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Lydia Anggraini ✉; Putri Laila Anggraina; Temmy Wikaningrum



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Biosilica Forming by Sol-Gel Extraction Method of Rice Husk Ash

Lydia Anggraini^{1, a)}, Putri Laila Anggraina^{2, b)} and Temmy Wikaningrum^{2, c)}

¹Study Program of Mechanical Engineering, President University, Cikarang, Bekasi, West Java, Indonesia

²Study Program of Environmental Engineering, President University, Cikarang, Bekasi, West Java, Indonesia

^{a)}Corresponding author: lydia.anggra@president.ac.id

^{b)}putrianggraina@president.ac.id

^{c)}temmy@president.ac.id

Abstract. Indonesia, as an agricultural country, produces much waste, especially from rice husk, which is a source of silica (SiO₂) production. Rice husk contains about 87% - 97% SiO₂ after complete combustion. SiO₂ extraction from ash of rice husk is carried out using an extraction process of solid-liquid with an alkaline as a solution solvent. The solid-liquid extraction process was done with 10 grams mass of rice husk ash added with 80 ml of potassium hydroxide (KOH) solution with a concentration of 10%, 15%, and 20% to extract the SiO₂ content with an operating time of 60 minutes. After the extraction process is complete, the solution is added with 1 N hydrochloric acid (HCl) to precipitate the SiO₂. The SiO₂ formed is then separated from the rest of the solution by filtration. The drying process is carried out to remove the moisture content of the resulting SiO₂. In this systematic study, HCl-washed rice husks were carried out in a muffle furnace for 60 minutes. The results showed that the samples produced SiO₂ with a polycrystalline structure, as confirmed by the results of analysis of the Energy-Dispersive X-ray Spectroscopy (EDS) that could be produced by solid-liquid extraction of KOH from rice husks ash. The amorphous SiO₂ has potential application as natural filler in rubber and environmentally friendly natural compounds.

INTRODUCTION

Recently, waste has become a new problem all over the world. Indonesia is one of the countries that face this problem. Many types of waste generate in Indonesia. As one agricultural countries, a rice husk as using a Silica (SiO₂) source is produced. Figure 1 shows the list of countries which produced milled rice in 2019/2020. Indonesia is in the third position to produce 34.7 million metric tons the milled rice after China and India. Meanwhile, more than 75% rice-growing countries, and more than 97% of husks are produced by developing countries [1, 10–17]. Rice is the basic staple food for Indonesians, which is also in line with the increase in staple food production in the other agricultural countries. The planted area expansion was measured with range from 11.786.400 to 14.116.600 ha in 2006 to 2015, respectively, with a 19.77% expansion rate, which is driven by increased rice production. Rice production was 54.459.900 and reached 75.397.800 tons in 2006 to 2015, with a 3.84% production rate per year [2]. On average, the top 10 rice producers from 2016 to 2019, Indonesia ranks third in the world as a rice-producing area, after China and India. China ranks first with an average rice production exceeding 211,378,225 tons, followed by India with 171,140,232.5 tons. Indonesia is in third place with increasing rice production, with annual rice production exceeding 58,156,641.75 tons in 2019 [3].

In addition to rice producing, rice husks also produced as a by-product. Dry milled rice is produced as 80 million tons in Indonesia per year in 2017, moreover, there are around 16 million weight tons of rice husks per year. The rice husks composition is controlled on the rice variety, situation of geographic and fertilizer type. Organic components can be converted into 20 percent of carbon dioxide, air, and ash via rice husks burn. The rice husk ash main component consists of 90-98 percent SiO₂, and Indonesia will produce 3.2 million tons of SiO₂ from rice husk ash per year [4].

In all rice-producing countries, considered waste material is rice husk. Many husks of rice usually disposed of or burned in open fields. This can cause disturbance of the soil and pollution in environmental. Many attempts to utilize rice husks have been made, as well as SiO₂ [5]. After complete combustion, one of the primary sources of SiO₂ production is rice husk, 87–97%. SiO₂ ash is formed from ash of rice husk by controlled combustion at 500–600°C of high temperatures, which various chemical processes can be used [6]. SiO₂ is a compound of silicon dioxide that can be used in a variety of ways, is a significant standard material in the glass, ceramics, refractories industry, and for the manufacture of solutions of silicates, silicon, and their alloys is an essential raw material.

