Utilization of rice husk silica as solid catalyst in the transesterification process for biodiesel production

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Abstract. Biodiesel from palm oil is a promising renewable fuel for substitute petro-diesel either be used directly or as a diesel mixture. To improve reaction rate and biodiesel yield, adding a catalyst with excess alcohol is needed in transesterification process. The high content of silica in rice husks is very prospective for the development of a heterogeneous catalyst. The study was carried out to investigate catalytic activity of the silica from rice husk produced by the impregnation process and various calcination temperatures at various amounts of it in the transesterification process for biodiesel production. A preliminary study was carried out to determine the amount of catalyst in the transesterification process. The amount of catalyst producing the highest yield of biodiesel was used in the next study. In the main study, the catalyst from rice husk silica was synthesized through an impregnation process used 1 N KOH and calcination processes at 200, 300, 400, and 500 °C. The experimental result showed the crystallinity degree of the catalyst first increased and then decreased with increases in calcination temperatures. The calcination at 300 °C resulted in the highest surface area of the catalyst (7.21 m²/g). The biodiesel produced through transesterification process using catalyst from rice husk silica with impregnation of KOH 1N and calcination at 300 °C resulted in the highest methyl ester (94.39 %), total acid number of 0.09 mg KOH/g, total glycerol of 0.57 %, saponification number of 186.76 %, free glycerol of 0.01 %, and moisture content of 650.55 ppm.

1. Introduction
Currently, the amount of energy from fossil fuel commonly used by the world population is limited and its reserve is being depleted. In addition, awareness of environmental protection related to petroleum-based fuel consumption has led to increased studies and development efforts to find renewable and environmental-friendly alternative energy sources, such as biodiesel. Biodiesel is a promising renewable fuel produced from vegetable oils or animal fats. Various studies have been reported that vegetable oil is the best raw material of biodiesel due to its sustainability, renewability, high-energy content, and energy security [1]. Biodiesel derived from vegetable oils has various advantages such as a renewable, nontoxic, biodegradable, and environmentally friendly. It almost similar to regular diesel, which can substitute petro-diesel perfectly and be used directly or as diesel mixture in engines with little changes [2–5].
Indonesia is the world’s largest crude palm oil producing country. The commodity has potential as a raw material to produce biodiesel due to its abundant availability. Biodiesel can be produced through transesterification of palm oil with methanol in the presence of a suitable catalyst. Transesterification is a reaction process of the formation of methyl esters from triglycerides with the help of alkyl alcohol and by-products obtained in the form of glycerol [6]. The transesterification process generates biodiesel converted from lipid feedstocks. One mole of triglyceride reacts with three moles of alcohol to produce three moles of mono-alkyl ester and one mole of glycerol. High conversion with relatively low cost, mild reaction conditions, product properties are closer to the petro-diesel, and applicable for industrial-scale production can be obtained by the transesterification process [5].

To improve the transesterification process performances such as rate of reaction and biodiesel yield, adding a catalyst with excess alcohol is needed, which shifts the equilibrium to the product side since the reaction is reversible [4], [7], [8]. Generally, the transesterification process uses methanol or ethanol and homogeneous catalysts such as sodium hydroxide, potassium hydroxide and sulphuric acid [9–11]. Nevertheless, this method has several disadvantages such as extensive separation process, wastewater generation, and equipment corrosion [11–14]. To overcome these problems, implementation of heterogeneous catalyst has been proposed by researchers in various studies, specifically silicates compounds.

Rice husk (RH) is an abundant and underutilized rice milling by-product in Indonesia. The material is an agricultural biomass that has a high silica content, which is 15-20% [15–17]. The silica extraction technology from rice husks using technical grade chemical has been developed by Setyawan [18], with a purity level of 86.17%. The high content of silica in rice husks is very prospective for the development of silica-based products. The abundant availability and easily obtained of rice husks are the advantages of rice husk silica compared to mineral silica. Silica extracted from rice husk is a promising heterogeneous catalyst to produce biodiesel from palm oil. The study aims to investigate catalytic activity of the silica from rice husk produced by the impregnation process and various calcination temperatures at various amount of it in the transesterification process for biodiesel production.

2. Materials and Methods
2.1. Materials
The rice husk ash (RHA) was obtained from Karawang District, West Java, Indonesia. All chemicals used to extract silica in this study included NaOH 98% (PT Tjiwi Kimia), KOH 98% (PT Tjiwi Kimia) and HCl 32.27 % (PT Brataco) were technical grade chemicals. NaOH 1 N and KOH 1 N (analytical grade) were used for impregnation process. Water and distilled water were applied for extraction and treatment process respectively. The commercial palm olein oil was used in transesterification process to produce biodiesel.

