Biodiesel Synthesis from Nyamplung (*Calophyllum Inophyllum*) Oil Using Heterogenous Modified Geopolymer Catalyst Derived from Kaolin

Panca Setia Utama¹*, Nabil Syahada¹, Barata Aditya Prawiranegara², Edy Saputra¹

¹Department of Chemical Engineering, Universitas Riau, Pekanbaru 28293, Indonesia
²Department of Chemistry, Universitas Riau, Pekanbaru 28293, Indonesia

Abstract. This work aims to develop a new type of solid base catalyst for biodiesel synthesis from “nyamplung” oil. A heterogenous catalyst was synthesized by modifying kaolin into a geopolymer. The geopolymer catalyst was activated using ammonium nitrate. The microstructure, specific surface area, pore diameter, pore volume, and crystalline phase of the catalyst were characterized. It was possible to achieve the highest biodiesel yield of 95.14%. The effects of reaction temperature, reaction time, oil-to-methanol molar ratio, and catalyst loading on the yield of biodiesel were examined. As per ASTM D6751 and SNI 7182:2015 standards, the biodiesel obtained is of satisfactory quality.

1 Introduction

In 1979, Joseph Davidovits developed the concept of "geopolymers" as inorganic materials. These materials are created through the geopolymerization of aluminosilicates with alkali and alkali earth metal hydroxides, carbonates, or silicates. Geopolymers are amorphous materials that resemble semicrystalline forms of certain zeolitic minerals. They possess exceptional qualities like great strength and resilience to fire and erosion. The automotive industries, non-ferrous factories and metallurgy, the construction sector, the plastics industry, waste management technologies, and heterogeneous catalysts are among the industries that may employ geopolymers (1–3). Copolymerization, which is exothermic (1), entails several complex step reactions, such as the dissolving of Si and Al elements by hydroxide ions, the polycondensation of aluminosilicate, and structural reorganization (2,4).

Similar to low-silica zeolites, the amorphous form of the geopolymer is a three-dimensional structure consisting of AlO₄ and SiO₄ tetrahedra linked by oxygen corners with a (1–3) Si/Al ratio (5). The manufacturing of geopolymers requires silicon and aluminum as basic materials. This ingredient was derived from industrial waste, including clay, rice hull ash, bottom ash, fly ash, and slag ash (6). Clays are commonly utilized as the starting materials for the creation of geopolymers. The percentage of Al₂O₃ and SiO₂ in the clay ranges from 70 to 90%. Whereas the origin and geology of the place affect the composition of clay. The most common way to create a geopolymer is to combine an alkali silicate solution with aluminosilicate directly. The geopolymer paste is mixed, then crushed in molds and allowed to cure at ambient temperature or a little bit hotter (20–80°C).

Biodiesel is produced by transesterifying fatty acids that have a long chain from renewable resources, such as plant-based and animal-based fats, with monohydric alcohol with the assistance of a catalyst (9). Higher flash points and a cetane ignition rating are two characteristics of biodiesel, which is also readily available, non-toxic, carbon neutral, and good for the environment (7–11). Depending on the type of biogenic oil, either an acid or a basic catalyst—which should be carefully selected—catalyzes the reaction. Because base catalysts are more active than acid catalysts, they are typically chosen (5). The four primary methods for producing biodiesel are thermal cracking, transesterification, microemulsions, and immediate utilization and/or mixing with raw oils (10).

The main goal of this work is to synthesize a geopolymer catalyst from kaolin and activate it using ammonium nitrate. The catalyst was employed in the transesterification of “Nyamplung” (*Calophyllum inophyllum*) (CI) oil to produce biodiesel. The novelty of this research is that the geopolymer from kaolin has great strength and is easy to mold into the desired shape, so it has great potential to be used as a catalyst. Investigations were conducted on the effects of catalyst loading, reaction temperature, reaction time, and oil-to-methanol molar ratio on biodiesel yield.

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2 Experimental

2.1 Materials and Chemicals

Merck provided the following: potassium hydroxide, sodium silicate, sodium hydroxide, methanol, and ammonium nitrate. The crude CI oil was bought from the Kebumen local market.

2.2 Catalysts preparation

The geopolymer was made by mixing 10 g of kaolin, 12.2 g of sodium silicate, 1.1 g of sodium hydroxide (NaOH), and 0.7 g of demineralized water. After 48 hours of polymerization in a closed vessel at 60 °C, the geopolymer matured for a week. The geopolymer was mixed with a 0.5 M NH₄NO₃ solution at room temperature and stirred for 12 hours. After that, the product was washed at least five times. The geopolymer was obtained after a drying period at room temperature.

2.3 Characterization of catalysts

The microstructure of the catalyst was determined using a scanning electron microscope (SEM) (JEOL JSM-5800LV, Japan). A surface area analyzer (Quantachrome Nova 2000 e, USA), the Brunauer-Emmett-Teller (BET), and the Barrett-Joyner-Halenda (BJH) were used to determine the specific surface area (SSA), pore diameter, and pore volume. The mineral phase in the geopolymer catalyst was identified through X-ray diffraction (XRD) characterization (Philips X'Pert MPD, Philips, Netherlands).

