Optimal Combustion of Rice Husks and Recycling of Amorphous Silica

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INTRODUCTION

Rice husk accumulates a large percentage of silica by weight. Since silica is used for a variety of purposes, rice husk has been previously considered as a possible silica source, although it has currently been abandoned. Rice husk could potentially be considered a bio-ore of silica, rather than a waste (Tateda 2016a). Much research has been conducted on silica for being used as a fertilizer (Ishibashi 1958, Tateda 2016b), and many other industrial purposes have been considered (Ramchandra 2016). An essential requirement for silica to be used as a resource is an amorphous physical state (Tateda 2016b). "Amorphous" is, however, very vague, and cannot be clearly defined. Iker (1979) divided amorphous silica into three types; vitreous silica, silica M, and microamorphous silica. Vitreous silica was made by fusing quartz, silica M was formed when either amorphous or crystalline silicas are irradiated with high speed neutrons, and microamorphous silica consists of particles less than a micron in size or have a specific surface area greater than about 3 m^2/g. Alexander et al (1954) showed identical structures for amorphous silica among finely divided powder, wet silica gel, and colloidal particles in the form of a sol. The state of silica in rice husk ash is evaluated by its solubility, a useful tool since the formation of silica is amorphous when its solubility is high and crystalline when its solubility is low. Since the solubility of silica in water is extremely low (Alexander et al 1954), it is usually measured by using a NaOH solution. The fundamental objective for our study, then, was to find how the solubility of silica could be measured with NaOH. In Japan, there is no standard method for measuring the solubility of the silica in rice husk ash. Solubility measurement protocols vary from place to place, and the values cannot, therefore, be compared with each other. In light of this, the purpose of this study was to propose an appropriate measurement method for the solubility of silica in rice husk ash. Factors that affect the solubility of the silica were assessed and the current standard procedure was simplified based on the results. If the same measurement method is adopted worldwide, it will be easy to share the information about solubility and the physical state of silica produced in any part of the world, especially Asian countries.

MATERIALS AND METHODS
Rice Husk Source

Rice husk from Koshihikari (*Oryza sativa L.*) was used in this study. The city where Toyama Prefectural University is located generates approximately 600 tons of rice husk annually, half of which (300 tons) is used as flooring material for domestic animals and in water drainage systems for rice paddies. However, such usage of rice husk is not stable and sustainable, and the entire amount of 600 ton/year will soon have to be treated as waste. The density of rice husk is very low, at 0.1-0.2 ton/m^3, meaning that extremely large storage spaces would be necessary for disposal unless recycling methods are developed.

Ash Preparation

Two types of rice husk ash, black and white, were prepared for analysis. Black ash was produced from the boiler described in Tateda (2016b) without washing (retention time in the boiler: less than 3 days). White ash was produced with a laboratory scale electric furnace (Koyo, KBF794N1) after washing rice husks with acetic acid (5 %) (retention time in the furnace: 2 hours). Fig. 1-1-1 shows the appearance of black and white ash produced.
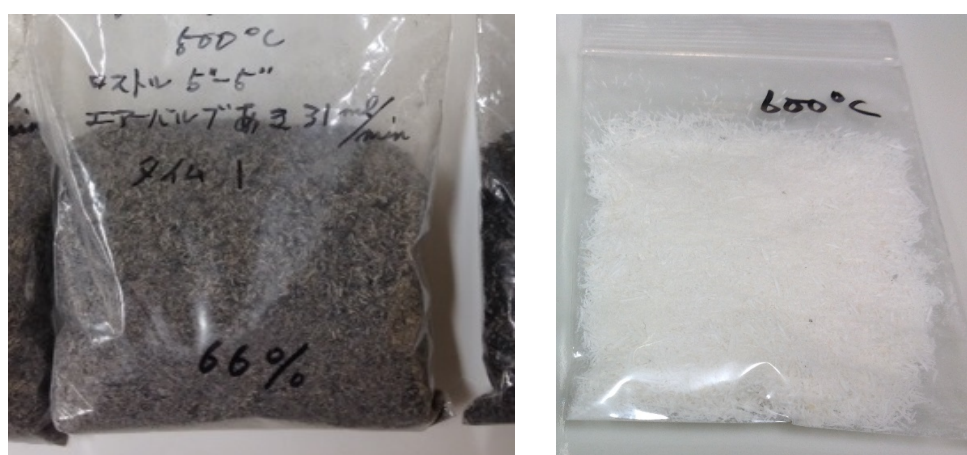
Fig. 1-1-1. Sample appearance: Black ash (Left), White ash (Right)

Qualitative Analysis of Crystallized or Amorphous State of the Silica in Rice Husk Ash

The physical state of the silica in the rice husk ash was determined by X-ray diffraction analysis (XRD: MultiFlex 40 kV, 30 mA, RIGAKU, CuKα, 2θ:5-80°). The samples burned at 500-1,000˚C were grinded into powder and measured by XRD.

Measurement of Fixed Carbon, Ash, Volatile Matter, and Moisture

Fixed carbon, ash, volatile matter, and moisture content in the rice husk ash samples were determined following the Japanese Industrial Standards (JIS) M 8812-8, -6.4.1, -7.2.4, and -5.2.4a, respectively (JIS 2006).

