



## Crystalline silica in compressed rice hull coke ash

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### Abstract

Compressed rice hull coke was produced by compressing rice hulls ground to less than 200  $\mu\text{m}$  diameter at  $1.22 \times 10^6 \text{ N/m}^2$  and  $310^\circ\text{C}$  with an oxygen deficient atmosphere. The compressed rice hull coke had a 5 cm outer diameter, a 1.5 cm inner diameter and 35 cm length. The density of the coke is 1.2, and, the heat value is  $16570 \text{ kJ}\cdot\text{kg}^{-1}$ . In this study, 2 kg coke was combusted at the average temperature of  $850^\circ\text{C}$  for 104 min with a maximum temperature of  $860^\circ\text{C}$ . The ash was colored black-grey, and the form remained coke. The ash contained 95.4% silica with 9.2% cristobalite and 86.2% amorphous silica. The occupational exposure limits of respirable fraction of crystalline silica such as cristobalite and quartz in floating dust less than the diameter of  $7 \mu\text{m}$  is  $0.025 \text{ mg/m}^3$ ; however, no respirable cristobalite was detected during combustion of the compressed rice hull coke. Cristobalite was not present in floating dust because it melted during the crystallization of amorphous silica to cristobalite.

## 1. Introduction

Rice hulls consist of 80 wt% organic matter (e.g., cellulose, hemi-cellulose, and lignin) and 20 wt% inorganic matter. Combustion of the organic matter is used for heating and power generation. The inorganic matter consists of around 90 wt% silica [1]. Silica is an essential substance for growing rice plants. Rice plants absorb silicic ions in soil and/or irrigation water via their roots; the silicic ions are transported to the wall of the trachea and cuticle layers of outer and inner epidermis of rice hull via the transpiration stream; then they lose water by transpiration and change to amorphous silica. The rice hull silica is originally amorphous state and changes to cristobalite and/or tridymite, depending on the combustion temperature and impurities such as  $\text{K}^+$  [2-7]. Potassium compounds in rice hull ashes decrease the surface area due to melting of silica particles and acceleration of the crystallization of amorphous silica to crystalline silica such as cristobalite. The amorphous silica in rice hulls is deposited in the cuticle, which is continuous films of cutinlocated outside of epidermis of rice hull, and disperses at a molecular level in the cuticle. The amorphous silica resulting from the combustion of rice hulls is in the form of very fine particles with primary particles having 20-30 nm diameters [8]. Combustion is usually done

with rice hulls in a state of suspension like a floating circulating combustor and a fluidized bed combustor [9]. In fire grate combustor, rice hulls are blown into the furnace with air because of 0.1 relative density of rice hull. In these combustors, rice hulls collide with each other, furnace wall and/or fluidizing bed medium and burn, resulting in rice hull ash being very fine particles. Some fine crystalline silica particles are emitted with the combustion of rice hulls, even if the flue gas is passed through a dust collector. Electrostatic precipitator can collect 98% of the dusts having a diameter more than  $0.01 \mu\text{m}$ . Respirable particles with a diameter of less than  $7 \mu\text{m}$  travel from the atmosphere through nose or mouth and arrive at the alveolus, which is deep in the respiratory system, and easily cause pneumoconiosis [10]. Respiratory crystalline silica particles (e.g., cristobalite, tridymite and quartz) floating in the air may cause silicosis or lung cancer; thus, NIOSH has set the occupational exposure limit of the respirable fraction at  $0.025 \text{ mg/m}^3$  for cristobalite and quartz and at  $0.05 \text{ mg/m}^3$  for tridymite [11] ( $0.03 \text{ mg/m}^3$  in Japan [12]). The silicosis caused by crystalline silica in rice hull ashes has been studied epidemiologically, experimentally and etiologically [13].

$\text{SiO}_2$  melts when crystallized to cristobalite by potassium in rice hulls and solidified when the temperature decreases [3]. Pieces of rice hulls adhere each other by the tar formed by thermal

decomposition of rice hulls under an oxygen deficient atmosphere near 300°C and the same time change to solid and dense rice hull coke by compression. Since the compressed rice hull coke does not burn in the state of suspension, the crystalline silica produced is not discharged as floating dust, because the crystalline silica melts and remains in the ash and solidified.

