

Eluted Soluble Silica Content in Rice Husk Charcoal Produced by Rice Husk Burner

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This study aims to compare burner combustion method with conventional method from the viewpoint of total amount of eluted soluble silica in rice husk charcoal (RHC). RHC was prepared in an electric furnace by controlling the combustion temperature and time. The amount of eluted soluble silica in RHC was measured by the molybdenum blue absorptiometric method. The amount of unburned carbon and the crystallization of silica were measured by weight change between RHC production and by the specific surface area and pore volume of RHC, respectively. As a result, RHC combusted at 900°C for 3 min as a developed rice husk burner contained 60% of the amount of eluted soluble silica in RHC combusted by conventional method at 400°C for 60 min. With regard to the mechanism of silica elusion, in short-term combustion assuming a developed rice husk burner, high temperature was suitable for increasing the amount of eluted soluble silica because it was determined by eliminating the plant fiber covering silica in rice husk. On the other hand, in long-term combustion assuming conventional method, low temperature combustion showed the possibility for increasing the amount of eluted soluble silica because it was determined by the crystallization of silica.

本研究の目的は、籾殻燻炭 (RHC) に含まれる可溶性シリカ量について、もみ殻燃焼炉による燃焼方法と従来法の燃焼方法の比較を行うことである。RHC は燃焼温度と時間を制御して電気炉で作製した。RHC の可溶性シリカの溶出量はモリブデン青吸光度法によって測定した。また、未燃炭素量とシリカの結晶化を、RHC 作製過程での重量変化および比表面積と細孔容積によってそれぞれ測定した。その結果、もみ殻燃焼炉を想定して 900°C で 3 分間燃焼した RHC の可溶性シリカの溶出量は、従来法である 400°C で 60 分間燃焼した RHC の可溶性シリカの溶出量の 60% を示した。可溶性シリカの溶出メカニズムにおいて、もみ殻燃焼炉を想定した短時間燃焼では、可溶性シリカの溶出量は籾殻中のシリカを覆っている植物繊維の除去具合によって決定されるため、可溶性シリカの溶出量を増やすことができる高温燃焼が適することが明らかとなった。一方、従来法を想定した長時間燃焼では、可溶性シリカの溶出量はシリカの結晶化によって決定されるため、可溶性シリカの溶出量を増やすことができる低温燃焼が適する可能性を示した。

Key Words

Combustion temperature, Combustion time, Crystallization, Rice husk charcoal, Soluble silica,
Unburned carbon

1. Introduction

Although the rice yield is decreasing year by year, approximately 8 million tons of brown rice is still harvested in Japan every year¹⁾. Rice husk, which is produced in the process of paddy rice husking after harvesting and drying,

is an unused biomass resource. Considering that rough rice is approximately 1.25 times as heavy as the mass of brown rice and rice husk accounts for approximately 20% of the mass of rough rice, approximately 2 million tons of rice husk is assumed to be produced in Japan per year. However, more than 20% of rice husk is not used and often disposed of by burning because of its difficulties to be decomposed²⁾. Some studies have reported the use of rice husk as a concrete admixture^{3) 4)}; however, a sustainable method to use rice husk within the agricultural field is desired because it is currently used only as a concrete admixture.

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Rice husk is expected to be used as a raw material for generating alternative energy resources for grain drying and greenhouse heating in the agricultural sector because the moisture content of rice husk obtained after drying process is very low. Rice husk is expected to be used as a raw material for not only generating energy resources but also producing rice husk charcoal (RHC), which is used for soil amendments. The development of an effective rice husk combustion system will promote the use of energy recycling systems in rural areas.

Conventionally, a farmer produces RHC by burning the rice husk produced within the farmland for over 60 min. However, the modernization and mechanization of agriculture have increased the stock of rice husk gathered at cooperative grain drying facilities⁵⁾. Therefore, a resource recycling system for the heat generated by a rice husk burner installed near a cooperative grain drying facility and for the by-product reuse of the RHC produced by the rice husk burner is desired⁶⁾. Recently, a rice husk burner was developed that could control combustion conditions such as combustion temperature and combustion time^{6) ~ 8)}; hence, this burner could produce homogenous high-quality RHC.

Rice husk contains high quantities of silica⁹⁾, which is a fertilizer component, and RHC is effective as a fertilizer for producing drought-resistant and lodging-resistant rice^{10) ~ 12)}. Silica is classified either as crystalline or amorphous or as soluble or insoluble (Table 1). When RHC is used as a fertilizer in soil, silica exists in the form of silicon dioxide (SiO₂). SiO₂ changes to a form of soluble silica, i.e., silicic acid (Si(OH)₄), when it is absorbed by a plant body. Therefore, the effectiveness of RHC as a fertilizer is decided by the amount of eluted soluble silica contained in RHC¹³⁾. In this research, silicic acid was assumed to be the same as soluble silica.

In previous studies^{5) 14)}, it was reported in the combustion temperature range of 300-900 °C, the RHC combusted at 400 °C had the largest amount of eluted soluble silica. In these studies, the combustion time was set to 60 min assuming conventional method and the combustion temperature was changed. This result is in agreement with that of the conventional method of RHC production by farmers, wherein high-quality RHC is produced by carrying out combustion at approximately 400 °C

for 60 min. However, recently, a rice husk burner was developed that could raise the combustion temperature rapidly and enable the combustion of rice husk at a high temperature for a short-term. The effectiveness of RHC as a fertilizer is assumed to be decided by not only the combustion temperature but also the combustion time because the amount of eluted soluble silica in RHC is determined by the amount of unburned carbon and the crystallization of silica⁵⁾.

This study aims to compare burner combustion method with conventional method from the viewpoint of total amount of eluted soluble silica in RHC with changing the combustion temperature and time, and propose hypothetical mechanism of silica elusion. First, RHC was prepared in an electric furnace by controlling the combustion temperature and time. The amount of eluted soluble silica in the prepared RHC was measured by the molybdenum blue absorptiometric method. Moreover, to estimate the factors affecting the amount of eluted soluble silica in RHC, the amount of unburned carbon and the crystallization of silica were measured by the weight change before and after RHC production and by the specific surface area and pore volume of RHC, respectively. In addition, the amounts of eluted soluble silica in RHC produced in the electric furnace and rice husk burner were compared to consider the characteristics of soluble silica elusion.