Measurement of the Solubility of Silica in Rice Husk Ash

Japan has standard methods for measuring the solubility of silica in fertilizers (4.4.1.a-c) (FAMIC 2015). The testing method 4.4.1.a is for silica that can be dissolved in acid, the method applied to blast furnace slag, which is usually used for silica fertilizer. Method 4.4.1.b is for silica that can be dissolved in alkali, and silica solubility of gel fertilizer can be measured by this method. Method 4.4.1.c is for silica that can be dissolved in acid and alkali and was used for the foundation of measurement in this study. In our analysis, the 2011 version was used even though it is slightly different from the 2015 version. Flow charts of 4.4.1.c are presented in Fig. 1-1-2. The KCl solution was prepared by dissolving KCl (150 g) in ethanol (250 mL) and distilled water (750 mL), which is half of the typical amount because of the difficulty in dissolving KCl in solution. Soluble silica (S-Silica) as a weight percentage (%) was then calculated as:

$$\text{S-Silica (\%)} = \text{vs} \times \text{C} \times \text{f} \times \frac{V1}{V2} \times \frac{15.021}{W} \times \frac{100}{1000} \quad (1)$$

where,

VS	:	Volume of NaOH solution (0.2 mol/L) consumed for titration (mL)
C	:	0.2 mol/L (Estimated concentration of NaOH solution)
F	:	1.000 (A factor of 0.2 mol/L NaOH solution (Wako) as provided on the bottle) (Unitless)
V1	:	250 mL (Volume of Solution A)
V2	:	5 mL (Volume of aliquot taken from each Solution, A or B)
15.021	:	1 mL of 0.2 mol/L NaOH = 1.5021 mg of SiO_2 (mg·L)/(mL·mol)
W	:	1 g (Sample taken)
100	:	A factor to obtain percentage (%)
1000	:	1000 mg/g (Conversion factor for mg to g)

According to Kato (1998), the silica in slag dissolves as a result that the formation of Si with alkali metals was broken down due to alkali metals such as Na, Ca, and K being extracted by the acid. The resulting silica is often referred to as "free silica (Deshmukh 2012)." The silica of silica gel, conversely, dissolves by becoming ionized in an alkali environment. However, the testing method for the silica in rice husk ash has not been designated since the physical characteristics of the silica were not yet known. Solubility of the silica in rice husk ash was therefore investigated based on the method of 4.4.1.c, which uses both acid and alkali

treatments (4.4.1.c-Whole, Fig. 1-1-2). For alkali-only treatment, the procedure for making Solution A was skipped and the process for making Solution B proceeded after taking one gram of Sample (4.4.1.c-Solution B w/o acid, Fig. 1-1-3). Method 4.4.1.c-Solution B with acid measured dissolution of silica in acid (Fig. 1-1-4).

Sample 1 g — Using a beaker (300 mL) and taking precisely to 1 mg scale

— Adding approx. 150 mL of HCl (1+23)* *:1 HCl to 23 Distilled water)

Heating — Stirring 10 minute interval for 1 hour at 30 ±2 ˚C

Filtering → **Rinsing** — Twice with distilled water

Using the type 3 (5 μm) filter into a flask (250 mL)

Residues on filter **Filtrate** → **Solution A**

Adding distilled water to the volume of 250 mL

Transferring — Transferring residues with a filter into a plastic beaker (300 mL)

— Adding approx. 150 mL of NaOH (20 g/L)

Heating — Stirring 10 minute interval for 1 hour at 65 ±2 ˚C

Cooling → **Filtering** — Using the type 3 (5 μm) filter into a flask (250 mL)

— Rinsing and adding distilled water to the volume of 250 mL

Solution B

Mixture of Aliquots — Each 5 mL of Solutions A and B is taken into a plastic beaker (300 mL)

— Adding approx. 10 mL of HCl (conc,)

— Adding approx. 15 mL of KF solution (58 g/L)

— Adding approx. 2 g of KCl

Stirring → **Cooling** → **Filtering** — Using a plastic Buchner funnel and the type 6 (3 μm) filter

In ultrasonic — In a refrigerator for 30 minutes

Rinsing — 7-8 times with **KCl solution
**:Described in the text

Transferring ← Transferring residues with a filter into a beaker (300 mL)

— Adding distilled water to the volume level of 200 mL

Heating → **Titlating** — Dropping NaOH solution (0.2 mol/L) and stopping titration when the solution turns to slightly red color

At 70-80 ˚C

Adding few drops of phenolphthalein solution (1 g/100 mL)

Fig. 1-1-2. Testing method 4.4.1.c for soluble silica for fertilizer

Sample 1 g — Using a beaker (300 mL) and taking precisely to 1 mg scale

Adding approx. 150 mL of HCl (1+23)*   *:1 HCl to 23 Distilled water)

Heating — Stirring 10 minute interval for 1 hour at 30 ±2 ˚C

Filtering → Rinsing — Twice with distilled water

Using the type 3 (5 μm) filter into a flask (250 mL)

Residues on filter   Filtrate → Solution A

Adding distilled water to the volume of 250 mL

Transferring — Transferring residues with a filter into a plastic beaker (300 mL)

Adding approx. 150 mL of NaOH (20 g/L)

Heating — Stirring 10 minute interval for 1 hour at 65 ±2 ˚C

Cooling → Filtering — Using the type 3 (5 μm) filter into a flask (250 mL)

Rinsing and adding distilled water to the volume of 250 mL

Solution B

Solution B — Five mL of Solutions B is taken into a plastic beaker (300 mL)

Adding approx. 10 mL of HCl (conc.)

Adding approx. 15 mL of KF solution (58 g/L)

Adding approx. 2 g of KCl

Stirring → Cooling → Filtering — Using a plastic Buchner funnel and the type 6 (3 μm) filter

In ultrasonic   In a refrigerator for 30 minutes

Rinsing — 7-8 times with **KCl solution **:Described in the text

Transferring — Transferring residues with a filter into a beaker (300 mL)

Adding distilled water to the volume level of 200 mL

Heating → Titlating — Dropping NaOH solution (0.2 mol/L) and stopping titration when the solution turns to slightly red color

At 70-80 ˚C

Adding few drops of phenolphthalein solution (1 g/100 mL)

Fig. 1-1-3. Testing method 4.4.1.c-Solution B w/o acid

Sample 1 g — Using a beaker (300 mL) and taking precisely to 1 mg scale

Adding approx. 150 mL of HCl (1+23)*   *:1 HCl to 23 Distilled water)

