Solubility and physical composition of rice husk ash silica as a function of calcination temperature and duration

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Abstract
Purpose The solubility of silica is a key parameter affecting its suitability as a rice fertilizer. Therefore, this study determined the effect of calcination temperature and duration on the physical composition of silica derived from rice husk ash.
Method Rice husks were calcined at 100–900 °C for 15–120 min in an electric furnace. The solubility and physical composition of the samples were measured, and the appearance of the calcined rice husk ash was determined via visual observations.
Results The appearance of the rice husk ash changed drastically at a calcination temperature of 300 °C. The husk exhibited the whitest color at 500 °C and 120 min of calcination. The solubility of silica in the rice husk ash increased up to a calcination temperature of 500 °C and then started to decrease. The silica in the rice husk ash exhibited a gray zone between the amorphous and crystalline structures.
Conclusion For actual field applications of silica derived from rice husk ash as a fertilizer, calcination conditions of 400–800 °C and 15 min are proposed to improve solubility. The optimal calcination temperature should be determined based on the heat recovery efficiency.

Keywords Rice-husk ash, Silica, Fertilizer, Calcination, Recycling, Solubility

Introduction
The recovery of heat from rice husk burning and the recycling of silica from burned rice husks are important techniques for reducing environmental contamination caused by discharging rice husks into the environment (An et al. 2011, Deshmukh et al. 2012, Shweta and Jha 2015). Fig. 1a shows a typical rice husk discharging scene in a rice-growing country and the rice husk recycling scheme proposed by Sekifuji et al. (2019). In this method, rice husk ash is recycled into paddy fields as fertilizer. The silica in rice husk ash can be used for many purposes, such as concrete materials, rubber filters, insulators, solar applications (Soltani et al. 2015), foods, and cosmetics (Pode 2016). We propose that the best way to recycle rice husks is to use the silica in rice husks as a fertilizer because silica is essential for healthy rice growth. Specifically, a lack of silica leads to insufficient moisture in rice plants, resulting in severe damage to the plant from insect invasion and lodging (Ma 2003). Therefore, rice plants must absorb sufficient silica from the water to support and protect themselves; indeed, rice plants are known as a “major silicon accumulator” (Raven 2003). The ideal agriculture loop shown in Fig. 1b also successfully achieves heat recovery.

When considering the use of silica from rice husk ash, the physical form of the silica is extremely important. This is because heat treatment can change silica from the amorphous form found in rice husks to a crystalline form that is difficult to dissolve in water (Tateda 2016). Therefore, crystalline silica is essentially useless for rice plant growth. The silica in rice husks is greatly affected by the heating temperature.
Fig. 1 (a) Discharged rice husks. (b) Ideal agriculture loop

and duration (Tateda et al. 2016a). Japan has previously proposed approved parameters for the “silica solubility for fertilizers” (Tateda et al. 2016b), which are used to evaluate whether a target silica material can qualify as an authorized fertilizer. For example, the solubility of silica-gel fertilizer and wollastonite must be 80% and 20%, respectively, to qualify as authorized fertilizers (FAMIC 2015). It should be noted that the Japanese standard definition of solubility is related to alkali or acid solutions, not to the solubility in water. Moreover, solubility is a good indicator of the physical form of the silica, i.e., amorphous or crystalline. High solubility values indicate that the silica is amorphous and appropriate as a fertilizer. Therefore, a relationship exists between the solubility and the amorphous structure of silica (Tateda et al. 2016b). Moreover, the amorphous silica structure in rice husk ash is strongly influenced by the heating temperature and duration, which can also influence the solubility (Tateda et al. 2016a).

In this study, the solubility and physical composition of silica derived from rice husk ash are discussed as a function of calcination temperature and duration. Sekifuji et al. (2017) previously reported the physicochemical differences of silica under different calcination temperatures; however, the present study is more comprehensive. The results of this study can help determine the optimal rice husk calcination conditions for producing effective silica fertilizer. Therefore, this research ensures that rice husk resources are returned to paddy fields for future rice plant growth.

Materials and methods

All experiments were triplicated, and the mean values were taken for the production of figures.

Rice husk variety and ash preparation

Rice husks of the most popular rice variety, Koshihikari (Oryza sativa L.), were used in this study. The rice husks were used without further preparation, i.e., without washing, and calcinated in a laboratory-scale electric furnace (KBF794N1, Koyo). In the field, a boiler is used to incinerate rice husks to recover heat and generate ash. In this study, an electric furnace was used to generate ash.

