Synthesis of silica from rice husk by sol-gel method

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Abstract. Rice husk is an abundant and underutilized agricultural by-product in Indonesia. The silica contained in the waste could be used as a substitute natural silica for various purposes. The extraction of silica from rice husk (RH) has been done using the sol-gel method without involving high energy. Extraction was carried out with KOH at concentrations of 7, 10, and 13% for 90, 120, and 150 minutes. Experimental results showed that the highest extraction yield was obtained at the extraction process using KOH 7% (average 9.03%). The minimum concentration of KOH could produce the maximum yield of silica. Characterization by XRD showed that the silica had the same pattern as that of commercial products and it was categorized as amorphous silica indicated with the broad peaks at 2θ = 22°. Amorphous silica with high purity was produced from rice husk by KOH 7% at 120 min (95.34%). The process condition resulted in high reactivity and a high BET surface area. The washing process needs to be intensified to improve the purity of silica.

1. Introduction
Rice husk (RH) is a by-product of rice milling which amounts to approximately 20% of the weight of unhulled rice. This amount will be abundant in some countries where rice is a staple food of their majority population. Hence, the RH needs to be processed to obtain high added-value products and also to reduce environmental problems due to its presence. In recent years, there have been quite a lot of studies reported on silica extraction from RH to become a solution to the problem of the abundance of this agricultural waste.

Some studies have claimed that RH is agricultural biomass that has a high silica content, namely 15 - 60% [1][2][3]. In its application, silica has many uses in various industries such as an anti-caking agent, beverage purifier, oil refining [4], fertilizer, pharmaceuticals products, detergents, adhesives, electronic semiconductors, catalysts, absorbents, corrosion inhibitors, and optical materials [1][2][5].

Silica obtained by an extraction process from RH combustion has been reported by some researchers [2][6][7][8]. Meanwhile, the combustion process to obtain rice husk ash has a negative impact on the environment due to producing air pollution. On this occasion, we hereby present the information on silica from ‘fresh’ dried RH without the burning process extracted by a sol-gel method with various concentrations of alkali solvent and extraction times. It is a technique which involves the simultaneous hydrolysis and condensation reaction of the metal alkoxide. This method has some advantages such as low-temperature synthesis and control of reaction kinetics by varying the composition of chemicals.
This study aims to investigate the optimum extraction process to produce high purity silica from RH. The properties studied include structure properties, SiO$_2$ content, and Brunauer Emmett-Teller (BET) surface area.

2. Materials and Methods

2.1. Materials
The RH was obtained from PT Jatisari Sri Rejeki rice mill, Jatisari, Karawang, West Java, Indonesia with a moisture content of 5.75%. KOH and HCl used were reagent grade obtained from Merck. Distilled water was applied for all extraction and treatment process. Commercial silica was used as a control.

2.2. Production of silica from rice husk
The preparation of silica was conducted following the procedures that have previously been applied by Sembiring [9]. RH was washed with hot water to remove contaminants of water-soluble organic matters present. The washing process was conducted by soaking RH in hot water (temperature 80°C) for 2 hours and repeated 4 times. RH was then dried at room temperature before the silica extraction process.

The silica from RH was obtained using an alkali extraction method previously reported by Sembiring et al. [10] with some modifications. 50 g dried RH was mixed with 500 ml of 7, 10, and 13 % KOH solution in a beaker glass. The mixture was boiled for 90, 120 and 150 min, and then allowed to cool to room temperature and left for 24 h.

