Recovery of silica and carbon black from rice husk ash disposed from a biomass power plant by precipitation method

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Abstract. In Thailand, air pollution caused by rice husk ash (RHA) disposed of biomass power plants has become more serious concerns. Recovery of silica and carbon black from RHA is an attractive solution to solve this problem. This study aims to extract silica and carbon black from RHA, which was burnt in a stoker firing at 800 – 850 ºC, by a precipitation method. RHA was dissolved in 2M sodium hydroxide at 105 ºC for 2 – 5 h. After that, carbon black was filtered out from sodium silicate solution. The solution was then precipitated by sulfuric acid to produce precipitated powder. The extraction parameters such as types of RHA (fly ash and bottom ash), dissolution time and precipitation time were studied. The precipitated powder was characterized by XRF for elemental analysis, XRD for crystallinity and BET for porosity analysis. The results showed that dissolution for 4 h and precipitation for 1 h could produce precipitated amorphous silica with the purity of 95–99 % SiO₂. The yields of silica extracted from bottom ash and fly ash were 85.66 wt% and 72.33 wt%, respectively. The yields of carbon black extracted from bottom ash and fly ash were 14.34 wt% and 27.67 wt%, respectively. The surface area of silica extracted from fly ash (410.72 m²/g) was higher than that of the silica extracted from bottom ash (296.98 m²/g).

1. Introduction

In Thailand, there are 178 biomass power plants. Common biomass fuels are rice husk, bagasse, and palm husk. Rice husk accounted for 15% of total biomass used in the power plants or about 8.1 Mt/year [1]. After combustion, 30% of rice husk is disposed of as rice husk ash (RHA). Some RHA is utilized for soil amendment. However, RHAs are mostly dumped in landfill. Particulate matters (PM) from RHA cause adverse impacts on air quality in the area nearby power plants. Thus, proper RHA management and RHA utilization would be alternative ways to reduce the environmental impacts from RHA. RHA contains silicon dioxide (SiO₂) approximately 60 – 80 percent which can be utilized as a silica source for various industries such as cement, ceramic, glass, paint, rubber etc. [2-6]. Apart from silica, carbon black can be separated from RHA during the process of silica extraction. Carbon black can be utilized as adsorbents, fillers, reinforcing materials etc.

Many researchers reported silica extraction methods from RHA. Sinyung et al. [7] extracted silica from rice husk ash (RHA) by precipitation. Rice husk ash (RHA) was pretreated with hot HCl and washed with distilled water. Then, it was dissolved in 1.5 M NaOH solution with a solid/liquid ratio (S:L) of 1:6 and constant stirring at 100 ºC for 1 h. This sodium silicate solution was adjusted to pH 7 by adding 1 M HCl and then the gel was cured at 50 ºC for 12 h. After that, the gel was centrifuged, washed with distilled water to remove salts and dried at 80 ºC for 48 h. The silica obtained from RHA...
contained 98.90% of SiO$_2$ and had a surface area of 312.4 m$^2$/g. Kalapathy, et al. [8] produced SiO$_2$ xerogel from rice husk ash by dissolving in 1 N sodium hydroxide for 1 h. The filtrates were titrated with 1 N HCl with constant stirring to pH 7 and aged for 18 h. Then, the gels were dried at 80°C for 12 h to produce xerogels. Xerogels produced from RHA contained 93% SiO$_2$ and 2.6% moisture. Loui, et al. [9] also used precipitation technique to extract silica from RHA. The optimum condition for sodium silicate preparation was soaking RHA in 1.5 M NaOH with the aging time of 12 h at pH 3. After that, sodium silicate was precipitated by 1 M hydrochloric, sulfuric, citric and oxalic acid. The purity of silica obtained from hydrochloric was 99.48% and its surface area was increased to 350 m$^2$/g, higher than sulfuric (89.39%, 319 m$^2$/g), citric (99.64%, 285 m$^2$/g) and oxalic acid (95.05, 313 m$^2$/g). According to the literature, it is observed that hydrochloric and sulfuric acid is commonly used for silica precipitation. For scale-up purpose, sulfuric acid is more preferable because it is compatible with common stainless steel. No special stainless equipment is needed. Moreover, the prices of both acids are similar.