2. Materials and Methods

2.1 Rice husk charcoal combusted in electric furnace

RHC was prepared in an electric furnace (Yamato Scientific Co., Ltd., FO100) by controlling the combustion temperature and time, and the amount of eluted soluble silica in the prepared RHC was measured. The details of the measurement method are described in the next subsection. One trial using about 1.0 g of rice husk in a combustion boat (30 mm × 150 mm × 15 mm) was repeated until gaining enough amount of RHC.

The rice husk of Koshihikari, *Oryza sativa* L., which was used in this research (Table 2), was grown at the farm of the National Agriculture and Food Research Organization, Institute of Agricultural Machinery. The fixed

Table 1 Definition of silica in this research

	Crystalline	Amorphous
Soluble	-	Silicic acid (Si(OH) ₄)
	Quartz	
Insoluble	Cristobalite	Silicon dioxide (SiO ₂)
	Tridymite	

Table 2 Technical and elemental analysis results of rice husk used in this research

Technical analysis					
Moisture [wt%]			Ash [dry wt%]		
13.6			18.2		
Elemental analysis [dry wt%]					
Carbon	Hydrogen	Sulfur	Oxygen	Nitrogen	Chlorine
44.4	6.2	0.03	30.8	0.28	0.036

carbon and volatile component in rice husk were assumed as approximately 14% and 60%, respectively based on a previous study¹⁵⁾.

The rice husk was prepared under 12 combustion conditions obtained using combinations of the combustion temperature (400, 500, 600, 700, 800, and 900 °C) and combustion time (3 and 60 min). Here, unlike previous studies, the combustion temperature of 300 °C was not considered because preliminary experiments showed that the combustion of rice husk at 300 °C for 3 min was not sufficient to combust rice husk and produce RHC. The combustion time was set based on conventional method⁵⁾ (60 min) and a developed rice husk burner explained in detail later (3 min) to clarify the difference of the amount of eluted soluble silica in RHC.

Rice husk was put into an electric furnace that already setting to target temperature and heated for 3 or 60 minutes. After that, it was picked up to outside and cooled to an ordinary temperature. Then, although there was a bit of fluctuation of inside temperature caused by opening/closing a door of an electric furnace, inside temperature in an electric furnace kept almost constant.

2.2 Measurement method of amount of eluted soluble silica

Based on a fertilizer analysis method^{16) 17)}, the amount of eluted soluble silica in RHC was measured by the molybdenum blue absorptiometric method. A reference solution of silicic acid was prepared to determine the standard curve of absorbance and soluble silica concentration. Then, the absorbance of the sample solution (including 0.4 g of the RHC combusted in an electric furnace) was measured at a wavelength of 810 nm, and the mass concentration of soluble silica, C_{sample} [ppm], was calculated from the determined standard curve. Considering a dilution magnification of five times and the difference between the added chemical reagent of a reference solution and sample solution, the amount of soluble silica per unit weight of RHC, M_{solSiO_2} [mg/g-ash], was determined (eq. (1)) by dividing C_{sample} by the mass concentration of RHC contained in 100 mL of the sample solution, X_{RHC} [g-ash/100 mL]. In this study, X_{RHC} of the RHC combusted in an electric furnace, $X_{\text{RHC-ef}}$, was determined to be 0.4 g-ash/100 mL.

$$M_{\text{solSiO}_2} = C_{\text{sample}} \times 5 \times \frac{29.5}{30.5} \times \frac{1}{X_{\text{RHC}}} \times 10 \quad (1)$$

The ratio of soluble silica to the total silica in RHC, $R_{\text{sol/total}}$ [%], was determined according to eq. (2) using the mass concentration of the total silica contained in the sample solution, C_{totalSiO_2} [ppm]. The total silica was found to contain crystalline and amorphous silica (Table 1).

$$R_{\text{sol/total}} = C_{\text{sample}} \times 5 \times \frac{29.5}{30.5} \times \frac{1}{C_{\text{totalSiO}_2}} \times 100 \quad (2)$$

2.3 Amount of unburned carbon and crystallization of silica

Two factors determine the relationship between the combustion temperature of RHC and the amount of eluted soluble silica: the amount of unburned carbon and the crystallization of silica⁵⁾. In this study, considering the combustion temperature and time, the amount of unburned carbon and the crystallization of silica in RHC combusted in an electric furnace were also measured.

The amount of unburned carbon was calculated from the ratio of the amount of RHC to the amount of rice husk that was thrown into an electric furnace or a rice husk burner. In the case of the complete combustion of rice husk, the weight ratio of the output amount of RHC to the input amount of rice husk approached 18.2% because the rice husk before combustion contained 18.2% of ash (Table 2). The difference between the ratio of the output amount of RHC to the input amount of rice husk and 18.2% was equal to the unburned part, and in the case of RHC, it was assumed to be the unburned plant fiber (unburned carbon).

The crystallization of silica was measured in terms of the specific surface area and pore volume of RHC. The specific surface area indicates the surface area of the target particle. The greater the number of pores in the RHC particle, the larger is the value of the specific surface area. The pore volume was measured in a given width along the pore diameter. The amorphous form of soluble silica (Table 1) is effective as a fertilizer; the effectiveness of soluble silica as a fertilizer decreases as crystallization proceeds. The values of the specific surface area and pore volume decrease as crystallization proceeds, and the value of the specific surface area becomes large as RHC remains amorphous. A nitrogen gas adsorption method (BET method¹⁸⁾) was used for measuring the specific surface area. A nitrogen gas desorption method (BJH method^{18) 19)}) was used for measuring the volume of the pores with diameters of approximately 2.6-200 nm, whereas a nitrogen gas desorption method (MP method¹⁹⁾) was used for measuring the volume of the pores with diameters of approximately 0.42-2 nm.