The mixture was filtered to separate the filtrate which contained silica (silica sol). To obtain solid silica, the sol was acidified by adding 10% HCl solution with constant stirring until the mixture was in pH 7 and the sol was converted into the gel. The gel was aged for three days and then rinsed repeatedly with distilled water 7 times to remove the excess acid or until clear sol. The gel was then oven-dried at 110°C for eight hours and then ground into powder using a planetary ball mill. The yield of silica was investigated to determine the optimum extraction process. It can be calculated by the following equation:

$$\text{Silica extraction yield (\%)} = \frac{\text{mass of produced silica}}{\text{mass of RH}} \times 100$$ (1)

2.3. Characterization
The samples were examined using scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray fluorescence (XRF), and Brunauer-Emmett-Teller (BET) surface area analysis. The SEM analyses of the silica from RH 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°. Silica content and metallic impurities were analysed by an Axios mAX WDXRF X-Ray Fluorescence (XRF) Spectrometer (Malvern Panalytical, The Netherland). Surface area, pore volume, and pore diameter of the prepared silica powder was measured using BET surface area analyser (Quantachrome NovaWin, USA).

3. Results and Discussion

3.1. Yield of silica
The yield of silica is shown in Table 1. It varies from 7.60 – 9.75 % and shows no significant difference between each combination of the concentration of KOH and extraction time investigated. This result concludes that the minimum concentration of KOH and extraction time can produce the maximum yield of silica.
Table 1. Silica extraction yield.

| Concentration of KOH (%) | Extraction time (min) | Yield* (%) | Means |
|--------------------------|-----------------------|------------|-------|
|                          | 90                    | 120        | 150   |
| 7                        | 9.05aA                | 8.30aA     | 9.75aA|
| 10                       | 8.55aA                | 8.60aA     | 7.60aA|
| 13                       | 8.50aA                | 8.35aA     | 8.20aA|
| Means                    | 8.70a                  | 8.41a      | 8.52a |

*Means followed by the same capital letters in a column and lower case letters on the lines do not differ significantly by the Duncan test (p < 0.05). *Values are means (n=2).

3.2. The structural features and composition of silica powders

XRD pattern of silica powders produced using various concentration of KOH and extraction times are shown in Figure 1. The XRD pattern of silica powder obtained in this study showed a similar pattern to that of commercial silica. It was categorized as amorphous silica indicated with the broad peaks at 2θ = 22° [11]. This XRD pattern also showed a similar pattern as reported by Setyawan [12]. Various peaks appear, show metallic impurities in obtained silica powder. The presence of impurities can be confirmed by the data shown in Table 2.

![XRD pattern of silica powders](image)

3.2.1. XRF analysis

XRF is used in identifying the chemical compositions and purity of silica powders produced from the RH. Table 2 shows the composition of silica (SiO$_2$) and various metallic impurities. The silica content of the powders produced from RH were from 81.99 – 95.34 %. The silica that was obtained using KOH 7% at 120 min showed the maximum reactivity. Therefore, according to the result of Table 2, the above conditions are suitable for the production of high purity silica (95.34%). This content was almost equal to that of commercial silica (95.37%). Silica was obtained from potassium silicate using a sol-gel method. Mittal [13] reported that the reaction of SiO$_2$ in RH with alkali solution is as follows:

$$\text{SiO}_2 + 2\text{KOH} \rightarrow \text{K}_2\text{SiO}_3 + \text{H}_2\text{O}$$ (2)

To obtain solid silica, the sol was acidified by adding 5% HCl solution until the sol was converted into the gel. This process occurred in pH 7 to obtain silica from potassium silicate by the following reaction:

$$\text{K}_2\text{SiO}_3 + 2\text{HCl} \rightarrow \text{SiO}_2 + 2\text{KCl} + \text{H}_2\text{O}$$ (3)
Table 2. Composition of silica powders.