Solubility measurement of rice husk-derived silica

The silica solubility derived from the rice husks was measured using a modified method described by Tateda et al. (2016b). This method is based on the Standard Method 4.4.1.c (FAMIC 2015) but omits the first hydrochloric acid treatment to save time while resulting in values similar to those of the Standard Method. Method 4.4.1.c was not designed for the silica fertilizer made from rice husks but for a fertilizer containing silica gel; therefore, no authorized method for measuring the solubility of rice husk-derived silica currently exists. There are extremely few studies that discuss silica solubility. The term “solubility” is used in this study; however, the Silica Activity Index, which indicates the degree of amorphousness of silica, was proposed by Deshmukh.
et al. (2012). Their concept of solubility was similar to that used in this study and was employed to measure the reactivity of silica in ricehusks.

**Measurement of the physical composition of rice husk ash**

The physical composition of the rice husk ash was determined according to the relative contents of fixed carbon, ash, volatile matter, and moisture (Sekifuji et al. 2017). The four proportions were determined following the Japan Industrial Standards (JIS) M 8812-5.2.4a, -6.4.1, -7.2.4, and -8 for water, ash, volatile, and fixed carbon, respectively (JIS 2004). Finally, visual observations were performed to describe the appearance of the rice husk ash.

**Solubility calculation**

The solubility of the silica in the rice husk ash was calculated according to Equation 1 (Tateda et al. 2016b):

\[
\text{Solubility (\%) = (1)}
\]

where VS is the volume of NaOH solution (0.2 mol/L) consumed for titration (mL), C is the estimated concentration of NaOH solution (0.2 mol/L), f is the factor of 0.2 mol/L NaOH solution (Wako) as provided on the bottle (1.000, unitless), V1 is the volume of the alkali-treated solution (250 ml, see Tateda et al. 2016b for details), V2 is the volume of aliquot taken from V1 (5 mL), 15.021 refers to 1 mL of 0.1 mol/L NaOH = 1.5021 mg of SiO\(_2\) (mg/l)/(ml·mol), W is the amount of sample taken (1 g, measured precisely to three decimal places), 100 is the conversion factor used to obtain a percentage (%), and 1000 is the conversion factor for mg to g (mg/g).

**Experimental procedure**

The rice husks were calcinated in an electric furnace at the Waste Management Laboratory of Toyama Prefectural University, Toyama, Japan. Calcination temperatures varied from 100 to 900 °C, and the calcination durations were 15, 30, 60, and 120 min. After calcination, an aliquot of the ash sample was taken to measure the silica solubility in the ash. Another aliquot of the ash sample was used to measure the physical composition of the ash. Measurements were performed in triplicate, and the mean values were used for subsequent analysis.

**Results and discussion**

**Appearance of rice husk ash as a function of calcination conditions**

Fig. 2 shows the appearance of the rice husk ash after heat treatment at different calcination temperatures and durations. According to Lui et al. (2013), the mass retention (%) and differential thermal analysis (DTA) (μV mg\(^{-1}\)) of rice husks showed a drastic reduction between 200 °C and 400 °C. In agreement with their results, the appearance of rice husks at 300 °C changed drastically from that at 200 °C. Conversely, rice husks calcined at 100 °C and 200 °C retained their original appearance, although rice husks calcined at 200 °C for 60 min and 120 min were slightly tainted. Moreover, the color of the rice husks became whiter at 400–800 °C as calcination time increased. All rice husks were black after 15 min of calcination at temperatures above 300 °C. They then became whiter as the calcination temperature increased before becoming darker after 500 °C, achieving the darkest color at 900 °C for all calcination durations. The whitest appearance was observed after 120 min at 500 °C. A similar study was conducted by Krishnarao et al. (2001) at calcination temperatures of 400–700 °C, but with no calcination time variation and with the rice husks washed in acid. In their study, the acid-washed rice husks became progressively whiter after 500 °C. This difference can be explained by the presence of alkali metals, especially potassium, in the rice husks, which transform to potassium oxide under heat treatment, then reacts with silica under high temperatures. These mixed potassium and silicon oxides begin to melt due to their low melting point, resulting in some combustible carbon remaining on the surface of the ash, producing a blackish appearance (Tanaka et al. 1989). The acid-washed rice husks appear whiter because the acid removed alkali metals. According to Fig. 2, the combustible carbon remained in the husk for 60 min and all carbon was completely oxidized at 500 °C after 120 min. The carbon in the rice husks should be easily oxidized and removed at high temperatures; however, the results showed that the ash became darker with increasing temperature over 500 °C. This suggests that, as the temperature increased, the mixed oxides of alkali metals and silica retained the combustible carbon faster than it could be removed from the ash surface by oxidation.
Solubility and calcination temperature

Fig. 3 shows the solubility of silica in the rice husk ash as a function of the calcination temperature. The solubility trends were almost identical after 60 and 120 min, exceeding 80% at 400 °C and 500 °C before decreasing after 500 °C to single digits at 900 °C. Among the four calcination times, 15 min resulted in the lowest solubility but exhibited the most stable solubility trend at 400–800 °C of approximately 48–51%. Then, the solubility decreased substantially to 35% at 900 °C. Calcination for 30 min showed an intermediate trend between 60 min/120 min and 15 min. At 800 °C, the solubility remained higher than that after 60 and 120 min but similar to that after 15 min. However, the solubility decreased drastically to 10% at 900 °C, similar to that after 60 and 120 min.