Heating — Stirring 10 minute interval for 1 hour at 30 ±2 ˚C

Filtering → Rinsing — Twice with distilled water

Using the type 3 (5 μm) filter into a flask (250 mL)

Residues on filter

Filtrate → Solution A

Adding distilled water to the volume of 250 mL

Transferring — Transferring residues with a filter into a plastic beaker (300 mL)

Adding approx. 150 mL of NaOH (20 g/L)

Heating — Stirring 10 minute interval for 1 hour at 65 ±2 ˚C

Cooling → Filtering — Using the type 3 (5 μm) filter into a flask (250 mL)

Rinsing and adding distilled water to the volume of 250 mL

Solution B

Solution B — Five mL of Solutions B is taken into a plastic beaker (300 mL)

Adding approx. 10 mL of HCl (conc,)
Adding approx. 15 mL of KF solution (58 g/L)
Adding approx. 2 g of KCl

Stirring → Cooling → Filtering — Using a plastic Buchner funnel and the type 6 (3 μm) filter

In ultrasonic   In a refrigerator for 30 minutes

Rinsing — 7-8 times with **KCl solution   **:Described in the text

Transferring

Transferring residues with a filter into a beaker (300 mL)

Adding distilled water to the volume level of 200 mL

Heating — Titlating — Dropping NaOH solution (0.2 mol/L) and stopping titration when the solution turns to slightly red color

At 70-80 ˚C

Adding few drops of phenolphthalein solution (1 g/100 mL)

Fig. 1-1-4. Testing method 4.4.1.c-Solution B with acid

Rice husk was burned as-is, whether by boiler or electric furnace, so that the ash maintained the shape of the rice husks. Since ash samples for solubility measurements were only one gram (Fig. 1-1-2), non-silica contents in the samples could have affected solubility of the silica. Samples were powdered by grinding 100 times manually in a grinding bowl and the solubility was compared to samples left as-is. Method 4.4.1.c-Whole was applied for the solubility measurements in this comparison. Solubilities of tridymite and quartz were also measured by the method 4.4.1.c-Whole.

RESULTS AND DISCUSSION

The values shown here are statistically significant ($p < 0.01$) values obtained from multiple replications, unless otherwise stated.

Necessity of an Acid Treatment Procedure

As described in Section "Measurement of the Solubility of Silica in Rice Husk Ash", the methods for dissolving the silica in slag and in gel are different. The silica in slag from a blast furnace dissolves in an acid solution, while the silica composed of silica gel fertilizer dissolves in an alkali solution. Table 1-1-1 shows the results measuring silica solubility in rice husk ash using 4.4.1.c-Whole, -Solution B w/o acid, and -Solution B with acid. Solubility shown here of the black ash (produced by the boiler, which uses a regular exothermic reaction) shows high, implying that silica in black ash produced by the boiler was completely amorphous.

Table 1-1-1. Solubility of the silica from using methods 4.4.1.c-Whole, 4.4.1.c-Solution B w/o acid procedures, and 4.4.1.c-Solution B with acid procedures

Sample	4.4.1.c-Whole (%)	4.4.1.c-Solution B w/o Acid (%)	4.4.1.c-Solution B with Acid (%)
A (Black ash)	67.5	60.0	67.8
B (Black ash)	63.9	57.3	64.4
C (Black ash)	55.8	52.0	56.1
D (Black ash)	75.0	70.5	75.2
E (White ash)	87.6	85.2	87.6
F (Black ash)	66.2	60.6	66.4
G (Black ash)	72.8	66.6	72.6
H (Black ash)	60.1	55.8	60.1
I (Black ash)	60.1	53.0	60.1
J (Black ash)	65.9	58.4	65.9

Solubilities of tridymite and quartz were 0.4 % for comparison. Values of solubility by only alkali dissolution were lower than that by acid and alkali dissolution, meaning that the silica in rice husk ash could be dissolved in acid, and that there might be free silica.

Due to the small difference in solubility of silica in Solution B measured by the methods 4.4.1.c-Whole and 4.4.1.c-Solution with acid, it was assumed that the silica dissolved in Solution A would be negligible ($\pm$0.5 point). The results, taken together, indicate that the silica in rice husk cannot be dissolved in acid, but that the solubility increases after acid treatment (2.4-7.5 points). Therefore, the analysis procedure shown in Fig. 1-1-2 can be shortened as shown in Fig. 1-1-4. In the modified procedure, only Solution B is needed for measurement, which lessens the complex manners of the measurement procedure.

Factors Which Influence Silica Solubility
Powdering ash samples as pretreatment
The results are given in Table 1-1-2.

Table 1-1-2. Comparison of solubility of black ash samples: Powdered and As-Is

Solubility of the Silica (4.4.1.c-Whole)	Powdered	As-Is
Mean Value (%)	65.5	65.5
Standard Deviation (%), n = 10	0.63	0.57

Mean values of "powdered" and "as-is" were the same, but the standard deviation of "as-is" was smaller than that of "powdered." These results indicate that ash samples do not need to be powdered prior to solubility measurements.

Inoue (1998) found that solubility increased as specific surface area (SSA) of rice husk ash increased, using rice husk ash with SSA 0.98-117 m^2/g. One of our previous experiments gave contradictory findings of decreasing solubility as SSA increased, using rice husk ash with SSA 40-196 m^2/g (data not shown). Results from our current study (Table 1-1-2) show the same trend as our previous study. We therefore conclude that SSA does not influence solubility of the silica, which contradicts the conclusion of Inoue (1998).

Fixed carbon, volatile matter, and moisture

Because only 1 g of ash was sampled for solubility measurements, it was possible that an impurity such as fixed carbon might strongly affect silica solubility. We investigated whether the percentage of fixed carbon decreased the solubility of silica. Representative data are given in Table 1-1-3.