Thus, this study aimed to extract silica and carbon black from RHA by dissolution with 2 M NaOH followed by precipitation by sulfuric acid. The effects of RHA type, dissolution time and precipitation time on the yields and properties of silica and carbon black were studied. The outcome of this study would be an alternative way to reduce the environmental impacts of RHA and produce value-added silica from RHA waste.

2. Materials and Method

2.1. Materials and Chemicals

The rice husk ash (RHA) samples used in this study were obtained from a biomass power plant in Nakhon Pathom Province. Rice husk was burnt in a stoker firing at 800 – 850 °C and then RHA was produced. Sodium hydroxide (Univar), sulfuric acid (QRëC), distilled water, paper filter (Whatman) were used for silica extraction.

2.2. Silica and carbon black extraction

RHA was dissolved in 2 M sodium hydroxide at 105 °C for 2 – 5 h with continuous stirring. After that, carbon black was filtered out from the sodium silicate solution. Then, silica gel was precipitated by adding conc. sulfuric acid into sodium silicate solution. The mixed solution was aged for 1 and 6 h. After that, the gel was washed by hot deionized water to remove soluble salts. The conductivity meter was used to detect the remaining salt after washing. The precipitated gel was dried at 105 °C for 12 h and ground to produce precipitated powder. The silica extraction was described as follows:

\[
\text{Rice husk Ash} + 2\text{NaOH} \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O} + \text{Carbon Black}
\]

(1)

\[
\text{Na}_2\text{SiO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{SiO}_2 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}
\]

(2)

2.3. Characterization of silica powder

The precipitated powder was characterized by X-ray Fluorescence Spectrometer (XRF) for elemental analysis, X-ray Diffractometer (XRD) for crystallinity, Brunauer–Emmett–Teller (BET) method for porosity analysis and the yields of silica and carbon black extraction were calculated by the following equation (3).

\[
\text{Extraction yield} = \left(\frac{\text{Mass of produced silica/carbon black}}{\text{Mass of RHA}}\right) \times 100
\]

(3)
3. Results and discussion

3.1. Effect of dissolution time on the yield of silica

Figure 1 shows the yield of silica extracted from RHA (bottom ash). The maximum yield was 88.33% for 5 h. However, this study selected the dissolution time of 4 h has a promising condition due to no significant difference found between the yields obtained from the dissolution time of 4 and 5 h. The yield of carbon black was 57.67%, 28.67%, 14.34% and 11.67% respectively.

The yields of silica extracted from bottom and fly ash with the dissolution time of 4 h were presented in Figure 2. The yields of silica extracted from bottom ash and fly ash were 85.66 wt% and 72.33 wt%, respectively. The yields of carbon black extracted from bottom ash and fly ash were 14.34 wt% and 27.67 wt%, respectively. These results are in accordance with the XRF results as discussed later.

Figure 1. The effect of dissolution time on the yield of silica extracted from RHA (bottom ash).

Figure 2. The yields of silica extracted from fly ash and bottom ash by the precipitation with the dissolution time of 4 h and the precipitation time of 1 h.
3.2. Effect of precipitation time on the yield of silica

Figure 3 shows the yield of silica extracted from RHA (bottom ash) with the precipitation time of 1 and 6 h. The yields of silica extracted from 1 and 6 h were 85.66 wt% and 87.67 wt%, respectively. It was noticed that there was no significant difference found between the yields obtained from the precipitation time of 1 and 6 h. This might because the precipitation was completely finished within 1 h. Thus, the precipitation time of 1 h was recommended for silica extraction.