2.4 CI oil pretreatment

Degumming and neutralization were used to remove impurities from CI oil. The purpose of degumming is to get rid of gum or impurities in oil (7). Phospholipids, unproven substances, proteins, carbohydrates, water, resin acids, and a trace amount of free fatty acids are some of the components that make up gum. A magnetic stirrer was used to stir 500 cm³ of CI oil while it was heated to 80°C. Stirring for 30 min after the temperature was reached, 0.3% (v/v) of an 85% phosphorus acid solution was added. After that, pour the oil into a funnel designed to separate the gum from the oil, and leave it there for a full day (8). A filter was then used to separate the oil from the remaining gum. Because the FFA content of the CI oil is 33 weight percent, producing high-quality biodiesel requires a two-stage process. During the esterification process, pre-heated oil was mixed with 1% (v/v) sulphuric acid and 20:1 methanol to refined oil in a reactor, which was stirred at 400 rpm for three hours at 60°C (9). Following the esterification process, the water and FFA contents in the oil were examined.

2.5 Transesterification of CI oil and methanol

The investigation of the transesterification reaction and the catalytic activity of the geopolymer catalyst was conducted in a 200 cm³ three-neck glass reactor equipped with a magnetic stirrer, a controlled-temperature electric heater, and a water-cooled condenser. Variations were made to the methanol-to-oil molar ratio, catalyst loading, reaction temperature, and reaction time to examine the impact on the biodiesel yield. This procedure involved first mixing the geopolymer catalyst with esterified CI oil, and then mixing various molar amounts of methanol. To separate the catalyst from the reaction product, filter paper was utilized. The methanol and glycerol were separated from the biodiesel, and then the biodiesel was washed and dried.

The following formula was used to determine the biodiesel yield.

\[
\text{yield} \% = \left( \frac{\text{weight of biodiesel}}{\text{weight of oil}} \right) \times 100
\]

3 Results and discussion

3.1 Characterization of kaolin-based geopolymer catalyst

The morphological characteristics of the geopolymer catalyst analyzed using SEM micrographs are shown in Fig. 1.

![Fig. 1. SEM micrograph geopolymer catalyst](image)

The microstructure of the geopolymer catalyst is typically a tubular halloysite or sheet (12). The surface morphology of the geopolymer catalyst reveals that it has a non-uniform shape, a hollow cavity, and a size that approaches the micrometer scale (2μm–10μm). More transesterification reactions on the catalyst surface will be possible because of the surface morphology of the catalyst (13). It is anticipated that the aluminosilicate source will maintain its original structure throughout the geopolymerization process because the geopolymer reaction system is a solid-liquid reaction system known as a gel system with low water content (14–16). The geopolymer's cavity volume and porosity are directly impacted by the ratio of liquid to solid reactants, which in
turn influences the geopolymer's properties (9). Based on the SEM results, showed that the form of the geopolymer catalyst is amorphous. This amorphous form can also be confirmed through XRD analysis which can be seen in Fig. 2. The geopolymer catalyst samples' diffraction pattern was examined using XRD analysis. The muscovite phase, which was an impurity in the crude clay, underwent a geopolymerization process as a result of the strong alkaline activation that followed the catalyst preparation process utilizing clay. The quartz phase, in contrast, is mainly non-reactive [17]. The result of this research is an amorphous product. This suggests that other factors, such as the curing time and the presence of an alkaline activator, affect the temperature-dependent crystallization process of geopolymers [17,18].

The N2 adsorption-desorption isotherm of the geopolymer catalyst is shown in Fig. 3. The N2 adsorption-desorption isotherm is similar to the type IV isothermic curve of the IUPAC and demonstrates the mesoporous nature of the adsorbent particles and their nearly slit-like pores [20].

![Fig. 2. XRD pattern of the geopolymer catalyst](image)

When it comes to catalyst activity, the active site and specific surface area are crucial. The surface area calculated using the BET method, the geopolymer catalyst's pore diameter, and the pore volume calculated using the t-plot and BJH method are all summarized in Table 1. The geopolymer catalyst's specific surface area, as determined by the BET method, is 52.74 m²/g, and its pore diameter, at 18.78Å, indicates that it is a mesoporous material.

![Fig. 3. N2 adsorption-desorption of geopolymer catalyst](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>SSA (m²/g)</th>
<th>Pore Diameter (Å)</th>
<th>Pore Volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geopolymer catalyst</td>
<td>52.74</td>
<td>18.78</td>
<td>0.0250</td>
</tr>
</tbody>
</table>

*a BET Method
*b BJH Method

3.2 Catalyst loading effect

In the transesterification reaction process of CI oil and methanol at a molar ratio of methanol: oil 12:1, reaction temperature 65°C, and reaction duration 120 min, the impact of catalyst amount on the FAME yield is displayed in Fig. 4.