Table 1-1-3. Physical properties of black ash samples and their solubility

| Ash sample | Dry base (%) | | | Wet base (%) | Solubility (%) |
	Fixed carbon	Ash	Volatile matter	Moisture	4.4.1.c-Whole
A	0.4	97.6	2.0	2.3	71
B	0.3	97.0	2.7	2.3	66
C	6.5	88.4	5.1	3.1	49

Solubility was lower when fixed carbon, volatile matter, and moisture content were also lower. Fixed carbon, especially, seemed to have a strong influence on solubility. Solubility was further measured by omitting the influence of fixed carbon (Table 1-1-4) by producing white ash (which does not contain fixed carbon). White ash was produced by burning rice husks at temperatures of 500-1,000 °C in a laboratory electric furnace.

Table 1-1-4. Physical properties of white ash samples and their solubility

| Ash sample | Dry Base (%) | | | Wet Base (%) | Solubility (%) |
	Fixed carbon	Ash	Volatile matter	Moisture	4.4.1.c-Whole
500	0.0	97.7	2.3	5.7	86.7
600	0.0	98.6	1.4	5.5	89.5
700	0.0	98.8	1.2	3.8	90.6
800	0.0	99.3	0.7	2.7	91.7
900	0.0	99.8	0.2	1.8	90.6
1,000	0.0	99.9	0.1	0.8	83.1

Volatile matter and moisture decreased as the burning temperatures increased. Conversely, ash increased with increasing temperatures. Solubility, volatile matter, and moisture were plotted as a function of temperature (Fig. 1-1-5).

Volatile matter and moisture both decreased as burning temperatures increased. Solubility increased up to 800 °C, and then decreased thereafter. From the results, existence of volatile

matter and moisture only seemed to affect solubility up to 800 °C, above which effects became negligible.

A Silica Activity Index (SAI) was introduced by Deshmukh et al. (2012). SAI is the percentage of available silica dissolved in an excess of boiling NaOH (0.5 M) during a 3-minute extraction period. They found that SAI is a function of burning temperature, and the solubility in Fig. 1-1-4 shows a similar trend. The SAI increased up to 500 °C and it decreased after the temperature to 900 °C.

The observed decline in solubility above 800°C was not influenced by volatile matter and moisture, since solubility increases as volatile matter and moisture decrease. Above 800 °C, the silica in rice husk ash might be crystalized. At high temperatures, the solubility of crystalized silica becomes low. To investigate the physical state of the silica, the ash burned at 500 – 1,000 °C were analyzed with an XRD (Fig. 1-1-6). The charts for 1,000 °C were chosen since the charts for 500 to 1,000 °C displayed the same trends. It was apparent that silica at any temperature did not crystalize, rather staying in an amorphous state. The question then became: What was the cause of decreasing solubility?