2.4 Rice husk charcoal combusted in rice husk burner

The characteristics of RHC combusted in a rice husk burner were considered based on the amount of eluted soluble silica in RHC combusted in an electric furnace. Using a vortex burner (Air-K, TSD-030, KANEKO Agricultural Machinery Co., Ltd.), which could provide

high-temperature, short-term combustion, the effect of the combustion temperature on the amount of eluted soluble silica was determined. The rice husk burner was controlled by the supply amount of rice husk and air with small amount of input energy from outside because rice husk has a nature of self-combustion. Then input energy per hour consumed by blower in higher temperature combustion was larger than in lower temperature combustion. However, regardless of combustion temperature, it was considered that input energy per the supply amount of rice husk consumed by blower was almost constant because higher temperature combustion could consume much amount of rice husk.

Rice husk acted as a fuel and began self-combustion as it circled in the rice husk burner, which was supplied with air. For stable self-combustion of rice husk, a combustion temperature greater than 600 °C was required to be provided to the rice husk burner. In addition, at high temperatures over 900 °C, there were some possibilities of the interiors of the rice husk burner being melted. Therefore, in this study, the combustion temperature in the rice husk burner was set to 600-900 °C. The combustion temperatures were selected as 711, 754, 774, 783, 814, and 898 °C because the combustion temperature in the rice husk burner was controlled by the supply of rice husk per unit time and it was difficult to set the combustion temperature to be the same as that in the electric furnace. The combustion time for rice husk in the rice husk burner was set to be short-term (3 min). The measurement method of the amount of eluted soluble silica was the same as that described in subsection 2.2, except that the amount of rice husk in the sample solution was 0.8 g. In this study, X_{RHC} of RHC combusted in the rice husk burner, $X_{\text{RHC-rhb}}$, was determined to be 0.8 g-ash/100 mL. In addition, for comparison, the amount of eluted soluble silica in commercial RHC combusted at 300-400 °C was also measured.

3. Results and Discussion

3.1 Amount of eluted soluble silica in rice husk charcoal combusted in electric furnace

The mass concentration of soluble silica in a sample, C_{sample} [ppm], was determined according to the absorbance of the sample, A_b [-], as follows:

$$C_{\text{sample}} = 3.5013 \times A_b - 0.0048 \quad (3)$$

Fig. 1 shows the amount of eluted soluble silica in RHC combusted in an electric furnace, $M_{\text{solSiO}_2\text{-ef}}$ [mg/g-ash], with respect to the combustion temperature and time. As shown in previous studies^{5) 14)}, in long-term combustion of conventional method (60 min), $M_{\text{solSiO}_2\text{-ef}}$ decreased as the

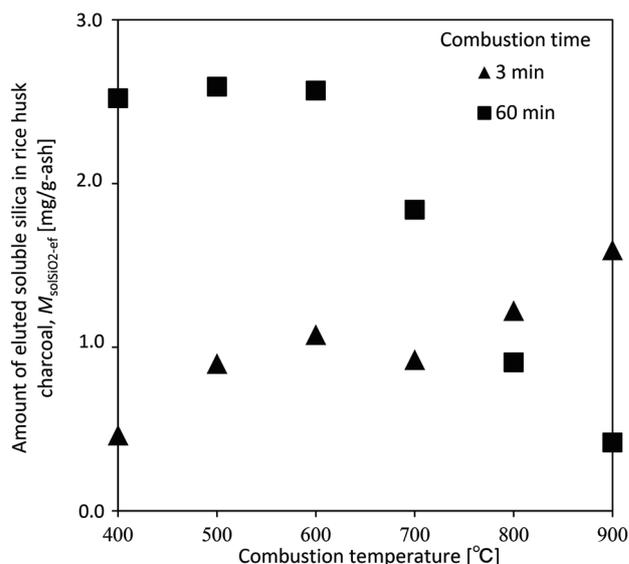


Fig. 1 Amount of eluted soluble silica in RHC combusted in electric furnace with respect to combustion temperature and time

combustion temperature increased. Although $M_{\text{solSiO}_2\text{-ef}}$ remained almost constant at 400-600 °C, it decreased rapidly above 700 °C. At 400 °C, $M_{\text{solSiO}_2\text{-ef}}$ was 2.5 mg/g-ash, whereas at 900 °C, it decreased to 0.42 mg/g-ash.

On the other hand, in short-term combustion of the rice husk burner (3 min), $M_{\text{solSiO}_2\text{-ef}}$ increased gradually as the combustion temperature increased. As the combustion temperature increased from 400 to 900 °C, $M_{\text{solSiO}_2\text{-ef}}$ increased from 0.46 to 1.6 mg/g-ash.

In long-term combustion of conventional method (60 min), the largest value of $M_{\text{solSiO}_2\text{-ef}}$ was 2.6 mg/g-ash at low-temperature combustion (500 and 600 °C). However, in short-term combustion of the rice husk burner (3 min), the largest value of $M_{\text{solSiO}_2\text{-ef}}$ was 1.6 mg/g-ash at high-temperature combustion (900 °C). Therefore, in the temperature range 400-900 °C, $M_{\text{solSiO}_2\text{-ef}}$ obtained under high-temperature and short-term combustion of the rice husk burner (900 °C, 3 min) was lower than that obtained by conventional method, *i.e.*, low-temperature and long-term combustion (400 °C, 60 min), and the former value reached more than 60% of that obtained by the conventional method.

Fig. 2 shows the ratio of soluble silica to the total silica in RHC combusted in an electric furnace, $R_{\text{sol/total-ef}}$ [%], with respect to the combustion temperature and time. In long-term combustion of conventional method (60 min), at 400-600 °C, $R_{\text{sol/total-ef}}$ was 31-32%, but above 700 °C, $R_{\text{sol/total-ef}}$ decreased rapidly and was less than 5% at 900 °C. It was assumed that although under low-temperature combustion at 400-600 °C, soluble silica was eluted, the elution was inhibited and the amount of eluted soluble silica decreased as the combustion temperature increased.