In this study, it was confirmed that melting occurred when silica in the ash of the compressed rice hull coke crystallized to cristobalite under the action of potassium, and that crystalline silica was not discharged as floating dust generated by combustion of compressed rice hull coke.

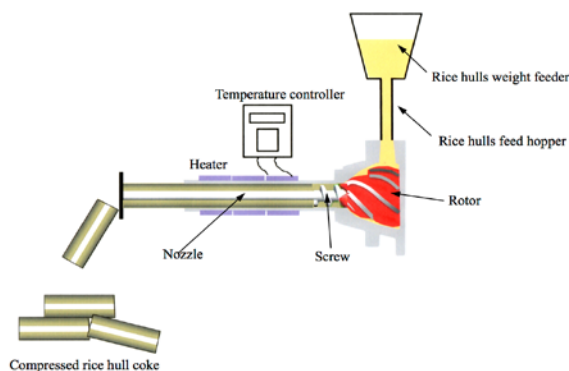
## 2. Experimental

### 2.1 Rice hulls and compressed rice hull coke

The raw material was rice hulls obtained from a rice mills in Naganuma, Hokkaido and Mihara, Hiroshima, Japan. Compressed rice hull coke was produced using a grind mill (Tromso Co. Ltd., TRM-120F) (Figure 1). Rice hulls collected at the rice mill in Mihara were set in the rice hulls weight feeder and were sent to the rotor part via the feed hopper. Rice hulls were ground in the rotor to coarse powder less than 200  $\mu\text{m}$  and compressed at  $1.22 \times 10^6 \text{ N/m}^2$  using the screw. At the same time, compressed crushed rice hulls with the pipe shape of 5 cm outer diameter and 1.5 cm inner diameter were heated at 310°C to prepare rice hull coke (Figure 2). As shown in our previous paper [3], the organic matter, the inorganic matter (ash), the organic matter decomposed to gas and tar at round 300°C, and the organic matter composed of solid carbon-rich organic compounds in rice hulls and compressed rice hull coke can be determined by TG-DTA analysis in the flowing air and  $\text{N}_2$ . The contents of organic matter (e.g., cellulose, hemicellulose and lignin), inorganic matter (e.g.,  $\text{SiO}_2$  and  $\text{K}_2\text{O}$ ), and water in rice hulls and the compressed rice hull coke are summarized in Table 1.

The surface and section morphology and the distribution of Si element of the section of rice hulls and the compressed rice hull coke were observed by a scanning electron microscopy (JEOL, JSM-5300) with an attached an energy-dispersive X-ray diffractometer (JEOL, JED-2100). The heat values of rice hulls and the coke were measured by a bomb calorimeter (Shimadzu, CA-4AJ). Thermal behavior

of rice hulls and the coke in air and nitrogen was analyzed using a simultaneous thermogravimetry/differential thermal analysis instrument (SII, TG/DTA 6200).



**Figure 1.** Scheme of the grind mill (Toromso, TRM-120F).



**Figure 2.** Compressed rice hull coke. (relative density:  $\sim 1.2$ , water content:  $\sim 5.5\%$ )

### 2.2 Crystallization of $\text{SiO}_2$ in ash

Rice hulls were heated at 500°C for 1 h in flowing nitrogen to obtain the carbonized rice hulls, which were combusted at 500°C for 1 h to obtain rice hull ash composed of amorphous silica and the impurities. The contents of Ca, Al, Fe, K, Mg, Mn, Na and P in the ash were analyzed using ICP-AES (Shimadzu, JSM-5200). The rice hull ash was heated in air stream of 100 mL/min at the temperature at 600 to 1500°C for 4 h to identify the crystalline phases using XRD (Rigaku, RINT2000 / PC) with  $\text{CuK}\alpha$  ray and a graphite monochromator.

To investigate the crystallization of amorphous rice hull silica without the impurities, 25 g rice hulls were washed with 0.5 L of 1N HCl solution at 100°C for 2 h to remove impurities such as  $\text{K}_2\text{O}$  and  $\text{CaO}$ .