Fig. 1-1-7 shows the physical appearance of the ash at each burning temperature, as taken by a handy zoom mobile recorder (Digital Micro Mobile Z, Biomedical Science) at 50-60x. The ash showed a broken and powdered-like state at low burning temperatures. The ash became bulky at high temperatures, however, and the shapes of rice husk remained as the temperature increased. These results indicate that the physical state of the silica shifted from amorphous to a more crystalized state. The silica was not fully crystalized, however, even at high temperatures, indicating that tiny parts of the amorphous silica might start to change to crystalline form (Fronde 1962, Kondo 2010).
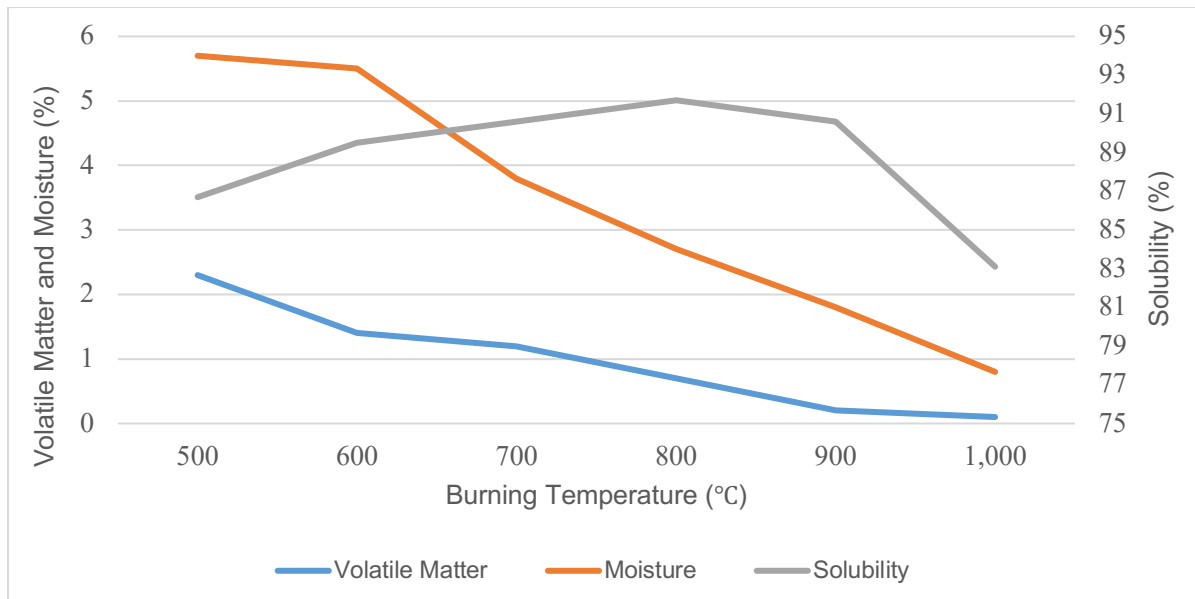
**Fig. 1-1-5. Trends of volatile matter, moisture, and solubility
as a function of burning temperature**
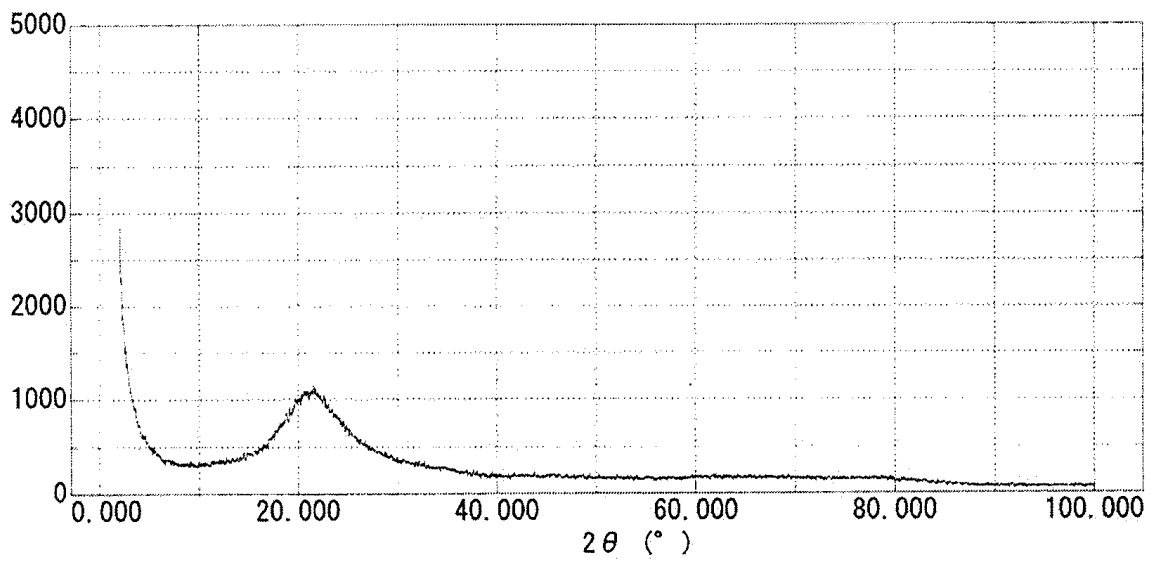
Fig. 1-1-6. XRD charts for 1,000 °C burning temperature
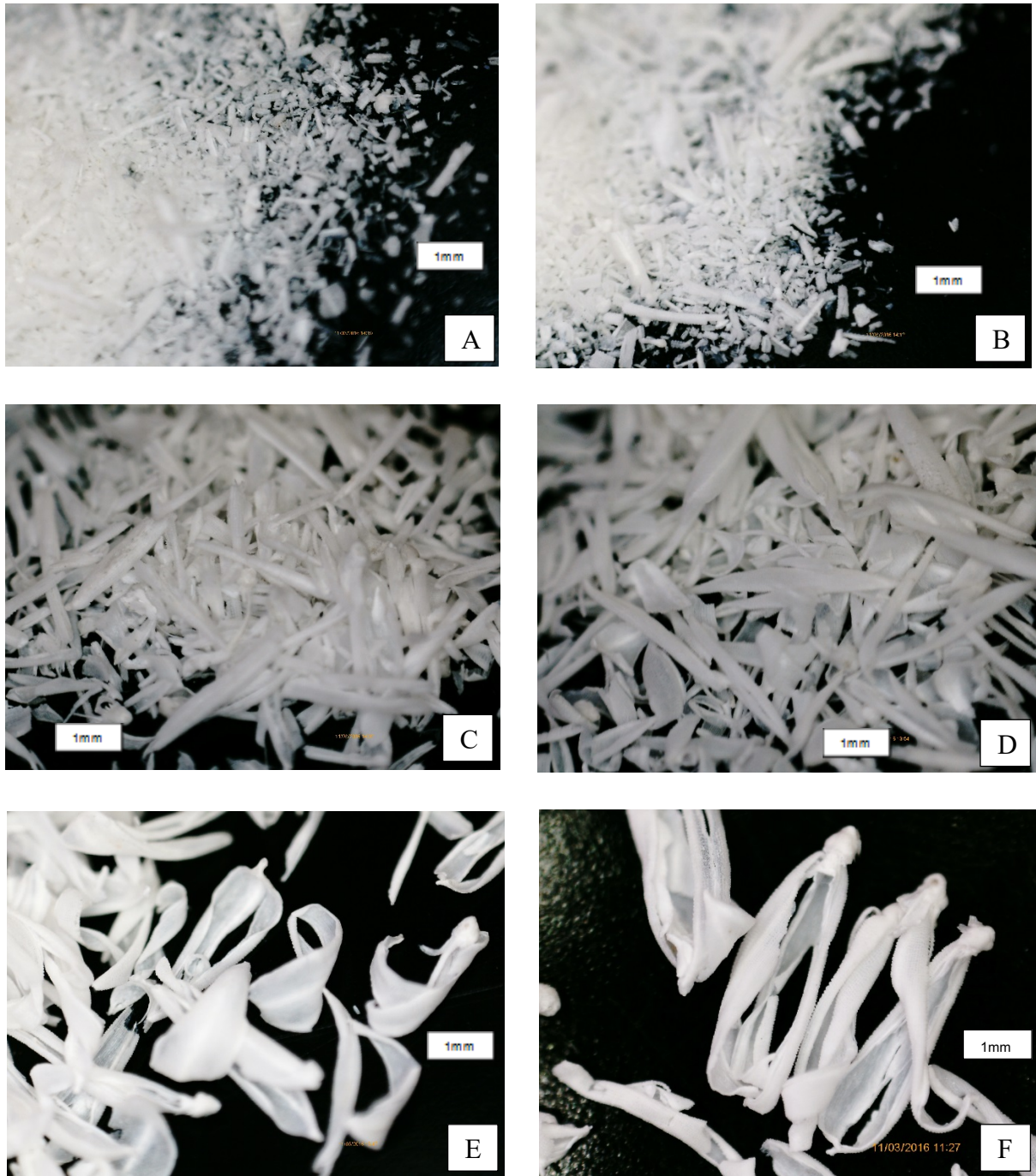
Fig. 1-1-7. Magnified appearance of rice husks burned at 500 °C (A), 600 °C (B), 700 °C (C), 800 °C (D), 900 °C (E), and 1,000 °C (F)