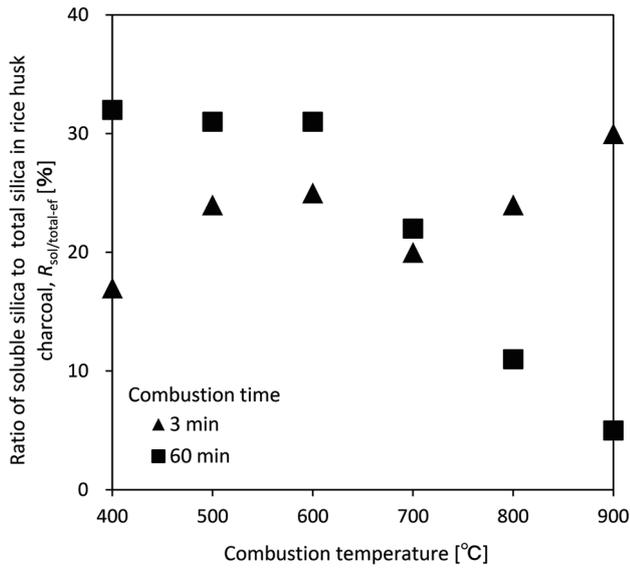


Fig. 2 Ratio of soluble silica to total silica in RHC combusted in electric furnace with respect to combustion temperature and time

On the other hand, in short-term combustion of the rice husk burner (3 min), $R_{sol/total-ef}$ tended to increase as the combustion temperature increased. $R_{sol/total-ef}$ was 17% at 400 °C and increased to 30% at 900 °C. It was assumed that as the combustion temperature increased, the inhibitor of elusion was eliminated and soluble silica could be easily eluted.

Therefore, the factors affecting the elusion mechanism of soluble silica in RHC were considered to be the amount of unburned carbon and the crystallization of silica, as mentioned in a previous study⁵⁾.

3.2 Amount of unburned carbon

Fig. 3 shows the weight ratio of RHC combusted in an electric furnace to rice husk [kg/kg-fuel] with respect to the combustion temperature and time. The weight of RHC was mainly composed of unburned carbon and silica. In long-term combustion of conventional method (60 min), the ratio of RHC to rice husk was approximately 18% regardless of the combustion temperature. On the other hand, in short-term combustion of the rice husk burner (3 min), the ratio was approximately 60% at 400 °C, and it decreased toward 18% as the combustion temperature increased.

The high value of the ratio of RHC to rice husk indicates the presence of a large amount of unburned carbon. It is generally known that 17% of the unburned remaining part in RHC exists as ash²⁰⁾, and the rice husk used in this study also included 18% ash (Table 2). Therefore, in long-term combustion of conventional method (60 min), regardless of the combustion temperature, it was assumed that plant fiber, which constituted the carbon part

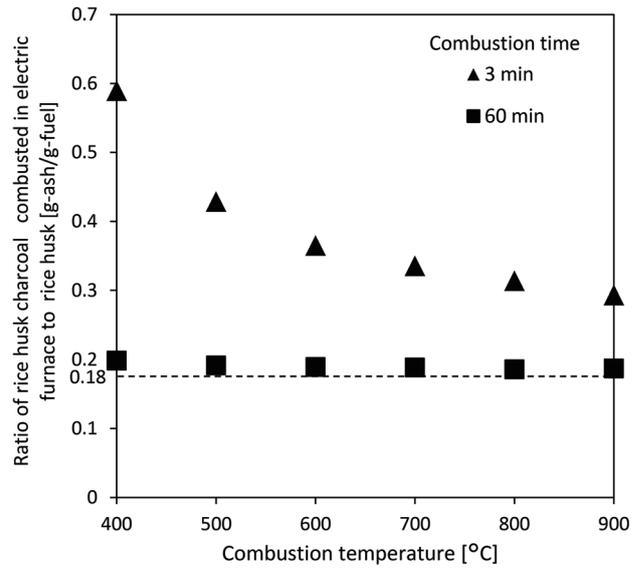


Fig. 3 Ratio of RHC combusted in electric furnace to rice husk with respect to combustion temperature and time

Table 3 Effect of combustion temperature and time on unburned carbon of rice husk plant fiber

	400° C	900° C
Long-term combustion of conventional method (60 min)	(a) Burned out	(b) Burned out
Short-term combustion of the rice husk burner (3 min)	(c) Remains	(d) Burned out

of rice husk, was almost burned and only ash remained (Table 3). On the other hand, in low-temperature and short-term combustion of the rice husk burner (400 °C, 3 min), the ratio of RHC to rice husk was high; hence, it was considered that combustion was not completed and most of the plant fiber was still unburned and remained in RHC (Table 3). Here, burned out means below 50% of the ratio of RHC combusted in an electric furnace to rice husk.

Fig. 4 shows time series variation of ratio of RHC combusted in an electric furnace to rice husk at 400, 600, and 800 °C. The ratio of RHC combusted in an electric furnace to rice husk decreased to the ratio of ash with increasing combustion time. From 3 min to 10 min, the ratio of RHC combusted in an electric furnace to rice husk decreased rapidly and from 10 min to 60 min, it decreased slowly regardless of combustion temperature. At 400 °C combustion, the variation of the ratio of RHC combusted in an electric furnace to rice husk were 0.02437 [1/min] from 3 min to 10 min and 0.00265 [1/min] from 10 min to 60 min. More, high temperature combustion (800 °C) shows lower ratio of RHC combusted in an electric furnace to rice husk that means large part of rice husk was burned out rather than low temperature combustion (400 °C).

