Optimalization of silicon extraction from husk ashes by excessive magnesium addition on increasing rate of temperature reduction

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Abstract. The Silicon can be extracted from rice husk ash by reducing silica with magnesium. In this study the use of Magnesium and Silica was 49:60 with various rate of increase in the reduction temperature (1 °C/minutes, 3 °C/minutes, and 5 °C/minutes). It was done in order to obtain silicon with a higher purity than previous studies. The results of EDX showed that the purity silicon with the increase rate of 1 °C/minutes and 5 °C/minutes were 1.78% and 29.39%, respectively. Then, silicon was not formed by increasing rate of 3 °C/minutes. Moreover, XRD results of the samples by using the increase rate of 1 °C/minutes and 5 °C/minutes showed that the pattern correspond to Silicon while the sample with increase rate of 3 °C/min corresponds to Silica. The FTIR spectra indicate the presence of stretching vibration an harmonic for functional groups of Si-O-Si with spring constant for the increase rate of 1 °C/minutes, 3 °C/minutes, and 5 °C/minutes respectively were 977.23 N/m, 1003 N/m, and 982.3 N/m. FTIR result was consistent with EDX and XRD result proving by the existence of Si-O-Si functional group which showed the purity silicon produced was not optimum and presence of OH-functional group indicate that sample contained water.

1. Introduction
Rice husk is waste rice cultivation results that are hard and rough, and nutrient levels are low and not worth economically. However, the current waste rice husks can already be used to fuel the red brick, cement base material, even the husk furnace fuel [1]. The results will appear burning other waste is waste rice husk [2]. Processing and utilization is not proportional to the amount of chaff is increasing every year. Therefore, the use of chaff should be maximized. Rice husk is the outer layer of the grain, which is a byproduct of rice milling process is currently done. From the rice milling process is usually obtained husk around 20-30% of the grain weight [3]. Husk waste is widely used as an alternative source of energy, one as rice husk furnace fuel.

Rice husk ash can be a source of synthesis of amorphous Silicon Dioxide bio ceramics at low cost because of its availability in abundance. Rice husk in general burned in the temperature range of 500 °C to 600 °C to obtain amorf [4]. Silicon dioxide Silicon dioxide produced can be extracted into silicon to reduce Magnesium. Silicon dioxide is a compound with a tetragonal structure that can be
found all around us and are widely used as raw material for the electronics industry. Pure silicon dioxide contained in three forms, namely quartz, tridymite, and cristobalite. Reduction magnesium silicon dioxide with a reductor at a temperature of 620 °C to 650 °C years. Silicon powder can be obtained from rice husk with ashing temperature of 1000 °C with a gray color that has such a shiny metal [5].

Rice husk ash research has been able to produce silica. In addition to silica, it turns ash from rice husk can also be extracted into a silicon purity can reach 60.87%. To obtain Silicon, Silica is reduced with magnesium at a temperature of 650 °C [6]. Silicon currently has a high selling power, the use of silicon is now no doubt. In the field of silicon technology is already widely used as a base for the manufacture of semiconductor components that are environmentally friendly. So that the waste generated does not damage the environment. Therefore, a challenge of exploiting the potential of Indonesia's natural resources one of which is rice husk. This research will be carried variation reduction rate of temperature increase between silica and magnesium, it is aimed to determine the rate of temperature rise is most optimum in producing high-purity silicon.

2. Material and Method

2.1. Materials
Bahan yang digunakan dalam penelitian sekam padi dari limbah pertanian, asam klorida (HCl), Magnesium (Mg) dan aquades. This study is divided into several stages, rice husk charcoal manufacture, extraction silica, and silicon extraction.

2.2. Rice husk charcoal manufacture
Making rice husk rice husk begins to weigh. Rice husk using sun dried and then weighed and then inserted into a furnace chaff. Rice husk produced subsequently weighed. Rice husk using sun dried and then weighed and then inserted into a furnace chaff. Rice husk produced subsequently weighed.

2.3. Extraction silica
The process of making silica, rice husk charcoal burned in a furnace at 400 °C for 2 hours. Furthermore, the heating temperature was increased to 900 °C for 1 hours with a heating rate of 0.9 °C/minutes. Rice husk ash was weighed and washed using hydrochloric acid (HCl 3%) to reduce the impurities present in rice husk ash so that only the silicon dioxide. Furthermore, washed using hot distilled water repeatedly until acid-free (tested using litmus paper), then filtered through ash-free filter paper. Results of screening (residue + filter paper) is heated in a furnace to temperature of 900 °C until white remaining silicon dioxide [7].