On the other hand, previous researchers (Kalapathy et al. in 2001, Pandiangan et al. in 2008, and Suka et al. in 2008) have researched SiO₂ extraction with alkaline solvents and SiO₂ deposition with acid [7–9]. Kalapathy et al. was examining the SiO₂ extraction from rice husks using sodium hydroxide (NaOH) for 1 N with an extraction method of two-cycle and yielded 91% yield at 2001 [7]. Pandiangan et al. was research the SiO₂ extraction from husks of rice using various concentrations of potassium hydroxide (KOH) solution and 10% nitric acid (HNO₃) solution as a trigger in 2008, and obtained from 50 grams of rice husk ash, the most enormous 1.8690 grams yield mass at a solution concentration of KOH, 1.5% for 30 minutes [8]. Another study conducted by Suka et al. was obtained the highest yield of 40.8% with the use of 5% KOH solvent with a reaction time of one hour in 2008 [9].

The purpose of this study was to confirm the conditions of the extraction process of rice husk ash into SiO₂ with different extraction times and concentrations of KOH and identify the formation of SiO₂ gel. The synthesis of SiO₂ gel by the extraction method is influenced by the concentration of the solvent, both acid and base. Generally, the acid solvents used such as sulfuric acid, hydrochloric acid, and nitric acid as inorganic acids. Furthermore, the reaction time and temperature also affect the microstructure and purity of the SiO₂ gel produced. The result of SiO₂ was confirmed through a sol-gel process with the influence of KOH concentration.

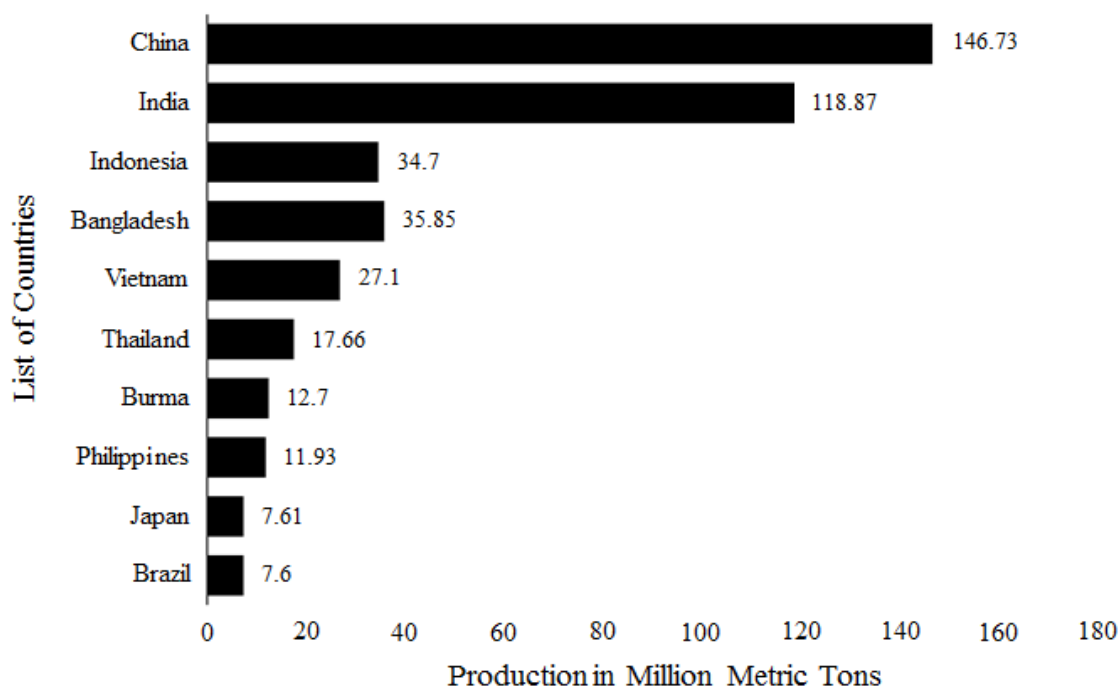


FIGURE 1. List of countries based on the production of milled rice in 2019/2020 [1].