2.2. Silica extraction process
Extraction of silica from RHA was conducted adapting the sol-gel method of Setyawan [18], Kalapathy [17], [19] and Handayani [20]. The RHA was mixed with alkaline solution 5%w/v in the ratio 1:5. In the preliminary study, NaOH was used as a chemical to extract silica from rice husk while in the main study used KOH. The RHA was extracted using hydrothermal process at 110-120 °C and 1.5-2 bar for 30 min. Solutions were then filtered and titrated with HCl 3.65%w/v with constant stirring to pH 7. The silica gel formed was aged for 12 h and washed repeatedly (5 times). The gel was dried at 60 °C for approximately 20 h and ground using fine milling.

2.3. Catalyst preparation and characterization
To prepare the catalyst, silica from rice husk was treated by impregnation and calcination processes. In the preliminary study, the silica was mixed with 1N NaOH solutions with ratio 1:10. The mixture was
heated at 100 °C for 1 h at a stirring speed of 350 rpm, filtered and dried at 110 °C. The silica was then calcinated at 500 °C.

The catalyst from rice husk silica used in the main study was synthesized through impregnation of KOH 1N and calcination at 200, 300, 400, and 500 °C with three replications. The catalyst obtained was then further analyzed included scanning electron microscopy (SEM), X-ray diffraction (XRD), and and Brunauer-Emmett-Teller (BET) surface area analysis. The SEM analyses of the catalyst was conducted on an EVO MA10 (ZEISS, Germany). The X-ray diffraction (XRD) patterns were obtained using a D8 Advance Discovery X-ray Diffractometer (Bruker, Germany) using Cu anode, LynxEye detector operated at 2Theta between 5° to 80°. Surface area, pore volume, and pore diameter of the obtained catalyst was measured using BET surface area analyser (Quantachrome NovaWin, USA).

2.4. Biodiesel production

Biodiesel production was carried out adapting the method of Guo [21]. The catalytic reactions were carried out in a 1000 mL three-necked round-bottomed flask equipped with a mechanical stirrer and a reflux condenser. The flask was charged with 300 g palm olein oil and immersed in a thermostat controlled water-bath. After achieving the temperature setting, a relevant amount of methanol and freshly prepared catalysts were added to the flask to start the transesterification. The transesterification was carried out at 65 °C for 60 min at a stirring speed of 1100 rpm. The molar ratio of methanol to oil was 3:1. The amount of silica used in the main study was selected from preliminary study (5 wt.% or 10 wt%) of the palm olein oil (300 g) producing the highest yield of biodiesel. 0.25 wt.% 1 N KOH was used as a control. Biodiesel obtained was then washed using distilled water and heated at 80°C. Methyl ester, total acid number, total glycerol, saponification number, free glycerol, and moisture content were analysed following the procedure of Indonesian National Standard/SNI 7182:2015.

2.5. Statistical analyses

Data were analyzed by ANOVA and means were separated by the least significant difference when significant F (P<0.05) values were observed (SPSS version 21).

3. Results and Discussions

3.1. Characterization of catalyst

The catalysts used in transesterification process to produce biodiesel were obtained silica through the impregnation using 1N KOH and calcination processes at 200, 300, 400, and 500 °C. Table 1 shows the yield of catalyst ranged from 39.05 to 40.34% and indicated no significant difference between variations in calcination temperature.

| No | Calcination temperature (°C) | Yield of catalyst (%) |
|----|-----------------------------|-----------------------|
| 1  | 200                         | 40.32<sup>a</sup>     |
| 2  | 300                         | 39.90<sup>a</sup>     |
| 3  | 400                         | 39.05<sup>a</sup>     |
| 4  | 500                         | 40.34<sup>a</sup>     |

Different superscript letters showed significant differences (p<0.05). Values were mean (n=3).

Figure 1 shows the XRD patterns of catalyst from rice husk silica produced by impregnation and calcination process. The XRD patterns of silica (control) presented the typical amorphous hump for 2θ = 15–30°. The result was similar pattern as reported by Setyawan [18]. In the figure 1, we can observe that the XRD patterns of catalyst produced by impregnation using 1N KOH and calcination processes at 200°, 300°, 400° and 500 °C possessed completely amorphous structures with a degree of
crystallinity ranging from 39.6-56.1%. This degree first increased and then decreased with increases in calcination temperatures. There were several peaks detected were derived from impurities contained in the catalyst produced by impregnation using 1N KOH and calcination processes at 200°, 300°, and 400 °C. Similar results were also reported by Guo [21] and Roschat [22]. Only the catalyst produced at 500 °C had minimum peaks and a similar pattern to a product without calcination process. The presence of impurities and different structure of catalyst from potassium silicate produced from calcination process may result in different catalytic behaviors in the transesterification.
Figure 1. XRD diffraction pattern of catalyst from rice husk silica produced by impregnation using KOH 1 N and calcination process at 200°C (A), 300°C (B), 400°C (C), 500°C (D), and control (E)