2.4. Silicon extraction
Silicon dioxide has been obtained is filtered with a micro filter so that the same particle size with Magnesium powders. Furthermore, Silicon dioxide is reduced by magnesium using comparison magnesium and Silicon dioxide at 49:60 which mass of magnesium is 0.82 grams and Silicon dioxide 1 gram. The reduction process in furnace at temperature of 650 °C with rise temperature variation 1 °C/minutes, 3 °C/minutes, and 5 °C/minutes. After the reduction process, a sample of the reduction was washed using HCl 3% to remove impurities. The washing process is done twice, washing first early samples of the reduction put in a beaker, then mixed with HCl 3% 80 ml, then heated above the bath for the process of stirring for 2 hours at temperature of 200 °C and a stirrer speed of 240 rpm. After that, followed by washing the latter. The same sample mixed with HCl 3% of 300 ml, then heated above the bath at a temperature of 200 °C for 1 hour with a stirrer speed of 240 rpm. Then, sample washed with hot distilled water repeatedly until acid-free (tested with litmus paper, pH 7, and then filtered with ash-free filter paper. Results of screening (residue) is heated in a
furnace to a temperature of 110 °C for 12 hours for drying. The results of this screening suspected as Silicon.

2.5. Analyzed EDX, XRD, and FTIR

Silicon analyzed using EDX (Energy Dispersive X-ray) to identify the composition of the elements contained in the sample so as to determine the purity of the silicon. Analysis of XRD (X-Ray Diffraction) to observe the silicon structure. This method to identify crystalline phases in the material by determining the parameters of the lattice structure as well as to obtain particle sizes. Analysis of FTIR (Fourier Transform Infra-Red) to characterize the functional groups and molecular bonding.

3. Results and discussion

EDX analysis results of samples Si of the silica reduction process with initial purity of 87.48% with magnesium were showed in Table 1. Table 1 showed different chemical composition on the rate of temperature rise is different. The ratio between magnesium and silica at 49:60, purity silicon obtained from variations in the rate of temperature rise of 1 °C/minutes, 3 °C/minutes, and 5 °C/minutes different from each other. At the rate of temperature rise of 1 °C/min, purity silicon by 1.78% because there are impurities Rubidium. But purity silica increased from 87.48% to 97.23%. At the rate of temperature rise of 3 °C/minutes percentage of oxygen element very much, but there are still remains of the magnesium reduction process, and there are impurities rubidium and potassium. This causes the sample yet to form pure silicon, even a silica purity of the sample was reduced to 49.23%. At the rate of temperature rise of 5 °C/minute percentage of the silicon element more than the element oxygen that purity silica increased to 99.99%. However, because there are still remaining Magnesium and there are impurities in the form of Rubidium, purity silicon obtained only by 29.39%. Purity silica and silicon calculated using the percentage of atoms detected on FTIR instrument.

| Elements       | Comparison Mg and SiO$_2$ | 1°C/minutes (%) | 3°C/minutes (%) | 5°C/minutes (%) | 1°C/minutes (%) |
|----------------|---------------------------|-----------------|-----------------|-----------------|-----------------|
| Oxygen         |                           | 63.37           | 73.31           | 42.98           | 26.09           |
| Magnesium      |                           | -               | 8.84            | 4.72            | -               |
| Silicon        |                           | 32.41           | 16.41           | 47.26           | 73.91           |
| Rubidium       |                           | 4.22            | 1.23            | 47.26           | -               |
| Potassium      |                           | -               | 0.22            | 5.04            | -               |
| Purity of silica |                         | 97.23           | 49.23           | 99.99           | 99.99           |
| Purity of silicon |                     | 1.78            | -               | 29.39           | 60.78           |

a Muzikarno [10]

Purity silicon produced in the study by Muzikarno [8] at the same rate of temperature rise is 5 °C / minutes compared to silicon in this study with a ratio of 49:60 has a smaller purity is 29.39%. Therefore, it can be concluded that the mass ratio of magnesium and silica used in this study was not a comparison that is optimum to produce high purity silicon. But with the variation of the rate of rise in temperature reduction can be seen that the greater the reduction in the rate of temperature rise, the purity of the silicon produced even greater. Although the rate of temperature increase rate of reduction used are not optimum for the reduction of temperature rise resulting silicon has not had a high purity. The purity of the silicon element rice husk ash depends on the content of the elements contained in
rice husk and the geographical situation of the region of origin of rice husk. Similarly, the presence of rubidium, depending on the type of rice used. In this study, after the extraction process had appeared silica impurities in the form of Rubidium, so that the process of extracting the silicon looks still remaining rubidium. This is due to the use of rice husks contains rubidium. Silicon which has the fewest impurities or without impurities is a good silicon, fewer impurities, the purity of the silicon will be higher. EDX results on the three variations of this study indicate rubidium and potassium is a metal residual silica in the sample. These metals are naturally present in the husk.