EXPERIMENTAL PROCEDURES

Rice husk ash with a mass of 10 g is used in this study. Meanwhile, as a mixture in the manufacture of 1N Hydrochloric acid (HCl) and KOH solvents, the neutral acid of SiO₂ gel is using the aquadest (H₂O). Solid KOH is used itself, which is dissolved using H₂O in specific ratios into various concentrations of 10%, 15%, and 20%. HCl is used at a concentration of 37% for 1 N. The rice husk ash main components are shown in Table 1.

An Erlenmeyer tube is used in this study as a container for liquid chemicals in the form of laboratory glassware. In addition, this glass is also often used for the titration process to accommodate the solution to be used. Measuring cups are also used as a tool to measure the volume of a solution or liquid that looks like a funnel or glass that has a volume size that varies in milli litre (ml). To obtain the homogeneous solution, the hot plate magnetic stirrer is also used to heat and stir the solutions with a stirring rod. In the heating process, a furnace is used, which is a tool commonly used to extract metals from ores or smelters or in oil refineries and other chemical plants, as well as other applications as a heat source for fractional distillation pipes. Moreover, the oven is also used to heat or dry the sample. Meanwhile to dry glassware in the laboratory, chemicals and organic solvents can be used in the oven before the equipment is used, as well as for wet materials. In addition, the oven is also used for dry air sterilization. This sterilizer is used to sterilize glassware such as Erlenmeyer tubes, Petri-disks or Petri dishes, test tubes, and other glasses. To smooth or crush coarse particles is use a mortar and pestle. The mortar is the part of the container, while the pestle is the part of the stem held in place. The grinding duration depends on the type of material and the strength of the grinder. A digital scale is used for measuring the weight or mass of materials. The glass spatula is used to pick up solid or powder chemicals at the time of weighing. In addition to picking up chemicals, another function of the spatula is used to stir the mixture in a solution.

TABLE 1. The main component in the rice husks

| Component | Content (% weight) |
|---------------------|--------------------|
| Water content | 9.0 |
| Crude protein | 3.0 |
| Fat | 1.1 |
| Crude fiber | 32.6 |
| Ash | 20.3 |
| Crude Carbohydrates | 13.7 |
| Carbon (Charcoal) | 20.3 |

The various ratio of alkaline solvent KOH is used for 10%, 15%, and 30% with an extraction time of 60 minutes. The particle size is 100/80 mesh, the ash weight is 10 g, the extraction temperature is 90°C, the acid solvent type of HCl 1 N is chosen with the mixing speed of 100 rpm. The research procedure's step by step is as follows; first 5 kg of rice husk charcoal is used, followed by a pound with a pestle until smooth. The husk charcoal that has been pounded is followed by a filter using an iron sieve measuring 60 meshes. Rice husk charcoal with 500 g mass is put into the furnace. The heating process of the rice husk charcoal is carried out at 700°C furnace temperature for 4 hours, until the ash form. The ash result is pounded using a pestle, followed by filter using a 100-mesh sieve.

In addition, the SiO₂ Extraction Process is started by a 10 g mass of dry rice husk ash to be dissolved in 80 ml of KOH with concentrations (10%, 15%, and 20%). The heating process is carried out using a hot plate at a temperature of 85°C with a magnetic stirrer for a 60 min time. After cooling, filter paper is used to filtered the solution to separate the residue and filtrate. The resulting filtrate is taken.

The process of making SiO₂ gel is as follows first is 30 ml of potassium silicate solution is prepared into a breaker glass. The second is gently dropping the potassium SiO₂ solution with 1N HCl solution while magnetic stirrer used to stirring until a white gel with a neutral pH is formed. Let the gel that has formed at room temperature for 18 hours. The third is to filter, rinse the SiO₂ gel, and to remove excess acid with distilled water. Fourth, dry the SiO₂ gel in an oven at 120°C until the weight is constant, then crushed with a mortar. Last is filtering with 40 mesh, and SiO₂ gel was obtained. The basic characteristic of dry rice husks and husk ash available in some areas in Indonesia, are shown in Table 2 [10]. In this basic chemical compositions, some elements i.e. Al₂O₃ or ZnO are not detected at very old technology when it used.