**Table 1.** Contents of organic and inorganic matter and H<sub>2</sub>O in rice hulls and compressed rice hull coke.

	Organic matter	Organic matter decomposed to gas and tar	Carbon-rich organic matter	Inorganic matter (Ash)	H <sub>2</sub> O
Rice hulls (Naganuma)	76.4	52	24.4	18.9	4.7
Rice Hulls (Mihara)	74.4	53	21.4	18.6	7
Compressed rice hull coke	71.4	40.4	31.9	24	4.6

They were washed to pH 7.0 with distilled water and were dried at 80°C for 1h in vacuo. The contents of Ca, Al, Fe, K, Mg, Mn, Na and P in the ash obtained by combustion of the HCl-washed rice hulls were analyzed using ICP-AES. The HCl-washed rice hull ashes were prepared using combustion at 500°C, and were heated in flowing air for 1h at 600 to 1500°C with heating rate of 10°C/min in air to examine the crystalline phases.

Next we investigated the effect of K on the crystallization of the amorphous rice hull silica, KCl was added to the amorphous rice hull silica because KCl, which is driven from a fertilizer, was detected on the ash of the compressed rice hull coke using XRD analysis. Reagent KCl (99.5% purity, Wako) of 0.5 to 5 wt% as potassium metal for SiO<sub>2</sub> was added to the acid-washed rice hull ashes, and the mixed samples were heated in air stream of 100 mL/min at 600 to 1500°C for 4 h to identify the crystalline phases using XRD. K<sub>2</sub>CO<sub>3</sub> (99.5% purity, Wako), K<sub>2</sub>SiO<sub>3</sub> (Wako), KOH (85.0% purity and H<sub>2</sub>O of 15.0%, Wako), KNO<sub>3</sub> (99.0% purity, Wako) and K<sub>2</sub>SO<sub>4</sub> (99.0% purity, Wako) in addition KCl were added to the rice hull ashes washed with HCl. NaCl (99.5% purity, Wako), NaOH (97% purity, Wako) and CaO (99.9% purity, Wako) were also used as additives.

For comparison with rice hull ashes, the commercial amorphous silica without impurities (reagent grade, Kanto Chemical) was used.

### 2.3 Capture and analysis of floating dust from combustion of compressed rice hull coke

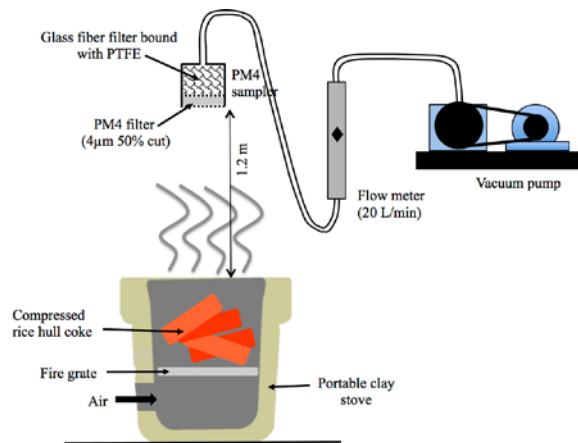
Crystalline silica such as cristobalite with respirable diameter smaller than 7 μm floating dust is capable of causing lung cancer [10]. The fine

amorphous silica in rice hulls change to cristobalite by potassium in rice hull ash during the combustion of rice hulls at 900°C [3] and the fine cristobalite particles in the ash contain in the floating dust of flue gas since the rice hull ash is fine. Floating dust was emitted with the combustion of compressed rice hull coke of 4 kg and the particles with the diameter of more than 7 μm were captured by the PM4 sampler (Shibata, NW-354), which respirable dust of cut-size 4 μm diameter (50% efficiency) can be captured [11]. A glass fiber filter bound with PTFE trapped particles less than 7 μm, from the flue gas of 3.8 m<sup>3</sup> for 190 min at a place 1.2 m away from the compressed rice hull coke stove (Figure 3). Particles less than 7 μm was analyzed by a XRD to detect the crystalline silica. Quantitative analysis of cristobalite was carried out by an internal standard method using XRD. Cristobalite (97% purity, Seto Yogyo Co.) was used as a standard substance; α-Al<sub>2</sub>O<sub>3</sub> (99.99% purity, Koujunndo Chemical Laboratory Co. Ltd.) was used as an internal standard substance; and TiO<sub>2</sub> (rutile, 99.99% purity, Koujunndo Chemical Laboratory Co. Ltd.) was used as a diluent.