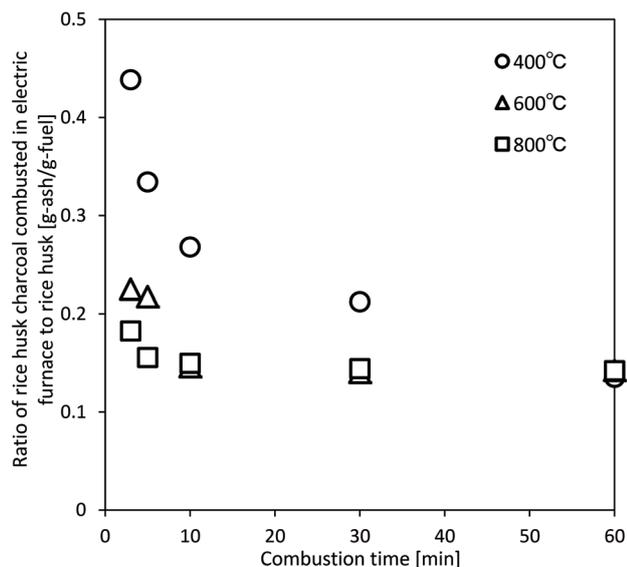


Fig. 4 Time series variation of ratio of RHC combusted in electric furnace to rice husk (400, 600, and 800 °C)

Shimizu *et al.*²¹⁾ reported that as the combustion temperature of rice husk increased at the rate of 20 °C/min, a rapid decrease in the mass and an increase in the heating velocity of rice husk were observed at 200 °C, and these trends peaked at around 340 °C. Furthermore, they reported that after the combustion of the volatile components in rice husk, solid carbon was combusted, and the former proceeded rapidly whereas the latter proceeded relatively slowly. Although it was difficult to compare the results to this research results directly, the tendency could be considered similar. Therefore, in low-temperature and short-term combustion of the rice husk burner (400 °C, 3 min), it was assumed that the ratio of RHC to rice husk was high because the combustion of volatile components proceeded rapidly and the time was too short to fully combust the volatile components. Accordingly, the combustion of solid carbon was assumed not to start. The remaining plant fiber was considered to physically inhibit soluble silica from eluting out of rice husk because the plant fiber part of rice husk (lignocellulose, cuticle layer, and so on) covered the silica (Fig. 5). Rice husk combustion caused the thermal decomposition of hemi-cellulose and cellulose at 250-550 °C⁴⁾. From the point of view of unburned carbon, long-term

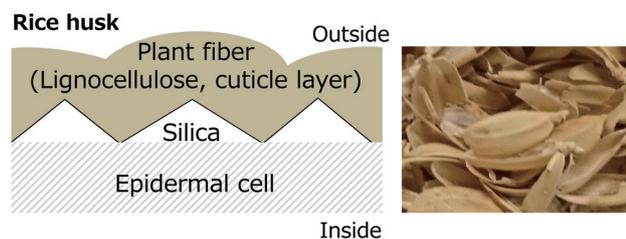


Fig. 5 Schematic view of rice husk

combustion of conventional method (60 min) was suitable for eliminating plant fiber; however, in short-term combustion of conventional method (3 min), an increase in the combustion temperature was desirable to eliminate plant fiber.

3.3 Crystallization of silica

The crystallization of silica was measured in terms of the specific surface area and pore volume. The measurement of these parameters serve as an activity measurement method, and their high values indicate that the tested sample is a high-quality fertilizer. The result of the specific surface area and pore volume of short-term combustion of the rice husk burner (3 min) over 700 °C and long-term combustion of conventional method (60 min) indicated the physical properties of ash because plant fiber was almost burned out and ash was remained as shown in Fig. 3. On the other hand, the result of the specific surface area and pore volume of short-term combustion of the rice husk burner (3 min) below 600 °C indicated the physical properties of ash and unburned plant fiber because plant fiber was not burned out.

Fig. 6 shows the specific surface area [m²/g] of RHC combusted in an electric furnace measured by the BET method¹⁸⁾ with respect to the combustion temperature and time. The specific surface area is related to the crystallization of silica. A smaller specific surface area indicates a progress in crystallization; however, a larger specific surface area, which represents amorphous silica, is desirable for an effective fertilizer. In general, a specific surface area of over 150 m²/g is assumed to indicate a high-

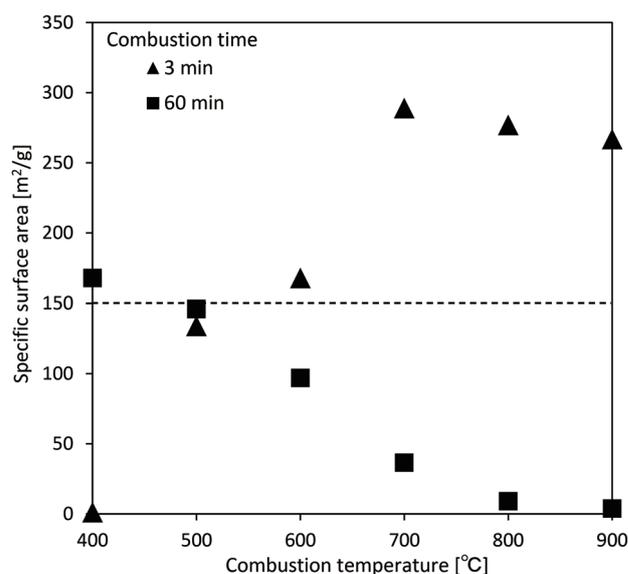


Fig. 6 Specific surface area of RHC combusted in electric furnace measured by BET method with respect to combustion temperature and time

activity resource⁵⁾.

In long-term combustion of conventional method (60 min), the specific surface area was the largest (168 m²/g) at 400 °C. As the combustion temperature increased, the specific surface area decreased and reached 3.94 m²/g at 900 °C. On the other hand, in short-term combustion of the rice husk burner (3 min), the specific surface area was the smallest (1.27 m²/g) at 400 °C. As the combustion temperature increased, the specific surface area increased rapidly and reached 267 m²/g at 900 °C.

In long-term combustion of conventional method (60 min), it was considered that the crystallization of silica is progressed as the combustion temperature increased. However, in short-term combustion of the rice husk burner (3 min), the specific surface area remained high even at high temperatures (700-900 °C), which means that the acceleration of the crystallization of silica was relatively slow. The specific surface area at 700-900 °C was supposed to reflect the physical properties of silica not plant fiber even plant fiber was still remained (Fig. 3).