Solubility and calcination duration

Fig. 4 shows the solubility of silica in the rice husk ash as a function of calcination duration. No solubility fluctuation was observed at 100 and 200 °C. Conversely, the solubility at 300 °C continued to increase with calcination duration. The solubility at 400 and 500 °C showed equivalent trends, reaching a maximum solubility after 120 min. At 600 °C, the maximum solubility was reached after 30 min and maintained until 120 min. At 700 °C, the solubility reached a maximum after 60 min and then decreased. At 800 °C, the solubility reached a maximum after 30 min and then decreased after 60 min before remaining relatively stable. For calcination at 900 °C, the maximum solubility was reached after 15 min, after which it continued to decrease.
Physical composition of rice husk ash as a function of calcination conditions

Fig. 5 shows the physical composition of the rice husk ash samples. Generally, the ash portion increased with increasing calcination temperature. In the ash portion, silica is the dominant component (Sekifuji et al. 2017), with the remainder consisting of metals such as potassium, calcium, sodium (Liu et al. 2013), iron, aluminum, titanium, and phosphorus (Bandara et al. 2020). The volatile portion comprises cellulose, hemicellulose, and lignin (Cai et al. 2017). According to Shimizu et al. (1978), the volatile portion consists of two types of volatile materials: easily volatile and resistant volatile materials. The former has low calories and the latter has high calories. The physical composition of the samples is discussed in more detail regarding the solubility results.
Relationship between appearance, solubility, and physical composition

Fig. 6a–i shows the physical composition, solubility, and appearance of ash calcined at temperatures of 100–900 °C for different calcination durations. At low calcination temperatures (100 and 200 °C), the volatile portion occupied a large percentage of the samples (Fig. 6a, b). The appearance of the rice husks remained the same and the solubility was stable, fluctuating within 14–17% as the calcination duration increased from 15 to 120 min. As mentioned earlier, the appearance at 300 °C changed drastically from that at 200 °C (Fig. 6c), turning to black ash. This was accompanied by a large percentage of fixed carbon in the samples. At 400 °C, the solubility increased as a function of calcination duration (Fig. 6d), and the ash became whiter as the calcination time increased, which corresponded to the decrease in the fixed carbon portion. The solubility finally became stable after 60 min of calcination, at which point the fixed carbon portion decreased. The trends at a calcination temperature of 500 °C were approximately the same as those at 400 °C (Fig. 6e), although the ash appeared whitest after 120 min of calcination at this temperature. At 600 °C, the solubility became stable after 30 min (Fig. 6f), and the ash became slightly black again after 120 min. Fig. 6g shows the trends at 700 °C. The fixed carbon portion decreased as calcination time increased to almost zero after 120 min; however, the ash appeared blackish. The solubility reached a max-
imum after 60 min of calcination and then decreased. At 800 °C, the solubility decreased by half after 30 min of calcination (Fig. 6h) to a minimum value after 120 min, and the sample was almost completely ash after 60 min of calcination. The solubility was at a maximum (35.1%) after 15 min and then decreased with calcination duration (Fig. 6i) to 1.79% after 120 min. The sample was almost completely ash after 30 min.

It was previously assumed that the solubility of rice husk ash with a whitish appearance would be higher than that with a blackish appearance. However, the results prove this assumption to be incorrect. This can be seen by comparing the appearance of rice husks calcined at 400 °C for 30 min (Fig. 6d), at 700 °C for 120 min (Fig. 6g), and at 600 °C for 30–120 min (Fig. 6f). Therefore, rice husk ash with a whitish appearance does not always make a better fertilizer.

Relationship between solubility and proportion of ash

Silica almost completely occupies the ash portion of rice husk ash. Therefore, considering the minimal metal contents and analysis errors, the entire ash portion is thought to be occupied with soluble silica up to a calcination temperature of 500 °C (Fig. 6a–e). At calcination temperatures above 600 °C, a gap appeared between the ash portion and the soluble silica portion (Fig. 6f–i). This gap gradually became larger as the calcination temperature increased. At the same temperature, the gap also increased with increasing calcination duration. This gap could be explained by a change in the form of silica in the rice husks upon heating to a less soluble crystallized form. At 700 °C, the gap was much larger than that at 600 °C (Fig. 6g). The soluble silica still occupied a large percentage of the ash portion after 15 min of calcination, but the solubility did not increase despite the ash portion increasing substantially and occupying almost the entire sample after 60 min and 120 min of calcination. At 800 °C, the inverse trend between solubility and the ash portion became more remarkable (Fig. 6h). However, the silica in the ash portion was not yet crystallized at this stage, according to our previous research (data not shown). At 900 °C, the solubility was 35%, yet the ash portion was approximately 70% after 15 min, which means that half the silica became insoluble and became crystalline. The silica in the rice husk ash was completely crystallized after 60 min and 120 min of calcination (data not shown) (Fig. 6i).