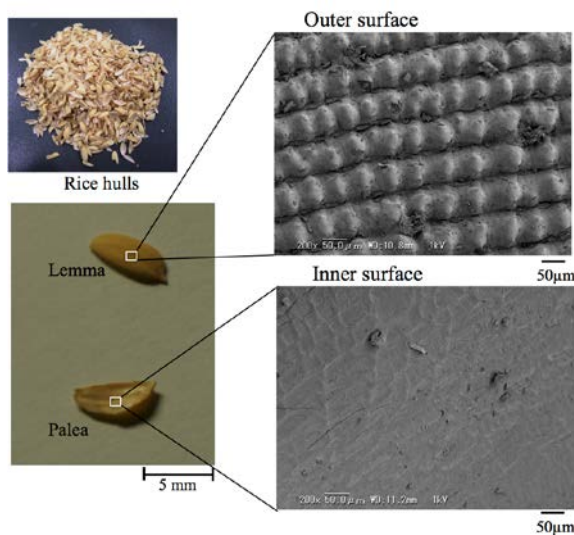
## 3. Results and Discussion

### 3.1 Rice hulls and compressed rice hull coke

Figure 4 presents SEM photographs of japonica (short-grain) rice hulls, and outer and inner surfaces of a rice hull. Rice hulls are composed of lemma and palea covering rice grain and have a 7 mm major axis, a 3 mm minor axis, and 70 to 120 μm thickness. Hemispheres with 30 to 40 μm diameter laid out a line longitudinally in the outer surface, and a smooth surface was observed in the inner surface.



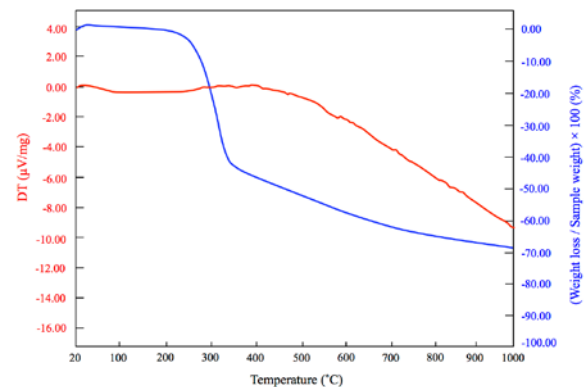
**Figure 3.** Schematic diagram of the capture method of respirable particles less than  $7\ \mu\text{m}$  diameter in floating dust from the combustion of compressed rice hull coke.



**Figure 4.** SEM photographs of outer and inner surface of rice hull.

The backscattered electron image and the  $\text{Si-K}\alpha$  image of the section of rice hull were presented in the previous report [8]. Organic matters such as cellulose existed in the center area of the section of rice hull, and silica existed in the cuticle layer located outside the epidermis and the inner epidermis. Sharma et al.[14] reported rice hulls contained 15.8~20.6 wt% silica, and the ratio of silica in the cuticle layer outside the outer epidermis and the inner epidermis was 2.4:1. In this research, silica was 17.4 wt% of rice hulls (Naganuma) and the ratio of silica was 10:1 for the cuticle layer outside the outer epidermis and the inner epidermis. XRD analysis of the crushed rice hulls indicated that the silica was amorphous.

Figure 5 plots the TG-DTA curves of rice hulls (Mihara) in flowing  $\text{N}_2$ . The sharp weight loss from  $220^\circ\text{C}$  to  $330^\circ\text{C}$  was thought to be due to the decomposition of organic constituents (e.g., cellulose, etc.) releasing gases such as  $\text{CH}_4$  and tar vapor. In the grind mill (Figure 1), the crushed rice hulls released the tar vapor at  $310^\circ\text{C}$  with an oxygen-deficient atmosphere, and the tar vapor solidified pieces of the crushed rice hull coke at the lower temperature, and produced the dense rice hull coke under the compression caused by the screw and the nozzle of the grind. The heat of the compressed rice hull coke was  $16590\ \text{kJ}\cdot\text{dry}\cdot\text{kg}^{-1}$  and that of rice hulls (Mihara) was  $16160\ \text{kJ}\cdot\text{dry}\cdot\text{kg}^{-1}$  because of the carbon content. The heat of the coke was greater than that of rice hulls, because polymerized organic matter with higher carbon content was formed due to decomposition of the organic matter.