More, in short-term combustion of the rice husk burner (3 min), the degree of decreasing unburned carbon (Fig. 3) and the difference of the specific surface area (Fig. 6) over 700 °C were relatively small because the factor controlling the burning velocity of solid fuel changed below and over 700-800 °C. The burning velocity was mainly controlled by chemical bond of solid fuel and oxygen at below 700-800 °C and by oxygen gas diffusion from heated surface of solid fuel toward outside to cause lack of oxygen near the surface over 700-800 °C.

Here, the specific surface area at 400-600 °C combustion for 3 min was extremely small. In general, silica never change from crystalline to amorphous that means the specific surface area never increase with increasing combustion time or temperature. Then, the specific surface area at 400-600 °C combustion for 3 min was supposed to reflect the specific surface area of plant fiber rather than silica owing to the fact that plant fiber covering silica was not sufficiently burned at 400-600 °C, as mentioned above. The result of unburned carbon at 400-600 °C (Fig. 3) that the ratio of RHC combusted in electric furnace to rice husk decreased with increasing combustion temperature corresponded to the result of the specific surface area (Fig. 6). Therefore, silica in RHC from 400-600 °C combustion for 3 min was supposed to be amorphous judged by irreversibility change from crystalline to amorphous, not by results of specific surface area.

From the viewpoint of the crystallization of silica, high-temperature and short-term combustion (900 °C, 3 min) was suitable, whereas high-temperature and long-term

combustion (900 °C, 60 min) was not suitable for this purpose (Table 4). Some amounts of crystalline silica, quartz, cristobalite, and tridymite also existed, and the ratio of these constituents changed as the combustion temperature changed. Under atmosphere pressure, tridymite and cristobalite are crystallized at 867-1470 and 1470-1727 °C, respectively^{9) 22)}. On the other hand, it was reported that the temperature of crystallization changes with the existence of alkali metal oxide when rice husk is combusted^{4) 23)}. In this study, the crystallization of tridymite was supposed to start in this target temperature range because alkali metal oxide existed when rice husk was combusted.

At 900 °C, although the specific surface area reduced in the 60-min combustion, it remained high in the 3-min combustion (Fig. 6). Therefore, it was suggested that even at high temperatures, short-term combustion did not cause crystallization to progress.

Figs. 7, 8, and 9 show the pore volume [cm³/g] with respect to the combustion temperature and time. The pore volume represents the volume of the pore measured by the specific surface area, and it measured the activity of samples like the specific surface area. Fig. 7 shows the pore volume

Table 4 Effect of combustion temperature and time on crystallization of silica in rice husk

	400 °C	900 °C
Long-term combustion of conventional method (60 min)	Amorphous	Crystalline
Short-term combustion of the rice husk burner (3 min)	- (supposed to be amorphous)	Amorphous

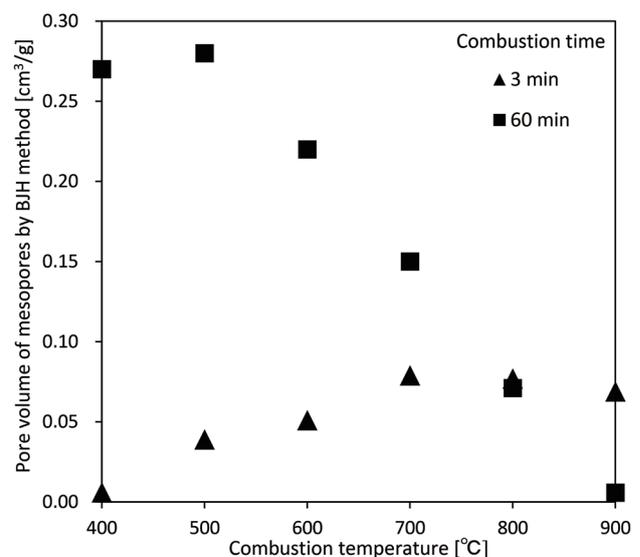


Fig. 7 Pore volume of mesopores (pore diameter: approximately 2.6-200 nm) of RHC combusted in electric furnace measured by BJH method on adsorption side with respect to combustion temperature and time

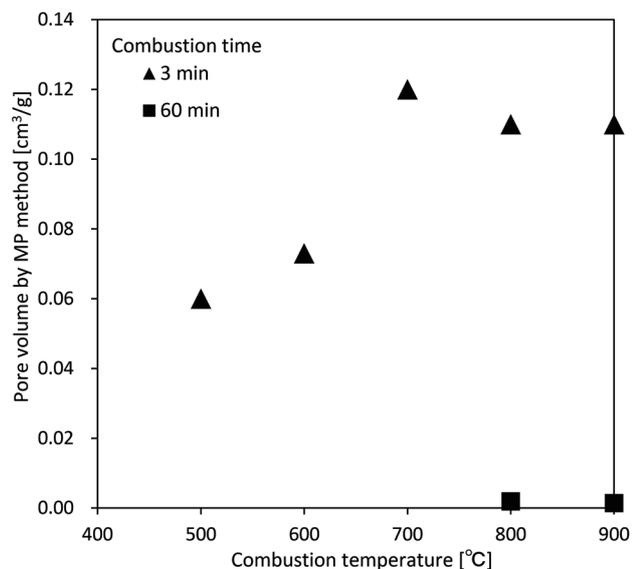


Fig. 8 Pore volume (pore diameter: approximately 0.42-2 nm) of RHC combusted in electric furnace measured by MP method with respect to combustion temperature and time