The gap is interpreted as a gray zone between amorphous and crystalline silica that became larger with increasing calcination temperature and duration, leading to the appearance of a probably amorphous silica that is not soluble but not yet crystalline. Therefore, the silica in the ash portion is not always amorphous or crystalline (Fig. 7).

Optimal calcination conditions of rice husks for fertilizer application

The solubility of silica in rice husk ash describes its availability to rice plants; availability is high if the solubility is high, and vice versa. There are two types of fertilizer currently used in Japan: regular fertilizers and special fertilizers. Regular fertilizers have their solubility criteria, which are stricter than those for special fertilizers; therefore, they sell at a higher price because...
their quality is guaranteed. Silica-gel fertilizer, one of the designated silica fertilizers in Japan, has its own criteria whereby the solubility must be 80% or higher. On the other hand, rice husk ash has not been designated as a regular fertilizer, although it has been prepared for application as a regular fertilizer by the Japanese Ministry of Agriculture, Forestry, and Fisheries.

For fertilizer applications, the solubility of silica in the ash should be as high as possible. According to Fig. 6, calcination at 400 °C and 500 °C produced the best results at all calcination temperatures. In this study, an electric furnace was used to burn rice husks in the laboratory. However, Tateda et al. (2016a) reported an actual field operation using a real boiler system where the rice husks were burned using their own calories. The residence time in the boiler system from the inlet to the outlet was less than 10 min; therefore, the calcination duration of 30–120 min used in this study are unrealistic. Hence, only the solubility after 15 min of calcination is realistic and considered here. Similar values were obtained at different temperatures after 15 min of calcination, i.e., 49.2%, 53.3%, 52.0%, 48.5%, and 50.6% at 400 °C, 500 °C, 600 °C, 700 °C, and 800 °C, respectively (Fig. 8). The burning temperature can be controlled by the air blowing rate into the incineration furnace; therefore, the optimal burning temperature should consider the heat recovery efficiency.

Further consideration should be given to the following two calcination conditions: after 120 min of calcination at 300 and 700 °C, the solubility was almost the same (57.3% and 55.7%, respectively) (Fig. 8); however, the physical composition was different. For the sample at 300 °C, soluble silica occupied the entire ash portion (57.3%), whereas soluble silica only accounted for approximately half of the ash portion in the sample at 700 °C. Therefore, these samples may exhibit a different dissolution of silica in water. According to Fig. 7, the sample at 700 °C had a larger gray zone; therefore, the effects of this gray zone on the dissolution of silica are an interesting topic for future research. Moreover, the samples calcined for 120 min exhibited a different appearance at 700 and 900 °C (Fig. 8). The sample at 900 °C was much darker than that at 700 °C, although the fixed carbon percentage was almost zero in both. The exact amount of fixed carbon might help explain this phenomenon; therefore, additional experiments are required.

**Conclusion**

The following conclusions were obtained in this study.
- The appearance of rice husk ash changed drastically at a calcination temperature of 300 °C (decrease of volatile portion and increase of ash portion and solubility) and was whitest at a calcination temperature and duration of 500 °C and 120 min (almost ash portion occupied). The rice husk ash became blackish after 500 °C, in contrast to the acid-washed rice husks.
- The solubility of silica in rice husk ash increased up to a calcination temperature of 500 °C and then began to decrease. The silica exhibited maximum solubility after calcination for 60 min and 120 min. Conversely, minimum solubility was observed after 15 min of
calcination but was stable from 400 to 800 °C.
- The ash portion in the rice husk ash increased with increasing calcination temperature.
- A whiter rice husk ash did not always indicate higher solubility.
- Regarding the field application of heat recovery using a boiler system, the optimum burning temperature should be between 400 and 800 °C because the residence time in the actual furnace is less than 15 min.
- Some samples exhibited almost equal solubility but very different physical compositions. Therefore, differences in the silica dissolution rate of the samples should be analyzed in future research.
- A gray zone between amorphous and crystalline silica was observed in the ash portion with increasing calcination temperature and time.

Compliance with ethical standards

Conflict of interest The authors declare that there are no conflicts of interest associated with this study.

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References


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