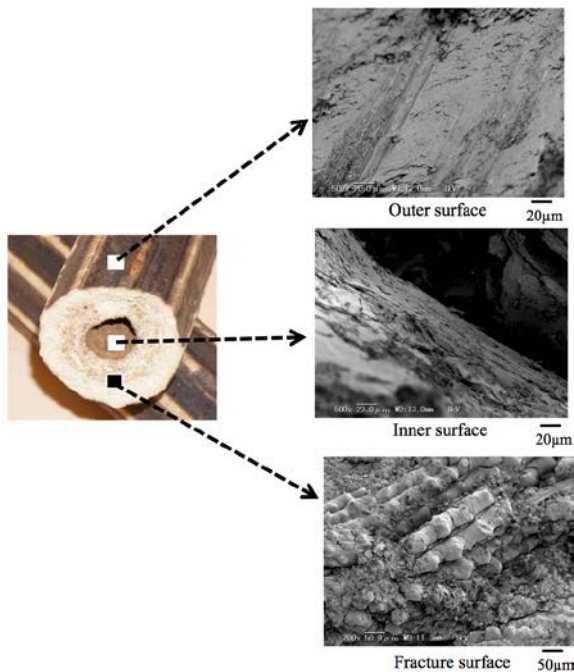


**Figure 5.** TG-DTA curves of a grain of rice hull (Mihara, Hiroshima) in flowing nitrogen of  $50\ \text{ml}\cdot\text{min}^{-1}$ . (Sample weight: 5.05 mg, Heating rate:  $10^\circ\text{C}\cdot\text{min}^{-1}$ , Thermocouple: R, 87% Pt/ 13% Rh-Pt by weight).

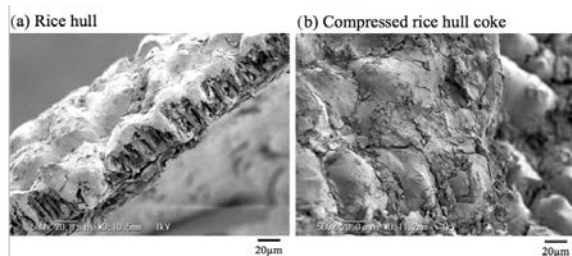
Figure 6 shows the SEM photographs of the outer and inner surface, and the fracture surface of the compressed rice hull coke. The inner and outer surface is smooth; however, the structure of rice hulls could not be observed because the crushed rice hulls rubbed the nozzle wall. The nozzle wall was heated at  $310^\circ\text{C}$ , and the outer surface was blackish-brown due to the thermal decomposition of the rice hulls. The fracture surface of the coke was yellowish, and pieces of cuticle and fine particles were observed.

Figure 7 presents SEM photographs of the fracture surface of (a) rice hull and (b) compressed rice hull coke. The cortex and pith composed of cellulose, hemicellulose and lignin of the coke were

particle and fine flakes; and pieces of hard cuticle containing silica remained because of grinding and compression during the processing of the rice hull coke. However, the cortex and pith of rice hulls were in the form of fiber with many cavities.



**Figure 6.** SEM photographs of compressed rice hull coke.



**Figure 7.** SEM photographs of the cross section of rice hull and compressed rice hull coke.

**Table 2.** Chemical composition of rice hull ash and rice hull ash produced by the combustion of rice hulls washed with diluted HCl.

Chemical composition (wt%)	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	MnO	Na <sub>2</sub> O
Rice hull ash	92.14	0.04	0.48	0.03	3.20	0.16	0.18	0.09
HCl- washed rice hull ash	99.84	0.04	0.02	0.03	0.00	0.01	0.01	0.00

### 3.2 Crystallization of SiO<sub>2</sub> in ash

Table 2 summarizes the content of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, Fe<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, MgO, MnO and Na<sub>2</sub>O in the ash prepared the combustion of rice hulls (Naganuma) at 600°C. The ash contains 92.14 wt% SiO<sub>2</sub>, 3.20 wt% K<sub>2</sub>O and other impurities.