![Fig. 4. Effect of catalyst loading (%) on methyl ester yield (%)](image)

The more catalysts used, the higher the yield of FAME. The FAME yield was 88.56% when only 1 weight percent of catalyst was used. When the catalyst content increased from 1 weight percent to 2 weight percent, resulting in a 92.12% increase in FAME yield from 88.26%. The maximum FAME yield of 95.14% was achieved with 3 weight percent of catalyst loading. More catalysts meant that there were more basic sites in the reaction system where methanol could form the methoxide anions required to produce biodiesel. However, the catalyst loading of 4 weight percent decreased the FAME yield. Because of the excessive loading of the catalysts, the CI oil-methanol system became more viscous, which contributed to the reduction in FAME yield [21].

3.3 Effect of oil to methanol molar ratio
Another important factor that significantly affects the yield of biodiesel is the molar ratio of oil to methanol. One mole of triglycerides can be converted into three moles of methyl ester (biodiesel) and one mole of glycerol using stoichiometry, which states that three moles of methanol are needed [22]. The yield of FAME produced increases with the amount of methanol used because the transesterification reaction is reversible and needs an excessive amount of methanol to drive the reaction to the product [23]. The molar ratios of oil to methanol in this study ranged from 1:12 to 1:3, 1:6, and 1:9. Fig. 5 shows the effect of the oil-to-methanol molar ratio on the FAME yield.

![Fig 5. Effect of oil to methanol molar ratio on methyl ester yield (%)](image)

At a molar ratio of 1:12, a maximum yield of 91% was attained, and the yield of FAME rose as the molar ratio of oil to methanol increased. This implies that when the mole ratios of oil to methanol used increase, so can the yield of FAME produced. When more methanol is added, the reaction will be accelerated up to a point before being inhibited once the maximum condition is met, forming the methyl ester product [22].

### 3.4 Effect of reaction temperature

The impact of reaction temperature on FAME yield at 50, 55, 60, and 65 °C is depicted in Fig 6.

![Fig 6. Effect of temperature on methyl ester yield (%)](image)

As the reaction temperature rises, the transesterification reaction rate increases dramatically. At 50°C, the lowest reaction temperature, the yield of FAME is 74.16%. The FAME yield rose to 86.16% when the temperature was raised to 65°C. The reaction temperature is capped at 65°C because any higher temperature—above methanol's boiling point at 70 °C—will result in a reduced FAME yield. The lower FAME yield is caused by methanol evaporating and staying in the vapor phase during the reaction at 70 °C, which lowers the methanol concentration in the reaction mixture and lowers the yield [23].

### 3.5 Effect of Reaction Time

The impact of reaction time on FAME yield is displayed in Fig. 7.

![Fig 7. Effect of reaction time on methyl ester yield (%)](image)

As reaction time increases, so does the yield of FAME. The lowest reaction time required to achieve a 77.14% FAME yield was 60 min. Reaction time increased to ninety min, and the FAME yield increased from 77.14% to 82.12%. The yield of FAME increased only slightly, from 86.16% to 86.66%, when the reaction time was increased from 120 to 150 min. This is because a longer duration leads to more fatty acids forming soap and increases ester hydrolysis, also known as reverse transesterification, which causes ester loss [23].

### 3.6 Biodiesel characterization

Table 2 displays the biodiesel product characterization results from CI oil.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>ASTM D6751</th>
<th>SNI 7182: 2015</th>
<th>Biodiesel Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester Alkyl</td>
<td>%</td>
<td>-</td>
<td>min</td>
<td>98.55</td>
</tr>
<tr>
<td>Content</td>
<td></td>
<td>96.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>kg/m³</td>
<td>-</td>
<td>850-890</td>
<td>882.3</td>
</tr>
<tr>
<td>Kinematic Viscosity</td>
<td>mm²/s</td>
<td>2.3-6.0</td>
<td>2.3-6.0</td>
<td>4.54</td>
</tr>
<tr>
<td>Acid Number</td>
<td>mg-KOH/g</td>
<td>max 0.5</td>
<td>max 0.5</td>
<td>0.38</td>
</tr>
<tr>
<td>Flash Point</td>
<td>°C</td>
<td>min 100</td>
<td>min 100</td>
<td>135</td>
</tr>
</tbody>
</table>
Based on SNI 7182:2015 and ASTM D6751, the properties of the biodiesel obtained from CI oil that were analyzed match the properties of the standard biodiesel.

4 Conclusions

Kaolin, sodium silicate, and NaOH have all been used to synthesize geopolymers. Geopolymer activated with NH₄NO₃ can be used as a heterogeneous catalyst when converting CI oil into FAME. The geopolymer catalyst is amorphous and can be categorized as a mesoporous substance. The FAME yield of 95.14% was attained at an oil-to-methanol ratio of 12:1, a temperature of 65°C, catalyst loading of 3% (wt), and a reaction duration of 2 hours. The quality of the synthesized FAME is in the range of biodiesel standards.

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References