**Figure 1.** XRD pattern of (a) Silikon 1 °C/minutes (b) Silikon 3 °C/minutes (c) Silikon 5 °C/minutes

Figure 1 showed the x-ray diffraction pattern of silicon with a variation of 1 °C/minutes, 3 °C/minutes, and 5 °C/minutes. The third picture above showed the diffraction pattern with a peak of almost the same. The highlight appears indicating their compounds x-ray exposure when tested XRD, the peak of silica and silicon compounds. After compared with the data of JCPDS ICDD 1997, the diffraction pattern in Figure 1 (a) seen the peak of silicon at an angle of 28.5°, 47.56°, 56.4°, 69.58°, and 76.8°. But there is still a silica compound indicated by peaks at 22°. The same is shown in Figure 1 (c), the diffraction pattern showed peaks of silicon and silica. Silicon peak at 28.4°, 47.3°, 56.1°, 69.1°, 76.3°. Silica peaks shown by angle of 22°, 23°, 32.2°, 35.89°, 36.2°, 40°, 52.2°. Figure 8 (b) shows the X-ray diffraction pattern of the same, namely the silicon peak at an angle of 28.3°, 47.4°, 56.1°, 69.1° and 76.2°, while silica peaks at 21.9°, 23°, 32.5°, 36°, 36.5°, 39.8°, 52.2°. Third diffraction pattern shows that the peak of the silica is still there. This indicates silica or silicon dioxide does not dissolve in HCl and do not react with magnesium [1,2,11,12].

Peak compounds of silicon dioxide (SiO$_2$) is not dominant, but in the data EDX oxygen atoms exist. It is suspected that the oxygen atoms do not form a compound of silicon dioxide (SiO$_2$) as shown in Figure 1, but is thought to form a compound of water (H$_2$O), in which the hydrogen atom is not detected in the data EDX. Moreover, the existence of rubidium and potassium were detected in EDX the data support the possibility of the formation of other compounds that cause the many peaks that form the XRD spectra of figure 8 (b) and (c). To convince them, it is necessary FTIR analysis. Table 2 showed Lattice constant of silicon sample. That table conclude structure of silicon is cubic.

| Silicon sample | Lattice parameters Å | Structure |
|----------------|----------------------|-----------|
| 1 °C/minutes   | 5.4416 5.4416 5.4416 | Cubic     |
| 3 °C/ minutes  | 5.4467 5.4467 5.4467 | Cubic     |
| 5 °C/ minutes  | 5.4416 5.4416 5.4416 | Cubic     |

Infrared transmittance silicon pattern shown in Figure 2 and the functional groups were detected shown by Table 2. In Figure 2 third IR spectra have a similar shape. The spectra are formed from silica each treatment has a dominant peaks same. At the rate of temperature rise 1°C/minutes absorption band appearing at wave number 494 cm$^{-1}$ indicate the presence of Si-O bending vibration of a siloxane (Si-O-Si) (20). Absorption at 791 cm$^{-1}$ and an absorption band at 1095 cm$^{-1}$ shows the
asymmetric stretching vibration of Si-O-Si-O Si (21). Absorption around 3421 cm\(^{-1}\) to 3823 cm\(^{-1}\) shows the OH stretching vibration of Si-OH or air (20). Main absorption peak is in an absorption band in 1095 cm\(^{-1}\), which is reinforced by the absorption band at 791 cm\(^{-1}\) indicating the asymmetric stretching vibration of Si-O siloxane groups (Si-O-Si) on a wave number of 1277.8 cm\(^{-1}\) with a spring constant of 977.23 N/m.