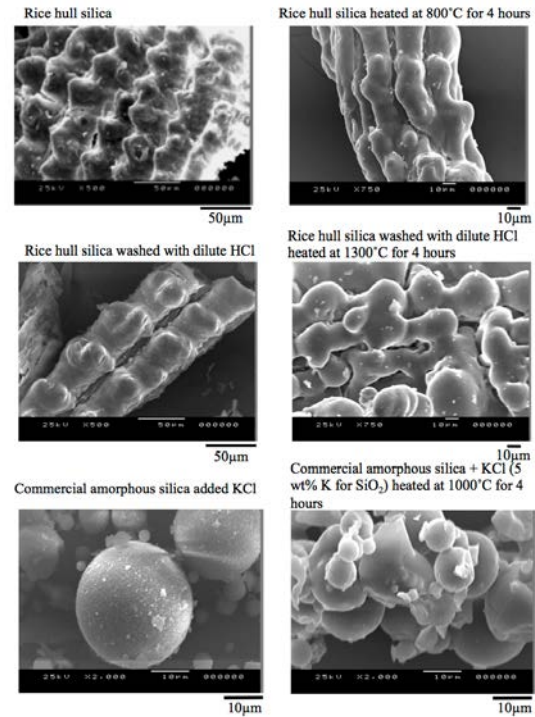
Table 3 lists the crystalline phases when the ash was heated from 600 to 1500°C for 4 h. Cristobalite was detected at temperature above 800°C and was also detected on tridymite at temperature above 900°C. However, cristobalite was detected at temperature above 1300°C on rice hull silica washed with dilute HCl, where the contents of K<sub>2</sub>O and Na<sub>2</sub>O was zero; those of CaO, MgO and MnO greatly decreased; and those of Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> did not change. Commercial amorphous silica with 100% SiO<sub>2</sub> was crystallized to cristobalite at temperature above 1300°C, and that with added KCl was crystallized to cristobalite and the small amount of tridymite at temperature above 1000°C.

Figure 8 presents SEM photographs of rice hull silica, rice hull silica washed with dilute HCl, and commercial amorphous silica with KCl added before and after crystallization. The shape of cuticle with half spheres containing mainly SiO<sub>2</sub> was observed in the rice hull silica and the HCl-washed rice hull silica. Particles of spherical silica and KCl (small particles on the spherical silica) were observed in the sample of commercial amorphous silica with added KCl. The surface of all samples heated at the temperature of the crystallization melted. The melt resulted in easy movement of the lattice of SiO<sub>2</sub> to crystallize to cristobalite from amorphous silica.

**Table 3.** Crystalline phases of rice hull silica, HCl-washed rice hull and commercial amorphous at various temperatures.

Additive Temperature (°C)	Rice hull silica	Rice hull silica washed with dilute HCl	Commercial amorphous silica	Commercial amorphous silica
	-	-	-	KCl (5wt% as K)
1500	C, T (t)	C	C	C, T (t)
1400	C, T (t)	C	C	C, T (t)
1300	C, T (t)	C	C	C, T (t)
1200	C, T (t)	A	A	C, T (t)
1100	C, T (t)	A	A	C, T (t)
1000	C, T (t)	A	A	C, T (t)
900	C, T (t)	A	A	A
800	C	A	A	A
700	A	A	A	A
600	A	A	A	A

A: amorphous silica, C: cristobalite, T: tridymite, (t): Small XRD peaks were detected.

**Figure 8.** SEM photographs of rice hull silica, rice hull silica washed with dilute HCl and commercial amorphous silica added KCl before and after crystallization.**Table 4.** Crystalline phases of rice hull silica washed with dilute HCl added with various compound additives heated at 600 to 1500°C for 0 h with heating rate of 10°C/min in air.

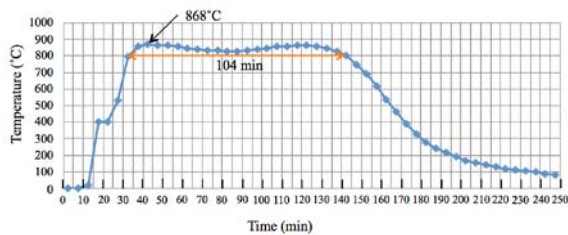
Additive Temp. (°C)	KCl (5 wt% as K)	KCl (1 wt% as K)	KOH (5 wt% as K)	K <sub>2</sub> CO <sub>3</sub> (5 wt% as K)	KNO <sub>3</sub> (5 wt% as K)	K <sub>2</sub> SiO <sub>3</sub> (5 wt% as K)	NaCl (5 wt% as Na)	NaOH (5 wt% as Na)	CaO (5 wt% as Ca)
1500	T, C(t)	C, T(t)	C, T(t)	C, T(t)	C, T(t)	C, T(t)	C, T(t)	C, T(t)	C, Q(t)
1400	T, C(t)	C, T(t)	C, T(t)	C, T(t)	C, T(t)	C, T(t)	C, T(t)	C, T(t)	C, Q(t)
1300	T, C(t)	C, T(t)	C, T(t)	C, T(t)	C, T(t)	C, T(t)	C, T(t)	C, T(t)	C, Q(t)
1200	C, T	C, T(t)	C, T(t)	C, T(t)	C, T(t)	C, T(t)	C, T(t)	C, T(t)	Q
1100	C, T(t)	C, T(t)	C, T(t)	C, T(t)	C, T(t)	C, T(t)	C, T(t)	C, T(t)	Q
1000	C, T(t)	C	C, T(t)	C, T(t)	C, T(t)	C, T(t)	C, T(t)	C, T(t)	Q, CaO, CaSiO <sub>3</sub> (t)
900	C, T(t)	C	C, T(t)	C, T(t)	C, T(t)	A	C	A	A, CaO
800	A	A	C, T(t)	C, T(t)	A	A	C	A	A, CaO
700	A, KCl	A	A	A	A	A	A, NaCl	A	A, CaO
600	A, KCl	A	A	A	A	A	A, NaCl	A	A, CaO