TABLE 2. Chemical compositions of dry rice husk and husk ash basis (%) [10]

| Content (origin) | Ash | SiO ₂ | CaO | MgO | Fe ₂ O ₃ |
|----------------------------|--------|------------------|-------|-------|--------------------------------|
| Rice Husk (Karawang) | 25.486 | 22.785 | 1.24 | 1.02 | 0.40 |
| Rice Husk (Tangerang) | 20.359 | 17.559 | 0.141 | 0.033 | 0.091 |
| Black Husk Ash (Karawang) | 33.572 | 31.189 | 0.433 | 0.137 | 0.315 |
| Black Husk Ash (Tangerang) | 33.555 | 30.822 | 0.504 | 0.115 | 0.342 |
| White Husk Ash (Karawang) | 99.095 | 91.306 | 0.759 | 0.164 | 0.572 |
| White Husk Ash (Tangerang) | 98.097 | 90.703 | 0.914 | 0.190 | 0.571 |

RESULTS AND DISCUSSIONS

Extraction is the process of separating a mixture using solvents. Solid-liquid extraction is the type of extraction used in this research. Solid-liquid extraction is a process that involves a mass transfer in between the phases. In this case, the rice husk ash acts as the solid phase and the KOH as the extractant. In extraction of solid-liquid, when mixing the extractant with the extracted material, the solid will react with the extractant to form an extract. In the solid-liquid extraction process, a very long reaction between the extractant and the solid is required. SiO₂ contained in rice husk ash is recovered by dissolving it in an alkaline solution. The reaction that occurs is between SiO₂ contained in rice husk ash and an alkaline solution. In this case, the KOH solution is occur on the reaction (1).



The SiO₂ compound formed is still in the form of a potassium silicate solution. Then the solution is added with 1 N HCl, which is used to bind potassium to produce SiO₂. The reaction that occur is described in the reaction (2). Figure 2 and 3 are shows the burning rice husk charcoal before and after entering into a furnace, respectively.



The result of dried coarse SiO₂ which generated from the rice extraction using the hydrochloric acid solution is shown in Fig. 2. The function of HCl is as a precipitation agent. SiO₂ compounds are easy to solve in alkaline conditions and will settle in an acidic atmosphere [7]. Based on this, to create SiO₂ compounds easily extracted from rice husks, an alkaline solvent, KOH solution, is used, and after that, an acid solution, 1 N HCl, is used to precipitate it again. After the SiO₂ compound are-settled, by drying in an oven, can be removed, the H₂O levels which affect the product moisture. In this process, SiO₂ deposits produced still contain a lot of coprecipitation. The following figure shows the stages of forming the extracted SiO₂ gel as shown in Figure 2.

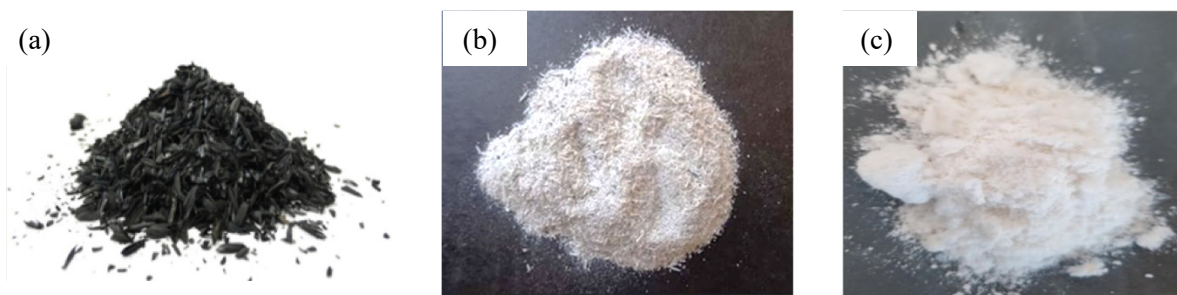


FIGURE 2. Step by step of SiO₂ forming. Burning rice husk charcoal (a) before furnace treatment, (b) after furnace treatment, and (c) dried coarse silica precipitate after sol-gel extraction

