Characterization of Ultrafine Silica Prepared from Rice Husk Ash by Sol-Gel Method

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Abstract. Rice husk ash that is removed from the combustion process in a furnace has a potential for silica source through the sol-gel process. The experiment was conducted in different concentrations of sodium hydroxide solution of 5.0, 7.5, and 10.0 % w/v in the preparation of the sodium silicate solution. For further observation, different pH values of the gel solution were also examined with values of 1 to 7. Particle Size Analyzer (PSA) has been used for size characterization of samples, while Energy Dispersive X-Ray Spectrophotometer (EDS) was used to determine the composition of the powder. The result shows that for all cases the silica products still contain carbon materials. The different pH values of the silica gel solution exhibit a different physical appearance of the gel. At pH values of 5 to neutral 7, the silica gel is completely formed, while in more acidic conditions there are only precipitates or none of both. Mostly, silica particles were in the size of micrometers with more than 90% in the range of 2-128 \( \mu \text{m} \). The composition characterization showed different percentages of silica and the good result was found at 5.0% of sodium hydroxide solution with a gel solution pH of 7.

1. Introduction
Rice is one of the biggest crops in the world. Rice production in Asia is accounted for about 87% of the total crop production in the world [1]. A high number of productions produces a high amount of waste products. In processing, only products that can be used as food are mostly taken. Meanwhile, side product such as rice husk is utilized as animal food or combustion materials. Rice husk contains 15% of silica and 75% of organic compounds [2]. These compounds can be processed to become more profitable materials.

Mostly, the purpose of synthesis silica is to produce fine silica in the dimension of micro and nanometer. The silica with high surface area and porosity is useful for various applications. Silica is widely applied as fertilizer [3], drug delivery [4], adsorption of \( \text{CO}_2 \)-containing gas mixtures [5], lithium-ion batteries [6], heavy metals adsorption [7], etc. In general, rice husk as a silica source was taken directly from the rice mill and then treated using the calcination process to obtain rice husk ash [8-9]. Silica contents in rice husk ash can reach up to 90%. In some reports, the rice husks are leached with acid before calcinations to remove dirt and other contaminants [10-11]. Nguyen et al. then continued the process with the sol-gel method to obtain fine high purity silica [12]. However, the utilization of rice husk as a fine silica source will consume a long step from the calcinations to the extraction process.

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In this research, rice husk that has been burned from the furnace pottery industry is used as a source of ultrafine silica. Besides, with rice husk ash as a source, the calcinations process is not required before silica extraction. Silica from rice husk ash was extracted using the sol-gel method because of its simple process and low energy requirement. The size, composition, and physical appearance of the silica that has been successfully synthesized were observed. Silica synthesis using rice husk as a source can become a solution to the management of natural resources and agricultural wastes.

2. Method

2.1. Materials
Rice husk ash (RHA) was obtained from the pottery industry located at Depok, West Java, Indonesia. The sol-gel method was executed using sodium hydroxide (NaOH) and hydrochloric acid (HCl). The materials used are technical grade (Semarang, Indonesia) without further purification.

2.2. Synthesis of Ultrafine Silica
The overall steps of ultrafine silica powder preparation are shown in Figure 1. RHA was continuously mixed and boiled in different concentrations of NaOH solution (5.0, 7.5, and 10.0% w/v) for 90 minutes at 90°C. The ratio of RHA and NaOH solution was maintained constant at 1:6 (mass to volume). The mixture then cooled down to room temperature and filtered to separate the sodium silicate solution and the remaining RHA residue. The residue was used again in the mixing process with NaOH solution until the filtration process.

Silica gel was obtained by neutralizing sodium silicate solution using HCl. The solution was titrated slowly drop by drop by hydrochloric acid in the concentration of 1 N while being stirred continuously. The solution was made at several values of pH 1 to neutral 7. This process result is a reaction of

\[ Na_2SiO_3(l) + 2HCl (l) \rightarrow SiO_2(gel) + 2NaCl (s) + H_2O(l) \]  

(1)

The gel was transferred to a closed jar and aged at room temperature for 18 hours. The silica gels were filtered and washed with distilled water several times to obtain clear gels. The gels were collected and dried 80°C for 18 hours to produce white silica solids. The solids were pulverized to powder using a mortar and screened through test sieve 200 mesh to obtain the micrometer size silica grains.

