Synthesis of geopolymer from rice husk ash for biodiesel production of *Calophyllum inophyllum* seed oil

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Abstract. In this work, geopolymer was prepared from rice husk ash (RHA) made into sodium silicate then synthesized by reacting metakaolin, NaOH, and water. The catalyst was characterized using Scanning Electron Microscopy (SEM), Energy-dispersive X-Ray analysis (EDX), Brunauer Emmet Teller (BET), and basic strength. Then, the catalyst used for transesterification of *Calophyllum inophyllum* seed oil in order to produce biodiesel. The variation of process variables conducted to assess the effect on the yield of biodiesel. The highest yield obtained 87.68% biodiesel with alkyl ester content 99.29%, density 866 kg/m³, viscosity 4.13 mm²/s, the acid number of 0.42 mg-KOH/g biodiesel and the flash point 140 °C. Generally, variations of % w/w catalyst provides a dominant influence on the yield response of biodiesel. The physicochemical properties of the produced biodiesel comply with ASTM standard specifications.

1. Introduction

Currently, petroleum is still the main dependent energy source in the world. However, along with population growth, fuel consumption from petroleum continues to increase every year. In addition to the fact, petroleum-based fuels can pollute the environment (e.g. particulate matter, carbon monoxide and sulfur oxides), encouraging the development of environmentally friendly alternative energy i.e. biodiesel. Besides its renewability, biodiesel also has high degradability and produces far fewer emissions (e.g. nontoxic, lack of aromatic compounds and sulfur, low COₓ, SOₓ, and particulate matter) thereby reducing environmental impact [1-3].

Biodiesel is produced from transesterification reactions of short-chain alcohols with triglycerides derived from vegetable oils or animal fats. The most commonly used catalysts for biodiesel are strong base homogeneous catalysts such as KOH and NaOH [4]. This high catalysts prices can cause biodiesel today to be more expensive than fuel derived from petroleum. It is necessary to develop an economical heterogeneous catalyst i.e. the geopolymer from rice husk ash. Large surface area and pore size, as well as strong base properties in geopolymer, made this material highly potential to serve as a catalyst for transesterification.

2. Experimental

2.1 Catalyst preparation

Rice husk was furnaced for 3 hours at 500 °C. Rice husk ash is filtered using 100 mesh strainer, then the silica from RHA was extracted which was carried out in the batch reactor. The extraction reacted RHA with 0.5 N NaOH (with SiO₂ / Na₂O mole ratio 1.9), at 100 °C for 60 min with 200 rpm stirring rate) [5]. After that, the mixture is filtered through the vacuum pump to separate the rice husk ash and filtrate as sodium silicate solution (Na₂SiO₃).
Metakaolin, sodium silicate, NaOH, and aqua DM were fed into a reactor with a weight ratio metakaolin: sodium silicate: NaOH: water = 10: 12.2: 1: 0.7. Polymerization was performed in a closed vessel at 60 °C for 48 h. After maturing of the geopolymer for one week, the geopolymeric monolith was ground [6]. Then, the catalyst was characterized by Scanning Electron Microscopy (SEM), Energy-dispersive X-Ray analysis (EDX), Brunauer Emmet Teller (BET), and basic strength.

2.2 Transesterification process
First, pre-treatment of Calophyllum inophyllum oil using 0.3% phosphoric acid from the weight of the oil, heated to 60 °C with stirring. Then, the transesterification was carried out with a mol ratio of oil: methanol 9:1, the temperature of 60 °C, 2 h reaction time with the variation of process variables %w/w catalyst 1-2%, stirring rate 200-600 rpm.

3. Result and discussion
The basicity (H_) of geopolymer catalyst was determined using Hammett indicators with the result of H_ >9.3, the catalyst is feasible to be used as a base catalyst in the transesterification reaction [7]. Then, for the surface area was determined by SAA (Surface Area Analyzer) instrument Brunauer Emmet Teller (BET) method with a result of 31.327 m²/g. Thus, the larger surface area has more contact area with reactant molecule to produce biodiesel and larger catalytic activity.