CONCLUSIONS

This study concluded the following:

- For solubility measurements of silica in rice husk ash, an acid treatment procedure is necessary to obtain accurate values.
- The Japanese standard method 4.4.1.c can be simplified to reduce the complexity of the measurement procedure
- Solubility increased as surface area of ash decreased.
- Powdering of samples was not necessary for solubility measurement (ash can be used as-is).
- Ash became bulky as the burning temperature increased.
- Fixed carbon may affect solubility, as well as volatile matter and moisture contents up to an 800°C burning temperature.
- Other, unstudied factors may exist that affect the solubility of silica in rice husks.

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Chapter II   Basic Studied for Physical Characteristics of Rice Husk Silica
based on Calcination Temperatures and Times

2-1. Observation of physio-chemical differences of rice husk silica under different calcination temperatures

INTRODUCTION

Rice husks are fundamental biomass resources because they are produced annually, making them sustainable and reliable. In contrast, wood biomass takes a long time to grow, so people have to wait to use it, which is not sustainable or reliable. Approximately 150 million tons of rice husks are generated globally per year, with two million tons from Japan (Pode 2016). Although rice husks have been proposed for many uses, there are few examples of sustainable applications using them, which could be due to farmers considering them to be a problem and paying a disposal fee for their management.

Rice husks have been used as adsorbents in wastewater treatment (Soltani et al 2015) and fuel for energy generation (Fang et al 2004). Rice husk "ash" has more options for application than the rice husks themselves. Rice husk ash has been widely proposed for various industrial uses including coatings, pigments, cement, insulators, rubber, and electronics (Pode 2016). Tateda (2016) proposed a method for recycling rice husks, using them as fuels in a proposed sustainable local energy system and suggested that rice husk ash could be used as a fertilizer for growing healthy rice plants.

To recycle rice husk ash, the ash must have a certain, essential condition - the silica in the ash must be amorphous. The silica in rice husks is also known as "plant opal," and is amorphous (Iker 1979, Kondo 2010). Soluble silica is assimilated by rice plants, and they use it to form their body structure for preventing damage from wind, evaporation of water from rice, and invasion by pests. As soluble silica is amorphous, plant opal is also amorphous.

Amorphous silica is transformed by exposure to temperature. Under high temperatures, amorphous silica turns to quartz, tridymite, or cristobalite. Rice husk silica must be carefully handled, because crystalized silica is a carcinogen, according to a WHO report (WHO International Agency for Research on Cancer 1997). The transformation, however, is not

always the same, and the existence of alkali metals and conditions of calcination would produce different materials.

For recycling rice husks, the production of rice husk ash has more advantages than the rice husks alone, as mentioned earlier. A burning process is required to remove unwanted materials for recycling, such as carbon, alkali metals, and volatile materials. Silica in the ash must remain amorphous, which is highly influenced by the burning temperatures.

There are many examples of rice husks being burned for recycling. Experiments have been performed at the following temperature ranges; 300—860 °C (Luan et al 1990), 600—700 °C (Bie et al 2015), 500—900 °C (Baker et al 2016), 300—900 °C (Moriizumi et al 2004), 400—900 °C (Xiong et al 2009), 700—800 °C (Saad et al 2016), 20—1,000 °C (Fernandes et al 2016), 400—900 °C (Inoue et al 1998), 250—600 °C (Wang et al 2016), 900—1,050 °C (Nayak et al 2010), 400—900 °C (Deshmukh et al 2012), 0—600 °C (Shimizu et al 1978), 600—850 °C (Honma et al 1989), and 700—900 °C (Ganesh et al 1992). The amorphous silica crystallizes at around 1,000 °C, but this depends on the conditions of the rice husks. None of the studies mentioned above provided comprehensive observations under changes in temperature, such as the transformation of amorphous to crystalline silica, which, to the authors knowledge, has had no studies.

To recycle silica in rice husk ash, the production of white rice husk ash is important. The lower the amount of fixed carbon in the ash, the better the quality of silica. In this study, physical and chemical changes in rice husk ash, especially the silica in the ash, were observed under minimal fixed carbon conditions. Two studies have used temperatures higher than 1,000 °C to observe the transformation from an amorphous to a crystalline state. Nakata et al (1989) conducted calcination from 400—1,500 °C but once pyrolyzed rice husks were produced, they were calcined. Sarangi et al (2011) chose burning temperatures of 400—1,200 °C, and the rice husks were calcined under N_2 gas to promote pyrolysis to produce crystalline silica, which is a completely different process. The silica ash turns to crystalline silica if alkali metals and fixed carbons remain in the ash. It is very important to understand physical and chemical changes as functions of calcination temperatures.

MATERIALS AND METHODS

All data were triplicated and their mean values were used to produce figures and tables.

Rice Husks and Ash Preparation

Rice husks from Koshihikari (*Oryza sative L.*) were used in this study. Rice husks were calcinated in a laboratory-scale electric furnace (KBF794N1, Koyo for 500-1,100 °C, Lindberg, Koyo for 1,500 °C) for two hours at 500-1,500 °C after being washed with acetic acid (5 %). The 500 °C minimum was selected from authors' previous study (Tateda 2016).

Qualitative Analysis of Amorphous and Crystallized State of the Rice Husk Silica

The physical state of rice husk silica was determined by X-ray diffraction analysis (XRD: MultiFlex 40 kV, 30 mA, CuKα, 2θ: 5-80°, Rigaku). The rice husks were ground into a powder and analyzed by XRD.