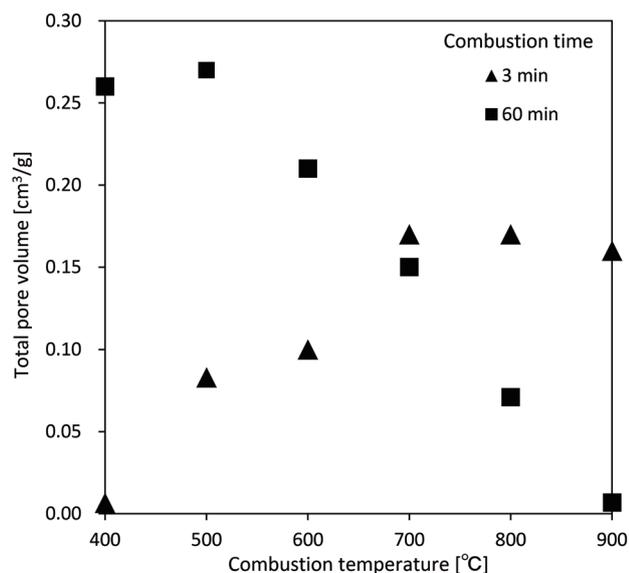


Fig. 9 Total pore volume of RHC combusted in electric furnace with respect to combustion temperature and time

of mesopores (pore diameter: approximately 2.6-200 nm) of RHC combusted in an electric furnace measured by the BJH method^{18) 19)} on the adsorption side with respect to the combustion temperature and time. Fig. 8 shows the pore volume (pore diameter: approximately 0.42-2 nm) of RHC combusted in an electric furnace measured by the MP method¹⁹⁾ with respect to the combustion temperature and time. Here, as shown in Fig. 8, only the RHC that was recognized to have micropores was analyzed. Fig. 9 shows the total pore volume of RHC combusted in an electric furnace with respect to the combustion temperature and time; this volume was measured under a relative pressure of

0.99. The results of pore volume at 400-600 °C combustion for 3 min was supposed to reflect the physical property of plant fiber rather than silica owing to the fact that plant fiber covering silica was not sufficiently burned at 400-600 °C, as mentioned above.

With regard to the pore whose diameter was approximately 2.6-200 nm (Fig. 7), in long-term combustion of conventional method (60 min), the pore volume decreased rapidly as the combustion temperature increased, and in short-term combustion of the rice husk burner (3 min), the pore volume increased gradually as the combustion temperature increased. The largest values of the pore volume were 0.28 cm³/g at 500 °C in long-term combustion and 0.079 cm³/g at 700 °C in short-term combustion.

With regard to the pore whose diameter was approximately 0.42-2 nm (Fig. 8), in short-term combustion of the rice husk burner (3 min), the pore volume increased as the combustion temperature increased; the pore volume was 0.060 cm³/g at 500 °C and 0.11 cm³/g at over 700 °C. In long-term combustion of conventional method (60 min), the pore volume was considerably smaller than that in short-term combustion of the rice husk burner (3 min); the pore volume was 0.0019 cm³/g at 800 °C. Pores were not recognized below 700 °C in the 60-min combustion.

With regard to all the pores (Fig. 9), in long-term combustion of conventional method (60 min), the pore volume decreased as the combustion temperature increased, as shown in Figs. 7 and 8. In short-term combustion of the rice husk burner (3 min), the pore volume increased as the combustion temperature increased. The largest values of the total pore volume were 0.27 cm³/g at 500 °C in long-term combustion and 0.17 cm³/g at 700 and 800 °C in short-term combustion.

From Figs. 7-9, it can be inferred that in long-term combustion of conventional method (60 min), the crystallization of silica progressed and the activity of RHC declined. On the other hand, in short-term combustion of the rice husk burner (3 min), although the total pore volume in the remaining plant fiber was small, a certain amount of the total pore volume was found to maintain the activity of the sample as a fertilizer at high temperature.

3.4 Relationship between amount of eluted soluble silica in rice husk charcoal and combustion temperature

With respect to maximizing the amount of eluted soluble silica (Fig. 1), the conventional method to produce RHC (low-temperature, long-term combustion) was considered to be the best. However, in this study, the possibility of using high-temperature, short-term combustion

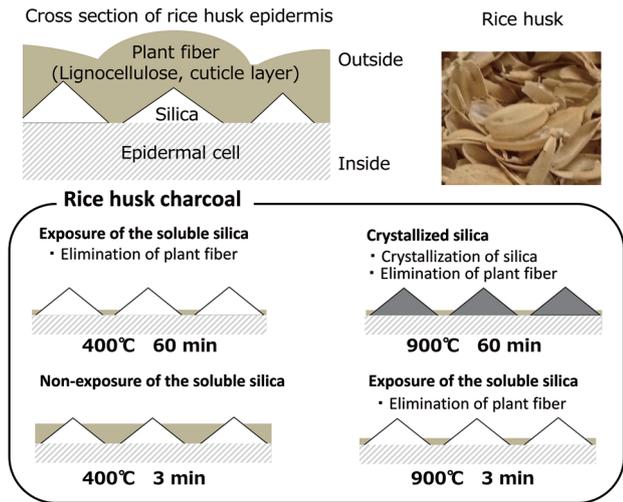


Fig. 10 Hypothetical mechanism of elution of soluble silica from RHC

was suggested. In addition, the combustion temperature and time were considered in this study, and the elusion mechanism of soluble silica in RHC was assumed to be decided by the amount of unburned carbon and the crystallization of silica, as was the case in a previous study⁵⁾ that considered the combustion temperature.

The hypothesis of the elusion mechanism of soluble silica in RHC was presented in Fig. 10. In short-term combustion of the rice husk burner (3 min), the amount of eluted soluble silica was determined by the elimination of plant fiber covering silica in rice husk (Table 3) because regardless of the combustion temperature, the crystallization of silica did not progress (Table 4). Consequently, a high temperature (900 °C) that was effective in eliminating carbon was suitable for increasing the amount of eluted soluble silica.

On the other hand, in long-term combustion of conventional method (60 min), the amount of eluted soluble silica was determined by the crystallization of silica (Table 4) because regardless of the combustion temperature, most of plant fiber was burned out (Table 3). Consequently, a low temperature (400 °C) that produced low crystallization of silica was suitable for increasing the amount of eluted soluble silica. Therefore, the amount of eluted soluble silica was decided by the balance of the two factors—the amount of unburned carbon and the crystallization of silica—which had a trade-off relationship, considering the combustion temperature and time.