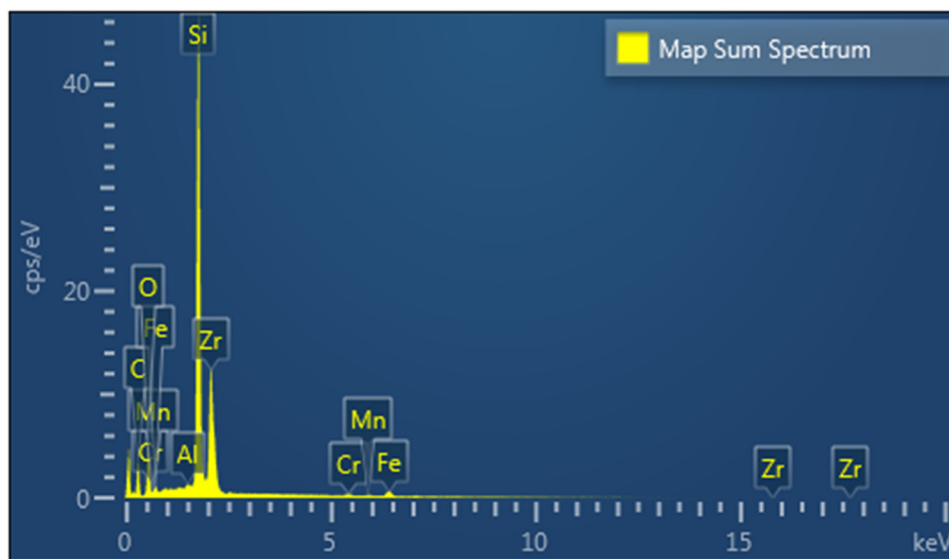
By various KOH concentrations and times are examined to obtain the sol-gel SiO₂, through the husk ash extraction process. It was obtained that there is a slight difference the density of SiO₂ gel with various in extraction times and KOH concentrations, from the results of this study. Factors that affect the density is due to extraction include the size of the material particle. The smaller size results of the particle, has resulted in the contact area larger between the solvent and the solid. The extraction temperature is also has slight affects on the density yield. The solubility of the extracted material and its ability to diffuse will increase with increasing temperature. However, too high a temperature can damage the extracted material, so the optimum temperature is used.

Energy Dispersive X-ray Fluorescence (XRF) is used to identify the purity of SiO₂ and the chemical composition, which is produced from the rice husk ash. Table 3 shows that contains a small number of metallic impurities and SiO₂ is the main component. It notice that KOH extraction was effectively removed metal impurities in rice husk ash. The other elements is appear such as MgO, P₂O₅, SO₃, and K₂O due of the effect during the extraction process or the possible contamination. Therefore, more specific analysis is done using the Energy-Dispersive X-ray Spectroscopy (EDS).

TABLE 3. Elements of SiO₂ in the KOH sol-gel extraction result

| Elements (%) | 10% KOH | 15% KOH | 20% KOH |
|--------------------------------|---------|---------|---------|
| SiO ₂ | 85.663 | 88.487 | 90.078 |
| MgO | 1.729 | 1.863 | 1.596 |
| Al ₂ O ₃ | 1.908 | 2.693 | 1.968 |
| P ₂ O ₅ | 1.583 | 2.058 | 1.971 |
| SO ₃ | 0.047 | NA | NA |
| K ₂ O | 0.350 | 0.011 | 0.045 |
| CaO | 0.063 | 0.061 | NA |
| MnO | 0.437 | NA | 0.545 |
| Fe ₂ O ₃ | 2.395 | 0.751 | 0.412 |
| ZrO ₂ | 1.543 | 1.271 | 0.645 |
| C | 0.500 | 0.338 | 0.543 |
| CrO | 3.782 | 2.467 | 2.197 |

Figure 3 and 4 show the EDS analysis data of polycrystalline SiO₂. The peak observed at 2θ around 45 eV indicates the formation of a non-crystalline SiO₂ phase in the sample. Under high-temperature conditions, the Si-O groups bond to give the low-temperature forms of cristobalite and tridymite crystalline [11, 12]. There is a versatile possibility of using heat-treated rice husks as a filler for elastomers, such as white ash is used as filler for polyethylene [13], polypropylene [14], and polystyrene [15]. SiO₂ with this amorphous crystalline structure contributes to tire durability, which measurable in terms of its efficiency factor [16]. The amorphous SiO₂ efficiency is confirmed as the additive dose ratio to the amount of rubber, which can be replaced to maintain the strength [17]. Thus, it is inevitable that by using a mixture of amorphous SiO₂, an eco-friendly tire filler can be produced in the future.