Measurement of Fixed Carbon, Ash, Volatile Matters, and Moisture

Fixed carbon, ash, volatile matter, and moisture content in rice husk ash were determined following the Japan Industrial Standards (JIS) M 8812-8, -6.4.1, -7.2.4, and 5.2.4a, respectively (JIS 2016).

Measurement of Element Contents in Rice Husk Ash and Content Estimation of Oxides

A length dispersive X-ray fluorescence spectrometer (WDX: PW2440, Spectris) was used to measure element content in rice husk ash, and, based on the results, estimate oxides.

Solubility Measurement of Rice Husk Silica (S-silica)

The solubility of rice husk silica (S-silica) was measured following the Japan Standard Methods for solubility of silica in fertilizers (4.4.1.c) (FAMIC 2015).

Measurement of Total Silica in Rice Husk Ash (T-silica)

The total silica in rice husk ash (T-silica) was measured following modified Japan Standard Methods for total silica content in fertilizers (4.4.1.d) (FAMIC 2015). The acid extraction process in the method was skipped.

Surface Observation of Rice Husk Ash

The surfaces of rice husk ash particles were observed at macro and micro scales by a hand zoom recorder (Digital Micro Mobile Z, Biomedical Science) and a field emission scanning electron microscope (FE-SEM, JSM-7001FTTLS, JEOL), respectively.

RESULTS

Solubility of Rice Husk Silica as a Function of Calcination Temperature

Solubility is presented as the percentage of soluble silica in the total silica. The degree of "amorphous state" silica in rice husks can be evaluated by "solubility." The higher the solubility, the better the amorphous state of silica in the rice husk ash (Tateda et al 2016a). Fig. 2-1-1 shows the solubility at each calcination temperature. Solubility was high through 500—900 °C, which means that more silica in rice husk ash was in an amorphous state. Solubility rapidly decreased at 1,000 °C, however. The same trend was observed by Tateda et al (2016b), but it was gentler and decreased to 83 % at 1,000 °C, compared to below 40 %, observed here. Solubility was 3.6 % at 1,000 °C, and decreased to 0.6 % at 1,500 °C. Deshmukh et al (2012) proposed a silica activity index that was based on the soluble fraction dissolving in boiling 0.5 M NaOH within 3 minutes. In this paper, solubility was discussed as the soluble fraction dissolved in HCl and NaOH, described in detail by Tateda et al (2016b), which could have similar values to the silica activity index.

Analysis of Four Contents of Rice Husk Ash

Four major components of rice husk ash; water, volatile matter, ash, and fixed carbon, were analyzed. The results are presented in Fig. 2-1-2. As the figure shows, fixed carbon was almost lost from the surface of ash at all temperatures, so the color of the ash under all temperatures was white. Tanaka et al. (1989) reported that the ash of pyrolyzed rice husks contains a fixed carbon content of 0.46 % at 500 °C, and it decreases to 0.02 % at 800 °C. This implies that more carbon remains on the surface of the rice husks after pyrolysis treatment. Volatile matter was eliminated at 800 °C, and water content was lost after 1,100 °C. After 1,100 °C, the ash component dominated rice husk ash.
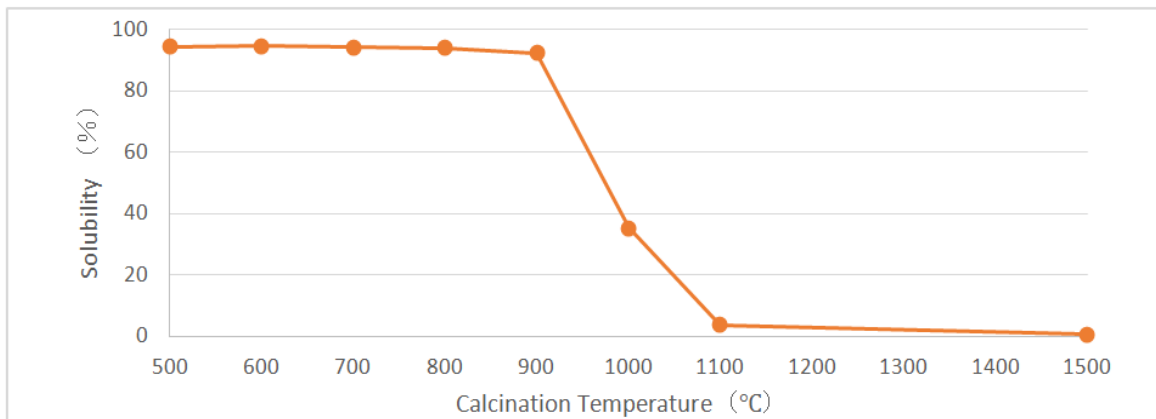
Fig. 2-1-1. Solubility trend as a function of calcination temperature
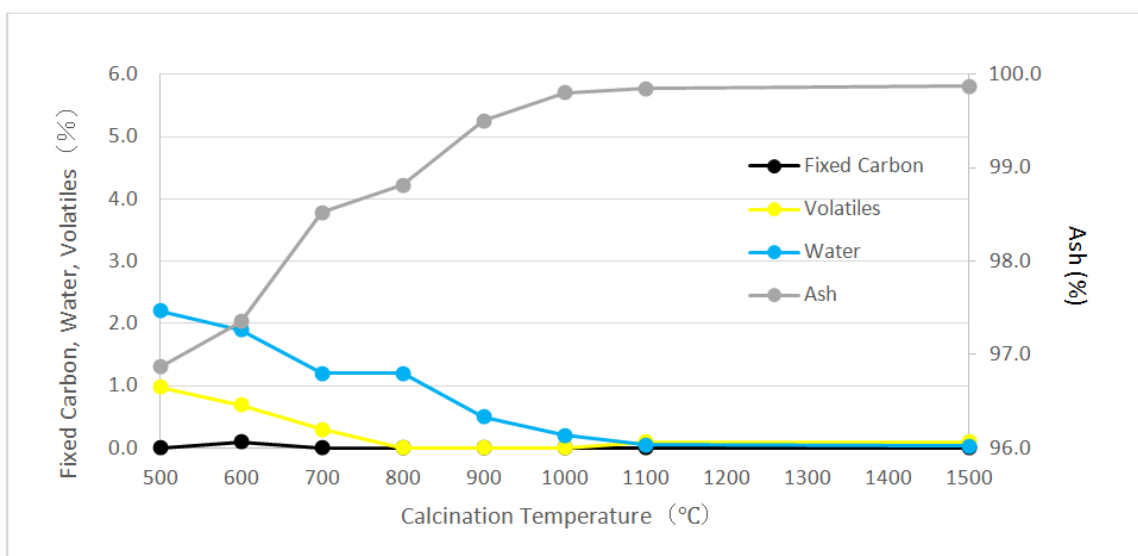
Fig. 2-1-2. Four components of rice husk ash