Figure 1. Schematic procedure of preparation ultrafine silica powder
2.3. Characterization
Particle size analysis was conducted using Laser Size Testing Report LLPA C-10 with a light source of He-Ne Laser ($\lambda=632.8$ nm) at an accuracy of <1% and range of measurement of 0.01-2000 micrometer. The composition characterization was evaluated using energy-dispersive X-ray spectroscopy (EDS, JEOL Ltd.).

3. Results

3.1. Physical appearances
Figure 2 represents the physical appearance of a sodium silicate solution (a) and formed gel at different pH values ((b) to (d)). Filtrates from the extraction step were yellowish transparent color sodium silicate solutions, while some research reported the solutions are transparent colorless [13-14]. The biggest possibility of yellow color is obtained from impurities from pottery clays and other impurities that were burned with rice husk ash and the use of technical grade materials. In the silica gel production step, different pH values from 1 to 7 have been examined to study the appearance of formed gel products. For pH above neutral, gels are hardly formed. In addition, Table 1 shows the appearance of different formed gel and solutions after the sol-gel process using hydrochloric acid. It is shown that different pH values, in conjunction with alkali solution concentration contributed to the forming silica gel. In a lower pH value, the gel formation is slow due to the conversion of siloxane (Si-O-Si) to silanol bonding (Si-O-H) and resulting in the composition of smaller silica primary [15]. Based on the reaction (1), acids donated the hydrogen ions to sodium silicate solution to produce a water component of silica gel product. When the moles of hydrogen increased, while oxygen and silicon were at the same amount, the remaining hydrogen ions bonded with silicon and oxygen bonding and formed the Si-OH bonding.

![Figure 2. Physical appearance of (a) sodium silicate solution and formed gel at pH (b) 4, (c) 5, and (d) 7 in the concentration of NaOH solution of 5%.](image)

| NaOH solution concentration (%) | pH value | Appearance |
|---------------------------------|----------|------------|
|                                 |          | Gel        | Precipitate |
| 10.0                            | 1 - 5    | No         | Slightly    |
|                                 | 6 - 7    | Yes        | No          |
| 7.5                             | 1-6      | No         | Many        |
|                                 | 7        | Yes        | No          |
| 5.0                             | 1-4      | No         | No          |
|                                 | 5-7      | Yes        | No          |
3.2. Particle size analysis

Figure 3 shows the particle size distribution of the prepared silica samples. The volume of each particle size is displayed by red square charts and the scattered curves show the cumulative particle size distribution. Slightly observed, the distribution of particle size of each sample is uniform with a maximum range of 2-400 μm, except for RHA that detected only until below 300 μm. In detail, the particle size range, mean, and the particle sizes bigger than 10, 50, and 90 weight percentiles (referred to as $d_{10}$, $d_{50}$, and $d_{90}$, respectively) were represented in Table 2.

![Figure 3](image_url)

**Figure 3.** Particle size distribution of (a) rice husk ash and silica at difference concentrations of NaOH solution of (b) 10%, (c) 7.5%, (d) 5% (gelation pH of 7), and (e) 5% (gelation pH of 5).
Table 2. Particle size range, mean, and the particle sizes bigger than 10, 50, and 90 weight percentiles

| Sample                        | Particle size range (μm) | Mean (μm) | d_{10} (μm) | d_{50} (μm) | d_{90} (μm) |
|-------------------------------|-------------------------|-----------|-------------|-------------|-------------|
| Rice Husk Ash                | 15.2-373.4              | 115.8     | 51.4        | 81.2        | 128.3       |
| 10.0% NaOH at gelation pH 7   | 2.1-932.6               | 160.4     | 20.6        | 51.4        | 128.3       |
| 7.5% NaOH at gelation pH 7    | 3.8-687.4               | 138.1     | 27.9        | 59.8        | 128.3       |
| 5% NaOH at gelation pH 7      | 7.1-506.6               | 122.0     | 37.9        | 69.7        | 128.3       |
| 5% NaOH at gelation pH 5      | 6.1-506.6               | 118.1     | 37.9        | 69.7        | 128.3       |