3.5 Amount of eluted soluble silica in rice husk charcoal combusted in rice husk burner

Table 5 lists the constituents of RHC combusted in the rice husk burner, as measured by the X-ray fluorescence

Table 5 Constituents of RHC combusted in rice husk burner at average temperature of 813 °C, as measured by X-ray fluorescence analysis

Constituent [wt%]				
SiO ₂	Al ₂ O ₃	TiO ₂	CaO	Fe ₂ O ₃
76.4	0.21	0.01	0.39	0.66
MgO	Na ₂ O	K ₂ O	P ₄ O ₁₀	
0.27	0.06	1.42	0.76	

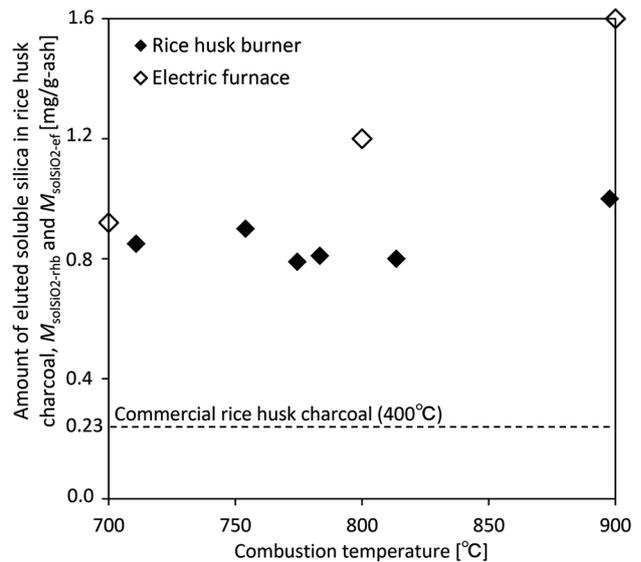


Fig. 11 Amount of eluted soluble silica in RHC combusted in rice husk burner and electric furnace at 700-900 °C in 3-min combustion

analysis.

Fig. 11 shows the amount of eluted soluble silica in RHC combusted in the rice husk burner, $M_{\text{solSiO}_2\text{-rhb}}$ [mg/g-ash], and in the electric furnace, $M_{\text{solSiO}_2\text{-ef}}$ [mg/g-ash], at 700-900 °C in the 3-min combustion. For comparison, the amount of eluted soluble silica in commercial RHC is also shown in Fig. 11.

Compared to $M_{\text{solSiO}_2\text{-ef}}$, $M_{\text{solSiO}_2\text{-rhb}}$ was small (less than 1.0 mg/g-ash) but the tendency of its highest value at 900 °C was the same as that of $M_{\text{solSiO}_2\text{-ef}}$. One of the reasons why $M_{\text{solSiO}_2\text{-rhb}}$ was smaller than $M_{\text{solSiO}_2\text{-ef}}$ was supposed to be that the combustion state in the rice husk burner was not stable and the combustion temperature fluctuated. It would be better to establish stable combustion in the rice husk burner for increasing the amount of eluted soluble silica. Compared to the amount of silica in commercial RHC, the value of $M_{\text{solSiO}_2\text{-rhb}}$ was high, and the rice husk burner produced high-quality fertilizer.

The mass concentration of the total silica contained in RHC combusted in the rice husk burner was higher only at 898 °C than the mass concentration of the silica contained in commercial RHC. However, the ratios of soluble

silica in the rice husk burner and electric furnace, which represented the ratio of valuable silica as fertilizer, were higher than that of commercial RHC under all conditions at 700-900 °C in 3-min combustion.

Shimizu *et al.*²⁴⁾ reported that in high-temperature combustion, the total amount of volatile components was larger than that in low-temperature combustion; in addition, with a high ratio of the vapor phase and a low ratio of the liquid and solid phases, thermal decomposition progressed more in high-temperature combustion than in low-temperature combustion. In addition, thermal decomposition progressed more at a rapid increase in the combustion temperature than at a gradual increase in the combustion temperature.

Therefore, the rice husk burner used in this study was suitable for combusting plant fiber to elute soluble silica because it could produce high-temperature combustion right from the beginning. In addition, the low ratio of the liquid and solid phases resulted in less tar and less clogging of the burner. Therefore, high-temperature, short-term combustion was considered to be effective in not only heat energy utilization by rice husk combustion but also producing RHC that could be used as a high-quality fertilizer.

4. Summary and Conclusions

- 1) This study clarified the differences between burner combustion method and conventional method from the viewpoint of total amount of eluted soluble silica in rice husk charcoal with changing combustion temperature and time, and estimated the mechanism of silica elusion.
- 2) Rice husk charcoal combusted at a high temperature for a short-term (900 °C, 3 min) of the rice husk burner contained 60% of the amount of eluted soluble silica contained in rice husk charcoal combusted at a low temperature for a long-term (400 °C, 60 min) of conventional method.
- 3) The hypothetical mechanism of the elusion of soluble silica with changes in the combustion temperature was supposed to be related to the amount of unburned carbon and the crystallization of silica. In short-term combustion (3 min), the amount of eluted soluble silica was determined by eliminating plant fiber covering silica in rice husk. Hence, a high temperature (900 °C) that was effective in eliminating carbon was suitable for increasing the amount of eluted soluble silica. On the other hand, in long-term combustion (60 min), the amount of eluted soluble silica was determined by the crystallization of silica. Hence, a low temperature (400 °C) that produced low crystallization of silica was suitable for increasing the amount of eluted soluble silica.
- 4) Although combustion in the rice husk burner was not as stable as that in the electric furnace, the amount of eluted soluble silica in rice husk charcoal combusted in the rice husk burner in a short-term (3 min) showed the same tendency as that in the electric furnace, and the highest value of the amount of eluted soluble silica was achieved in high-temperature combustion (900 °C).

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