| Elements | Concentration of KOH 7% | Concentration of KOH 10% | Concentration of KOH 13% | Commercial silica |
|----------|------------------------|--------------------------|-------------------------|------------------|
|          | 90 min | 120 min | 150 min | 90 min | 120 min | 150 min | 90 min | 120 min | 150 min |
| SiO₂     | 94.63  | 95.34   | 93.72   | 94.09  | 92.57   | 94.26   | 94.83  | 91.03   | 81.99   |
| K₂O      | 3.11   | 2.57    | 3.83    | 3.78   | 4.94    | 3.72    | 3.24   | 5.90    | 10.85   |
| Cl       | 0.77   | 1.03    | 1.67    | 1.52   | 1.78    | 1.38    | 0.93   | 2.43    | 6.28    |
| Al₂O₃    | 0.40   | 0.53    | 0.31    | 0.28   | 0.27    | 0.27    | 0.36   | 0.27    | 0.34    |
| ZrO₂     | 0.37   | 0.03    | 0.18    | 0.04   | 0.05    | 0.09    | 0.16   | 0.04    | 0.08    |
| Fe₂O₃    | 0.35   | 0.19    | 0.11    | 0.13   | 0.16    | 0.12    | 0.19   | 0.13    | 0.10    |
| MgO      | 0.12   | 0.08    | NA      | NA     | NA      | NA      | 0.08   | NA      | 0.13    |
| Na₂O     | 0.09   | 0.05    | 0.07    | 0.07   | 0.07    | 0.06    | 0.09   | 0.10    | 0.12    |
| CaO      | 0.06   | 0.04    | 0.04    | 0.02   | 0.03    | 0.02    | 0.02   | 0.02    | 0.03    |
| MnO      | 0.04   | 0.02    | 0.02    | 0.03   | 0.04    | 0.04    | 0.02   | 0.04    | 0.04    |
| P₂O₅     | 0.02   | 0.04    | 0.02    | 0.02   | 0.01    | 0.01    | 0.01   | NA      | 0.01    |

Values are the composition of silica powder analyzed by XRF (n=1)

3.3. Surface area, pore diameter and pore volume

The surface area, pore diameter and pore volume of silica powder extracted with various concentrations of KOH at 120 min (selected due to producing high purity SiO₂) are given in Table 3. The surface area of silica produced using KOH 7 and 10% (281.20 m²/g and 153.95 m²/g respectively) were higher than that of commercial silica. The surface area, pore diameter and pore volume of commercial silica were 143.95 m²/g, 22.7 nm, and 1.63 cm³/g respectively. The surface area of obtained silica from the extraction process using KOH 7% at 120 min was also higher than that of silica produced from RHA (274 m²/g) as reported by Yuvakkumar [14].

Table 3 shows increasing the concentration of KOH resulted in reducing surface area and pore volume and increasing the pore diameter. This phenomenon occurs due to the presence of potassium and other impurities (Table 2) contained in silica powder.

Table 3. Surface area, pore diameter and pore volume of silica powder.

| Samples | Concentration of KOH (%) | Extraction time (min) | Surface area (m²/g) | Pore diameter (nm) | Pore volume (cm³/g) |
|---------|--------------------------|-----------------------|---------------------|-------------------|---------------------|
| 7       | 120                      | 281.20                | 4.580               | 1.58              |
| 10      | 120                      | 153.95                | 9.70                | 0.74              |
| 13      | 120                      | 108.46                | 14.43               | 0.76              |
| Commercial silica | 143.95                   | 22.7                  | 1.63                |

3.4. Morphology of silica powders

The morphology of silica powders are shown in Figure 2. Figure 2 depicts the SEM morphology of the nano-silica. It showed that silica appears agglomerate and is not a single particle. However, the single-particle of silica has spherical shaped with an average particle size of 6 nm as reported by Rafiee [7].
Figure 2. Morphology of silica powders extracted with KOH 7% for 90 min (A), 120 min (B), 150 min (C); KOH 10% for 90 min (D), 120 min (E), 150 min (F); KOH 13% for 90 min (G), 120 min (H), 150 min (I); and commercial silica (CS).

4. Conclusions
The silica extraction process was conducted by the sol-gel method using KOH 7% resulted in maximum yield. Amorphous silica with purity above 95% was produced from rice husk by KOH 7% at 120 min. The process condition resulted in high purity amorphous silica with a high BET surface area.

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