**FIGURE 3.** EDS image of amorphous SiO₂ as the sol-gel extraction result

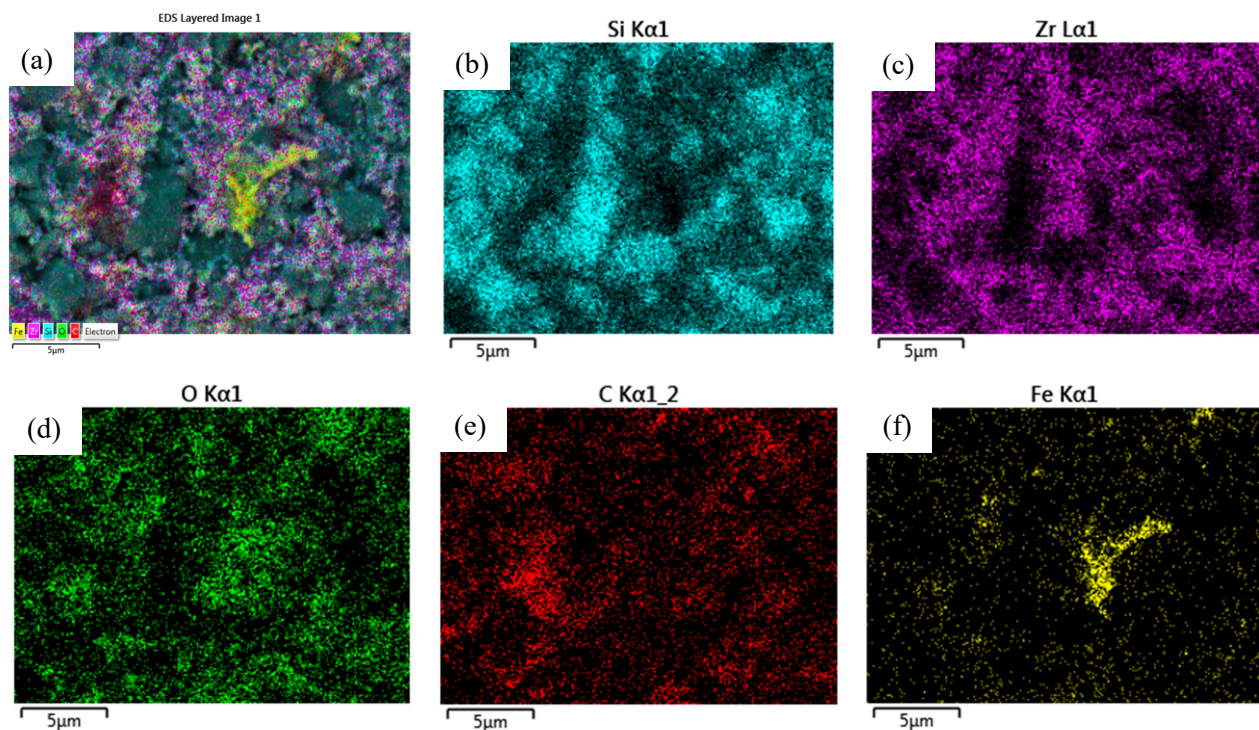


FIGURE 4. Scattering elements of (a) all, (b) Si, (c) Zr, (d) O, (e) C and (f) Fe elements

CONCLUSION

A polycrystalline SiO_2 was produced from rice husk by KOH solid-liquid extraction. By these process conditions, the SiO_2 was obtained and had potential application as in rubber filler as well as other types of compounding. In addition, the SiO_2 might be possible to applied as a catalyst support or adsorbent in the pure chemical synthesis.

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