The surface area, pore size and pore volume of catalyst from rice husk silica produced by impregnation and calcination process are given in Table 2. In general, increasing the calcination temperature decreased the specific surface area. The result is in agreement with the previous study as reported by Roschat [22]. The specific surface area of catalyst produced by calcination temperature at 300 °C was higher (7,205 m²/g) than that of catalyst produced by other calcination temperatures. The calcined potassium silicate in this study resulted in higher the specific surface area compared to that of calcined sodium silicate at the same temperatures as reported by Roschat [22]. However, the potassium silicate calcined at 200-500 °C showed lower specific surface area (2.47-7.21 m²/g) than that of catalyst produced without calcination process (345.44 m²/g). Guo [21] stated the low surface area showed abundance of the basic sites in the interior of the solid catalyst. This gives beneficial during transesterification process due to it allows more glyceride to diffuse into the interior of the catalyst.
Table 2. Physical features of catalyst from rice husk silica produced by impregnation and calcination process

| No | Calcination temperature (°C) | Specific surface area (m²/g) | Total pore volume (cm³/g) | Average pore diameter (nm) |
|----|-----------------------------|-----------------------------|--------------------------|--------------------------|
| 1  | 200                         | 2.47                        | 0.01                     | 9.32                     |
| 2  | 300                         | 7.21                        | 0.01                     | 4.10                     |
| 3  | 400                         | 5.48                        | 0.01                     | 2.64                     |
| 4  | 500                         | 5.51                        | 0.00                     | 1.25                     |
|    | Control                     | 345.44                      | 0.99                     | 5.72                     |

Figure 2 showed the images of catalyst from rice husk silica taken by SEM. The result showed that the catalyst produced by impregnation using KOH 1 N and various calcination temperatures had accumulated large number of agglomerates on the surface. The impregnation using 1 N KOH could increase particle size of catalyst due to accumulation of potassium. This result has been confirmed in previous study as reported by Mutreja [23]. The impregnation of potassium increase the presence of 85.59% of potassium and 14.41% of silicon demonstrated by SEM-EDX. Guo [21] reported that the loosely attached agglomerated structures can be used to the entry of triglyceride and methanol, so the basic sites of internal surface can also be exploited for the transesterification reaction.
3.2. Biodiesel production

The transesterification process to produce biodiesel in the main study used catalyst 5 wt.% of the palm oil (300 g) according to the result recommended in preliminary study. The amount produced higher yield of biodiesel (89.80 %) compared to catalyst 10 wt.% (78.50%).

Table 3 presented the characteristic of biodiesel produced through the transesterification process using various catalyst from rice husk silica. The catalyst from rice husk silica produced by impregnation of KOH 1N and calcination at 300 °C resulted in the highest methyl ester content (94.39 %) compared to that of other catalysts include KOH (homogeneous base catalyst). Biodiesel produced by this process had total acid number of 0.09 mg KOH/g, total glycerol of 0.57 %, saponification number of 186.76 %, free glycerol of 0.01 %, and moisture content of 650.55 ppm. The yield of methyl ester in this study (Table 3) was still lower than that of palm oil biodiesel catalyzed with rice husk-derived sodium silicate (98.6 %) as reported by Roschat [22]. However, this result was higher than that of biodiesel catalyzed with CaO-ZnO (76.95-84.91 %) as described by Santoso [6]. The physical appearance of the methyl ester produced using various catalyst can be seen in Figure 3.

Table 3. Characteristic of biodiesel produced through the transesterification process using various catalyst from rice husk silica

| Parameters                  | KOH (control) | Calcined at 200°C | Calcined at 300°C | Calcined at 400°C | Calcined at 500°C |
|-----------------------------|---------------|-------------------|-------------------|-------------------|-------------------|
| Methyl ester (%)            | 93.73         | 94.14             | 94.39             | 93.99             | 94.13             |
| Total acid number (Mg KOH/g)| 0.16          | 0.15              | 0.09              | 0.11              | 0.19              |
| Total glycerol (%)          | 0.59          | 0.58              | 0.57              | 0.57              | 0.57              |
| Saponification number (%)   | 173.97        | 182.20            | 186.76            | 174.51            | 181.48            |
| Free glycerol (%)           | 0.01          | 0.02              | 0.01              | 0.02              | 0.01              |
| Moisture content (ppm)      | 753.67        | 700.45            | 650.55            | 713.27            | 883.41            |
In this study, an attempt has been made to utilize rice husk silica as a heterogeneous base catalyst with the impregnation process and various calcination temperatures for biodiesel production through the transesterification process. The crystallinity degree of the catalyst first increased and then decreased with increases in calcination temperatures. The calcination at 300 °C resulted in the highest surface area of the catalyst (7.21 m²/g). The transesterification process using catalyst produced by impregnation of KOH 1N and calcination at 300 °C could result in biodiesel with the highest methyl ester content (94.39 %), the total acid number of 0.09 mg KOH/g, total glycerol of 0.57 %, saponification number of 186.76 %, free glycerol of 0.01 %, and moisture content of 650.55 ppm.

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