A: amorphous, C: cristobalite, T: tridymite, Q: quartz, (t): Small XRD peaks were detected.

Table 4 indicates the crystalline phase change of rice hull silica washed with dilute HCl with the addition of 5 and 1 wt% as K of KCl. The silica surface melted even with the low concentration K of 1% and the amorphous silica crystallized at 900°C in cristobalite. In potassium compounds except for KCl, the silica melted at the crystallization temperature. Crystallization of amorphous silica to cristobalite started at a lower temperature than the HCl washed rice hull silica at 1300°C. NaCl, NaOH and CaO additives resulted in acceleration of the crystallization of amorphous silica, similar to the potassium compound additives; however, these additives actually had no effect on crystallization because of their very low concentrations in rice hull ash.

### 3.3 Floating dust during combustion of compressed rice hull coke

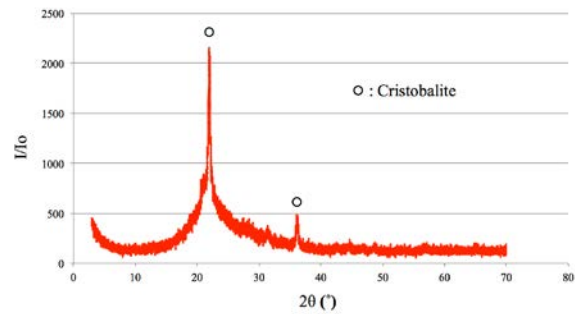
Figure 9 plots the temperature profile of combustion of 2 kg coke using a portable clay cooking stove under natural ventilation. The temperature was measured at the surface of the coke, and stable combustion at the average temperature of 850°C continued for 104 min. Table 5 indicates the chemical composition of the coke ash obtained from combustion of the coke plotted in Figure 9. The content of K<sub>2</sub>O was 1.96%, whereas the content of rice hull ash in Table 2 was 3.20%. The variety of product areas of rice hulls caused the difference of K<sub>2</sub>O content.



**Figure 9.** Temperature change with time of the combustion of compressed rice hull coke (2kg) using portable clay cooking stove.

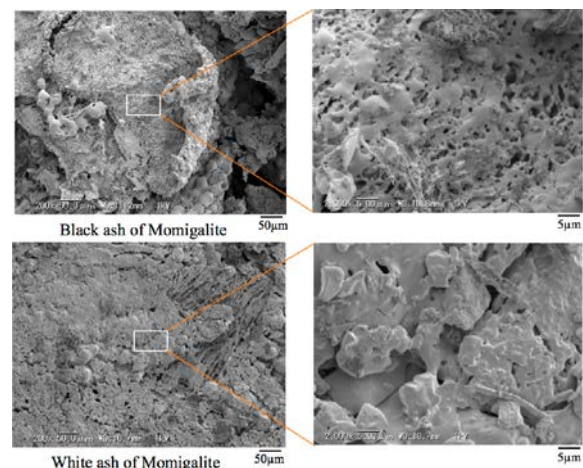
Figure 10 depicts cristobalite formed by the crystallization of amorphous silica, because the combustion temperature was more than 800°C, and 1.96 wt% of K<sub>2</sub>O was contained in the coke ash. Quantitative analysis of the coke ash by XRD indicated that the content of cristobalite in the ash was 9.2% of silica, as indicated in Table 6. The content of cristobalite of the ash for two-stage fluidized bed combustor that combusted rice hulls at the temperature less than 800°C (650 ± 50°C in the first stage bed and 750 ± 50°C in the

second bed) was 60% of silica [15]. The local temperature in the fluidized bed was assumed to be higher than 800°C.