![Figure 3](image_url)

**Figure 3.** The effect of precipitation times on the yield of silica extracted from RHA (bottom ash).

3.3. Elemental analysis

Table 1 shows the chemical characterization of RHA (bottom and fly ash) and the extracted silica. Major composition found in both bottom and fly ash was SiO$_2$ (80-95%). Common trace elements in RHA were K$_2$O, P$_2$O$_5$, CaO, SO$_3$, MgO, Fe$_2$O$_3$, CuO and MnO. After extraction, the content of SiO$_2$ was increased to 99% and the content of Na$_2$O was increased significantly due to the remaining sodium salt during precipitation.

| Composition | RHA (fly ash) | RHA (bottom ash) | Silica (Fly ash) | Silica (Bottom ash) |
|-------------|---------------|------------------|------------------|---------------------|
| SiO$_2$     | 80.20         | 95.10            | 99.3             | 99.4                |
| Na$_2$O     | ND            | ND               | 0.138            | 0.205               |
| K$_2$O      | 5.67          | 1.75             | 0.0695           | 0.531               |
| P$_2$O$_5$  | 3.89          | 0.942            | ND               | ND                  |
| CaO         | 1.67          | 0.885            | 0.0661           | 0.0686              |
| MgO         | 0.886         | 0.412            | ND               | ND                  |
| Al$_2$O$_3$ | 0.814         | 0.254            | 0.125            | 0.196               |
| SO$_3$      | 4.75          | 0.0917           | ND               | ND                  |
| Fe$_2$O$_3$ | 0.761         | 0.216            | 0.0203           | 0.0235              |
| Cl           | 0.629         | 0.0508           | ND               | ND                  |
| MnO         | 0.323         | 0.155            | 0.0223           | ND                  |
| ZnO         | ND            | ND               | 0.00327          | 0.0107              |
| CuO         | ND            | ND               | 0.00487          | 0.00518             |
| ZrO$_2$     | ND            | ND               | ND               | 0.00216             |
3.4. Crystallinity of the extracted silica
X-ray diffraction patterns of silica extracted from the bottom and fly ash were shown in Figure 4. The broad diffraction peak at 2 theta degree of 22 – 23 was attributed to amorphous silica [2]. It was found that our extracted silica from both bottom and fly ash was amorphous silica, similar to Kalapathy, et al. [8].

![X-ray diffraction patterns of silica extracted from the bottom and fly ash from this study (A) compared with that of Kalapathy, et al. [8] (B).](image)

3.5. Porosity of the extracted silica
The porosity of silica extracted from fly ash (SF) and bottom ash (SB) with the precipitation time of 1 h and 6 h was presented in Table 2. The appearance of fly ash before the extraction was fine particles and its particle size was much smaller than that of bottom ash. After extraction, the surface area of SF1 was the largest (410.72 m²/g), followed by SB1 (296.98 m²/g) and SB1 (176.51 m²/g). The surface area of SF1 and SB1 was larger than that of commercial silica. According to Thai industrial standards of silicon dioxide for rubber industries (TIS No.1070-2547), the extracted silica from this study could be applied as an additive in the rubber industry.
Table 2. BET surface area, pore size and pore volume of silica extracted from fly ash, bottom ash, commercial silica, and silica for rubber industries

| No. | Samples                      | BET Surface area (m²/g) | Total Pore volume (cm³/g) | Average Pore Size (nm) | SiO₂ purity (%) |
|-----|------------------------------|--------------------------|---------------------------|------------------------|-----------------|
| 1   | SF1                          | 410.72                   | 0.8070                    | 7.859                  | 99.3            |
| 2   | SB1                          | 296.98                   | 0.5699                    | 7.676                  | 99.4            |
| 3   | SB6                          | 176.51                   | 0.4730                    | 10.719                 | 99.1            |
| 4   | Commercial silica [10]       | 175 – 225                | ND                        | ND                     | 99.8            |
| 5   | Silica for rubber industries [11] | 110 – 240               | ND                        | ND                     | 98              |

4. Conclusions
This study investigated silica and carbon black extraction from RHA by precipitation and studied the effects of RHA types, dissolution and precipitation time on silica yields and silica properties. Silica was successfully extracted from both bottom and fly ash by precipitation method. The optimum dissolution time and precipitation time were 4 h and 1 h, respectively. The yields of silica and carbon black were 85% and 14%. After extraction, the purity of SiO₂ was increased significantly up to 99%. The extracted silica was the amorphous phase and had large surface area compared with commercial silica and silica for rubber industry. Thus, the process of silica extraction proposed from this study would be beneficial for RHA utilization. Not only solving ash disposal problem, but also adding value to RHA waste.

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