The silica and alumino content in geopolymer was determined using Energy Dispersive X-ray (EDX) spectrometry. The results are shown in Table 1. It can be seen that geopolymer has Si content of 14.17% and Al of 10.35%. Chemically, the geopolymer structure is similar to a low-silica zeolite with a Si/Al ratio between 1-3 [8]. The ratio of Si/Al in this research is 1.4. This indicated that the silica molecules were attached or incorporated into geopolymer structure during the impregnation process.

| Table 1. Composition of geopolymer component elements |
|--------------------------------------------------------|
| **Element**    | **Weight %** | **Atomic %** |
| C             | 24.86        | 34.36        |
| O             | 46.63        | 48.48        |
| Na            | 2.82         | 2.04         |
| Al            | 10.35        | 6.36         |
| Si            | 14.17        | 8.37         |
| K             | 1.17         | 0.50         |
| **Total**     | **100.00**   |              |

Furthermore, the catalyst was analyzed using SEM morphology catalyst in Figure 1.

![Figure 1. Surface morphology of geopolymer.](image)
Based on the results of the research is seen from Figure 2, that the use of catalysts affects the yield of biodiesel produced in the transesterification process. The use of catalyst concentration of 1% (400 rpm stirring rate, 2 h time, mol ratio oil: methanol 9:1, temperature of 60 °C), yield is 83.6%, while at catalyst concentration 1.5% biodiesel yield increased 86.56%, then at catalyst concentration 2% yield of biodiesel produced decreased i.e. 84.45 %. This suggested that the increasing of the catalyst concentration may increase the yield of biodiesel due to the increasing area that accelerated the reaction of reactant conversion into the product until the optimum condition reaches with the highest yield obtained at 87.68% at 1.5% catalyst, 400 rpm stirring rate.

![Figure 2. 3D graph plot and contour effect of stirring rate and catalyst on yield](image)

Figure 2. 3D graph plot and contour effect of stirring rate and catalyst on yield

The biodiesel obtained was determined its physicochemical properties. The content of the biodiesel product produced from this study was analyzed using GC-MS with 99.29% ester alkyl content presented in Figure 3, and Table 2.

![Figure 3. Calophyllum inophyllum biodiesel GC-MS analysis.](image)

Figure 3. Calophyllum inophyllum biodiesel GC-MS analysis.
Table 2. Calophyllum inophyllum biodiesel composition content

| R Time  | Component                              | %-weight |
|---------|----------------------------------------|----------|
| 39.383  | 9-Hexadecanoic acid, methyl ester       | 11.94    |
| 43.172  | 9-12-Octadecanoic acid, methyl ester   | 25.71    |
| 43.432  | 9-Octadecanoic acid, methyl ester      | 45.57    |
| 43.501  | 11-Octadecanoic acid, methyl ester     | 1.45     |
| 44.086  | Octadecanoic acid, methyl ester        | 14.23    |
| 47.358  | Hexadecanoic acid, 2-hydroxy-1,3-      | 0.11     |
|         | propanediyl ester                      |          |
| 48.350  | Eicasonoic acid, methyl ester          | 0.39     |
| 50.694  | 9-Pentadecadien-1-ol                   | 0.23     |
| 50.866  | 9-Octadecanoic acid                    | 0.37     |

The comparison of characteristic results of produced biodiesel in this study was compared with SNI 7182:2015 (Indonesia Standard) and ASTM D6751 presented in Table 3. The physicochemical properties of the produced biodiesel comply with SNI and ASTM standard specifications.

Table 3. Produced biodiesel comparison

| Parameter, unit                      | ASTM D6751 | SNI 7182:2015 | Produced biodiesel |
|--------------------------------------|------------|---------------|--------------------|
| Ester alkyl content, %               | Min 96.5   | 99.29         |                    |
| Density 40°C, kg/m³                  | 850-890    | 866           |                    |
| Kinematic Viscosity 40°C, mm²/s      | 2.3-6.0    | 2.3-6.0       | 4.13               |
| Acid Number, mg-KOH/g                | Max. 0.5   | Max. 0.5      | 0.42               |
| Flash Point, °C                      | Min 100    | Min 100       | 140                |

4. Conclusions

In this study, rice husk ash (RHA) geopolymer was prepared from metakaolin then by impregnation methods in sodium silicate solution from RHA extraction. The analyses of basicity, EDX, SEM, and BET showed the possibility of this economical catalyst being effective heterogeneous base catalysts for the manufacture of biodiesel. The RHA geopolymer catalyst provided the maximum biodiesel yield at 87.68% obtained in 2 h reaction time at 1.5% catalyst, 400 rpm stirring rate, a reaction temperature of 60 °C, methanol to oil molar ratio of 9:1.

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