In contrast with the pulverizing process, which using sieve 200 mesh (75 μm), while still many particles were detected more than that. This is probably due to particle agglomeration when stored before characterization and a small mass of bulk silica particles. In the 10% NaOH solution treatment, the mean of particle size obtained is the highest among others because of the broad particle size range. This result is similar to previous observations in the sieving process that large particle size intervals produce a large mean particle size [16, 17]. The other reason for this large particle size obtained is the presence of irregular dimensions, such as a rod-like shape that can pass transversally through the sieve pores [18]. However, according to fineness powder classification, these results exhibit up to 90% of very fine powder (<125 μm), under 10% ultrafine powder (<30 μm) for the treatment with 5.0% NaOH solution, and up to 10% ultrafine powder for the treatment with 10.0 and 7.5 % NaOH solution [19, 20].

3.3. Composition characterization (energy-dispersive X-ray spectroscopy analysis)

The composition of rice husk ash before synthesis treatment is shown in Figure 4. The result confirms the content of silicon (Si) and oxygen (O) in the percentage of 4.78 and 59.75%, respectively. Further composition analysis using stoichiometry of silica (SiO₂) shows a low amount of silica, and the remaining oxygen atoms are in charge of a high percentage of impurities, including Mg, P, and K. The EDS analysis of the synthesized silica is provided in Table 3. It is observed that carbon components still become a major impurity of samples, and others are components from the process, such as Na from NaOH in the extraction process and Cl from HCl in the gel formation process. The fractions of carbon components are decreased by decreasing the concentration of the NaOH solution in the sol-gel process. Major carbon composition indicated the possibility that chemical treatment did not completely dissolve silica in the rice husk ash. However, EDS only analyzes the surface of samples, so that the surface of the synthesized samples contains a large amount of carbon and did not reach the remaining silica compounds that placed not on the surface [21]. Interestingly, the sample treated using 5% NaOH solution concentration with different pH values shows a different percentage of components. In the pH value of 7, the silica content is higher than in the pH value of 5. This case is in agreement with the previous discussion in the physical appearance of gel that in the more acidic region, silica gel was hardly formed.
Figure 4. The EDS analysis of Rice Husk Ash before synthesis treatment

Table 3. The EDS analysis of silica samples prepared by the sol-gel method from rice husk ash

| Compound (mass%) | NaOH solution concentration (%) |
|------------------|----------------------------------|
|                  | 10.0 at gel pH 7 | 7.5 at gel pH 7 | 5.0 at gel pH 7 | 5.0 at gel pH 5 |
| C                | 64.25            | 47.62           | 22.50           | 34.43           |
| SiO₂             | 19.30            | 11.08           | 33.53           | 26.03           |
| Na₂O             | 9.27             | 21.02           | 22.88           | 16.35           |
| Cl                | 0.00             | 20.28           | 21.10           | 23.18           |

4. Conclusion
Silica from rice husk ash has been successfully synthesized through a sol-gel method using different concentrations of sodium hydroxide solutions. Further study was conducted using different pH values in the gelation process with hydrochloric acid. At pH values of 1 to 7, different results from different concentrations of NaOH solution were found. The silica gels were formed at pH values of 6-7, 7, and 5-7 for the concentration of NaOH solution of 10.0%, 7.5%, and 5%, respectively. The result of energy-dispersive X-ray spectroscopy analysis shows that for all cases the silica powder products still contain carbon materials and impurities. From the analysis of particle size, 90% of the products are in the range of very fine powder, while more than 10% are ultrafine powder. However, the particle size ranges still exhibit several large particles more than the size of the sieving mesh (75μm). Observations with other characterizations such as imaging are needed to see the surface morphology of silica due to the absence of large particle size and probably a rod-like particle shape.
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