Similarly, the pattern of absorption at the FTIR spectra of silicon at a rate of 3 °C/ minutes and 5 °C/minutes has a peak identical to the main absorption at 1092 cm\(^{-1}\). The second graph shows the cluster Si-O from the group siloxane (Si-O-Si) that is reinforced by the group Si-O in an absorption band 795 cm-1 for the rate of rise 3 °C/minutes, and the absorption band at 791 cm-1 for the rate of temperature rise of 5 °C/minutes. The presence of an absorption band at 791 cm-1 and 795 cm-1 indicates the asymmetric stretching vibration of Si-O and allow inharmonic oscillations that occur between the main absorption peak and an absorption band amplifier12-14. Where's the rate of temperature rise of 3 ° C/minutes had a constant vibration that occurs has a spring constant is 1003 N/m and for the rate of temperature rise of 5 °C/min was 982.3 N/m. Table 5 shows the wave number, frequency and spring constant of the vibration of Si-O an harmonic group of siloxane groups (Si-O-Si).

**Table 3. Functional groups of an harmonic vibration**

| Silicon | Wavenumber (cm\(^{-1}\)) | Functional groups |
|---------|--------------------------|-------------------|
| 1 °C/minutes | 463-493 | Bending Si-O |
|         | 791 | Stretching asymmetry Si-O (Si-O-Si) |
|         | 976 | Si-O-Metal |
|         | 1095 | Stretching asymmetry Si-O (Si-O-Si) |
|         | 1339 | Stretching Si-C\(_6\)H\(_5\) |
|         | 3421-3541 | Stretching –OH dari Si-OH |
| 3 °C/minutes | 471 | Bending Si-O (Si-O-Si) |
|         | 795 | Stretching asymmetry Si-O (S-O-Si) |
|         | 957 | Si-O-Metal |
|         | 1092 | Stretching asymmetry Si-O |
|         | 3259-3352 | Stretching Si-OH |
| 5 °C/minutes | 471 | Bending Si-O (Si-O-Si) |
|         | 791 | Stretching asymmetry Si-O (S-O-Si) |
|         | 1092 | Stretching asymmetry Si-O |
|         | 3379 | Stretching Si-OH |

**Tabel 4. Constant spring of Si-O an harmonic groups**

| Silicon | \(v_1\) (cm\(^{-1}\)) | \(v_2\) (cm\(^{-1}\)) | Wavenumber \((\bar{\omega})\) (cm\(^{-1}\)) | Frequency(f) (Hz) | Constant spring (N/m) |
|---------|----------------------|----------------------|------------------------------------------|-----------------|-----------------------|
| 1 °C/ minutes | 1095 | 791 | 1277.8 | 3.83x10\(^{13}\) | 977.23 |
| 3 °C/ minutes | 1092 | 795 | 1293 | 3.88x10\(^{13}\) | 1003 |
| 5 °C/ minutes | 1092 | 791 | 1281 | 3.84x10\(^{13}\) | 982.3 |
Figure 2. FTIR spectra of (a) Silicon with rate temperature 1 °C/minutes, Silicon with rate temperature 3 °C/minutes, 5 °C/minutes Silicon with rate temperature

Absorption peaks at wave number 3421 cm$^{-1}$ to 3823 cm$^{-1}$ showed absorption of Si-OH group and an OH group. Absorption band group Si-OH and OH on the data FTIR supports the XRD data, where the samples are oxygen atoms that do not form compounds of silicon dioxide (SiO$_2$), but form a compound of water (H$_2$O), in which the hydrogen atoms are not detected in the data EDX but in FTIR visible absorption peaks OH group.

4. Conclusions

The results were obtained silicon with a purity of 1.78% at a rate of temperature rise of 1 °C/minutes and 29.39% in the rate of temperature rise of 5 °C/minutes. While the rate of temperature rise of 3 °C/minutes has not been formed silicon. The results of XRD analysis with rate of temperature rise variations showed that XRD diffraction pattern which is not much different. Rate of temperature rise of 1 °C/minutes and 5 °C/minutes, the peak of silicon is more dominant than the peak of silica. Rate of temperature rise of 3 °C/minutes more dominant at the peak of silica. The data is the same as the EDX results showed that silicon is formed at a rate of temperature rise of 1 °C/minutes and 5 °C/minutes, while the rate of rise of 3 1 °C/minutes has not been formed is still in the form of silicon or silica. In addition, all three variations have a cubic structure. FTIR analysis results of three samples tested showed patterns of uptake that is not much different. The FTIR test results prove that the silicon produced in the sample still contained water compounds are not detected by the test EDX and XRD.

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