470.63 cm$^{-1}$ on Ni / Al$_2$O$_3$-bentonite shows the bending vibration of Si-O-Si in TO$_4$ layer, the occurrence of this Si-O-Si vibration wave swing rate indicates the occurrence Dealumination during intercalation and impregnation of Ni metals. Acid treatment does not cause the loss of silica sheet on bentonite. This is good because if the silica layer is damaged, it will decrease the ability of bentonite in its catalytic properties.

3.3 Crystallinity test of catalyst by X-ray diffraction (XRD)
In H / bentonite diffractogram (Figure 2 (c)) seen diffractogram montmorillonite structure shift from the value d = 14.62 Å to d = 13.05 Å this shows during the acidification process with H2SO4 0.5M resulted in the collapse of mineral montmorillonite. The peak of quartz (d = 4.40 Å) and feldspar (d = 4.05 Å) experienced a very significant increase in intensity, possibly due to the collapse of the montmorillonite structure to form quartz and feldspar structures.

![Diffractogram Image](image)

**Figure 2.** Difraktogram (a) initial bentonite, (b) HF-bentonite, (c) H/bentonite, (d) pillared bentonite (e) Ni/Al2O3-bentonite

The Ni/Al2O3bentonit diffractogram is showing the montmorillonite peak at d = 14.85 Å where the value is greater than H / bentonite. This shift occurs because of the presence of Ni metals in the bentonite layer, Ni metal with an neutral charge on bentonite will result in a decrease in the number of H2O molecules being hydrated. After the treatment of Ni metal impregnation, there was still quartz mineral at d = 4.15 Å with relatively high intensity and feldspar mineral at d = 4.02 Å.

### 3.4 Mineral deposits test on catalysts with X-ray fluorescence (XRF)

Qualitatively, the intercalation process will increase the composition of Al elements in bentonite this is evident from the XRF results show the increase in the composition of Al from 8.2% to 12%. The success of impregnation of Ni metal has been proven by XRF analysis result which shows an increase of Ni percentage from 0.20 % to 13.3%.

| Element | % in H/bentonite | % in Ni/Al2O3-bentonite |
|---------|-----------------|------------------------|
| Al      | 8.2             | 12                     |
| Si      | 47.9            | 49.7                   |
| Ni      | 0.20            | 13.3                   |
| Others  | 43.7            | 25.7                   |

Result of XRF test showed that impregnation using Ni metals has been conduct and it decrease the impurities content of the catalyst.

### 3.5 Determination of catalyst surface area by BET analysis

The treatment of impregnation of Ni metal on bentonite resulted in a specific surface area of Ni/bentonite of 37.630 m² / g, which is less than the surface area of H / bentonite of 79.078 m² / g. This shows the successful process of Ni metal embedding in bentonite. The mean pore size of Ni/bentonite is greater than...
H / bentonite. The average size of Ni/bentonite pore jores increased due to the presence of Ni metal in bentonite pore reduced the size of pore jores.

Table 4. Analysis Result of BET analyzer

| Sample                  | Surface area (m²/g) | Size pore jores (Å) | Pore volume (10⁻² cc/g) |
|-------------------------|---------------------|---------------------|-------------------------|
| H/Bentonite             | 79.078              | 88,9709             | 17.59                   |
| Ni/Al₂O₃-bentonite      | 37.630              | 140,563             | 13.22                   |

3.6 Hydrocracking Product Content Test
The result of this research, hydrocracking of nyamplung seed oil using H / bentonite catalyst produce a product with a yield of biogasoline equal to 39.83%. The dominant component of this hydrocracking is a component with a C11 chain of 9.31%, C14 of 9.30% and C16 of 8.22%. Hydrocracking nyamplung seed oil using Ni/bentonite catalyst produces biogasoline component (C6-12) with a yield of 60.37% product.

4. Conclusion
The hydrocracking process of nyamplung oil with H / bentonite and Ni/bentonite catalysts containing biogasoline fraction. The hydrocracking product contains 39.83% biogasoline fraction on the use of H / bentonite catalyst and 60.37% on the use of Ni / Al₂O₃-bentonite. The influence of bentonite characterization is the presence of Al₂O₃ pillar on bentonite layer structure increasing interlayer distance on bentonite structure so that Ni metal impregnation process can take place and increase Al amount on bentonite fraction from 8.2% (b / b) to 12% (b / b).

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