**Figure 10.** XRD pattern of compressed rice hull coke ash.

Floating dust with a diameter more than 7 μm was captured by the PM4 filter, and dust with a diameter less than 7 μm was captured by the glass fiber bound with PTFE set after the PM4 filter during the combustion of coke. Table 7 lists the amount of dust less than 7 μm diameter and the contents of free crystalline silica such as quartz, cristobalite and tridymite in the dust for coke combustion by natural and forced draughts. No XRD peaks of crystalline silica were observed in the dust. When amorphous silica crystallized to cristobalite, the silica particles melted (Figure 8). The compressed rice hull coke ashes in which the content of silica was 95.42% had the melting part, which was cristobalite (Figure 11). Therefore, the floating dust did not contain crystalline silica.



**Figure 11.** SEM photographs of compressed rice hull coke ashes produced with the combustion by the natural draught.

**Table 5.** Chemical composition of compressed rice hull coke ash.

Chemical composition (wt%)	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	MnO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>
Compressed rice hull coke ash	95.42	0.38	1.04	0.24	1.96	0.12	0.22	0.09	0.53

**Table 6.** Contents of cristobalite and amorphous silica in compressed rice hull coke and rice hull ashes.

Materials (Combustor)	Content of cristobalite	Content of amorphous silica
Compressed rice hull coke ash (Portable clay stove-stoker combustor)	9.2%	86.2%
Rice hull ash (Two stage fluidized bed combustor <sup>15</sup> )	60.0%	40.0%

**Table 7.** Amount of dust captured by the PM4 filter and content of free crystalline silica in the dust by the combustion of compressed rice hull coke.

	Amount of dust less than 7µm diameter (mg)+	Content of free crystalline silica (%)			Result of qualitative analysis
		Quartz	Cristobalite	Tridymite	
Compressed rice hull coke (natural draught)	4.55	0.1% or less*	0.1% or less*	0.1% or less*	No free crystalline silica
Compressed rice hull coke (forced draught)	7.10	0.1% or less*	0.1% or less*	0.1% or less*	No free crystalline silica

- +) Captured amount of dust by the PM4 filter during the combustion of compressed rice hull coke of 4 kg
- \*) Threshold of quantitative XRD analysis.
- No free crystalline silica: no XRD peak of quartz, cristobalite and tridymite.
- Temperature: 26.4°C, relative humidity: 66%.
- Natural draught: air supply by natural convection for the compressed rice hull coke combustion.
- Forced draught: 20 L·min<sup>-1</sup> air supply for 1 min every 10 min and air supply by natural convection for the compressed rice hull coke combustion.
- Suction amount of exhaust gas to the PM4 filter: 20 L·min<sup>-1</sup>.
- Time of exhaust gas sampling: 3 h 10 min.
- Total volume of exhaust gas sampling: 3.8 m<sup>3</sup>.
- Amount of compressed rice hull coke for combustion: 4 kg.



#### 4. Conclusions

Rice hulls were crushed to less than 200 $\mu$ m and then were compressed by 1.22x10<sup>6</sup> N/m<sup>2</sup> at 310°C to mold into pipe shape to produce compressed rice hull coke. The tar formed from thermal decomposition of the organic constituents of rice hulls (e.g. cellulose and lignin) acted as a binder between rice hulls. The heat value of the coke was 16,590 kJ/kg, and the density of the coke was 1.2, whereas the density of rice hulls was 0.1. The combustion temperature was normally higher than 800°C. Ash was obtained in 25.2 wt% of the dry coke, and silica was contained 95.4 wt% of the ash. Cristobalite was contained 9.2 wt% of the ash, because amorphous silica in the ash crystallized at the temperature above 800°C. Free crystalline silica (e.g. cristobalite) in a dust of flue gas is a carcinogen. No crystalline silica in the dust of the coke combustion was detected, because the compressed rice hull coke did not burn in the state of suspension, and crystallization to cristobalite resulted in silica melting, so that cristobalite was captured as the melt in the ash of the coke.

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