Analysis of Components of Rice Husk Ash after Removing Fixed Carbon

Based on the results of the previous section "Analysis of Four Contents of Rice Husk Ash," the ash did not contain fixed carbon, therefore it has three portions: ash, volatile matter, and water. The ash portion should consist of silica and non-silica components. By measuring the total silica in the ash, more details, especially in the ash portion, were estimated (Fig. 2-1-3).

In rice husk ash, the ash portion included T-silica and ash without T-silica. In the figure, T-silica includes both S- and non-S-silica. The ash without T-silica portion could have been decreasing as a function of temperature. The types of oxides which comprised the ash-except-T-silica portion were analyzed. Oxides such as P_2O_5, CaO, Fe_2O_3, and K_2O were dominant, which was also stated by Fernandes et al (2016) and Nakata et al (1989). The ash

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portion of rice husk ash mainly consists of T-silica and the oxides mentioned above. According to Bie et al (2015), K_2O decomposes at high temperatures, and holds more fixed carbon in ash. Fig. 2-1-2 shows that no carbon remained at high temperatures, which differs from the results of Bie et al (2015), because rice husks were burned after acetic acid washing, and the K_2O content was below 0.3 %. In contrast, rice husks burned without washing had a K content of 6.1—8.1 % (2.3—2.8 % as K_2O). The high percentage of K_2O influenced the residual fixed carbon in the ash. One type of the *Oryza sative L.* (Koshihikari) rice plant was used in this study and the ash content (oxidized elements in the portion of ash excluding T-silica) was dependent on where the rice plants grew (Shimizu et al 1978). This could be the consequence of differences in fertilizers. Due to differences in paddy field soil properties, farmers use their own fertilizers.

XRD Analysis

XRD analysis for each temperature was conducted to verify whether the silica in rice husk ash was amorphous or crystallized. Fig. 2-1-4 a)-c) shows the XRD curves for the ash samples, with calcination temperatures. Fig. 2-1-4 a) represented XRD curves from 500—1,000 °C because they were almost the same.

According to the figure, the silica in rice husk ash burned at 500—1,000 °C had an amorphous nature, while the silica burned at 1,100 °C had more of a crystalline nature, and at 1,500 °C it had a cristobalite nature. Deshmukh et al. (2012) conducted similar experiments and obtained XRD curves similar to those seen in Fig. 2-1-4. They washed rice husks with HCl followed by water, and then burned them at 400 to 900 °C. They concluded that amorphous silica turned crystalline at 900 °C. However, this phenomenon was not observed in the current study. It is highly unlikely that washing by HCl caused the difference because, in general, amorphous silica without impurities (such as alkali metals and fixed carbon) does not turn into crystalline form below 1,000 °C, as seen in this study. Notably, Deshmukh et al. (2012) do not specify the medium used to burn the rice husks in their study.

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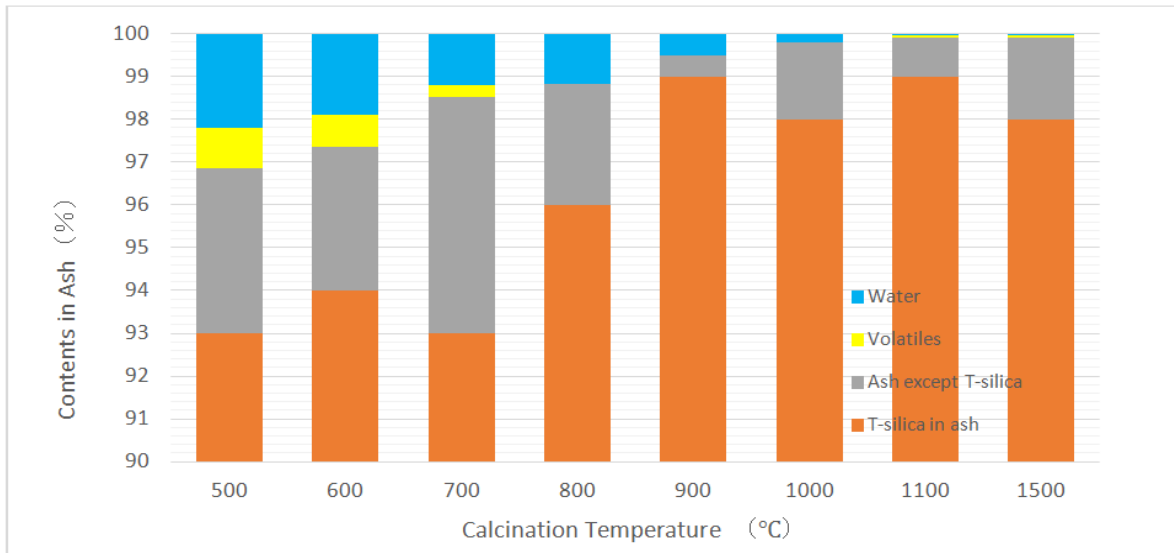
Fig. 2-1-3. Detailed content of the ash portion
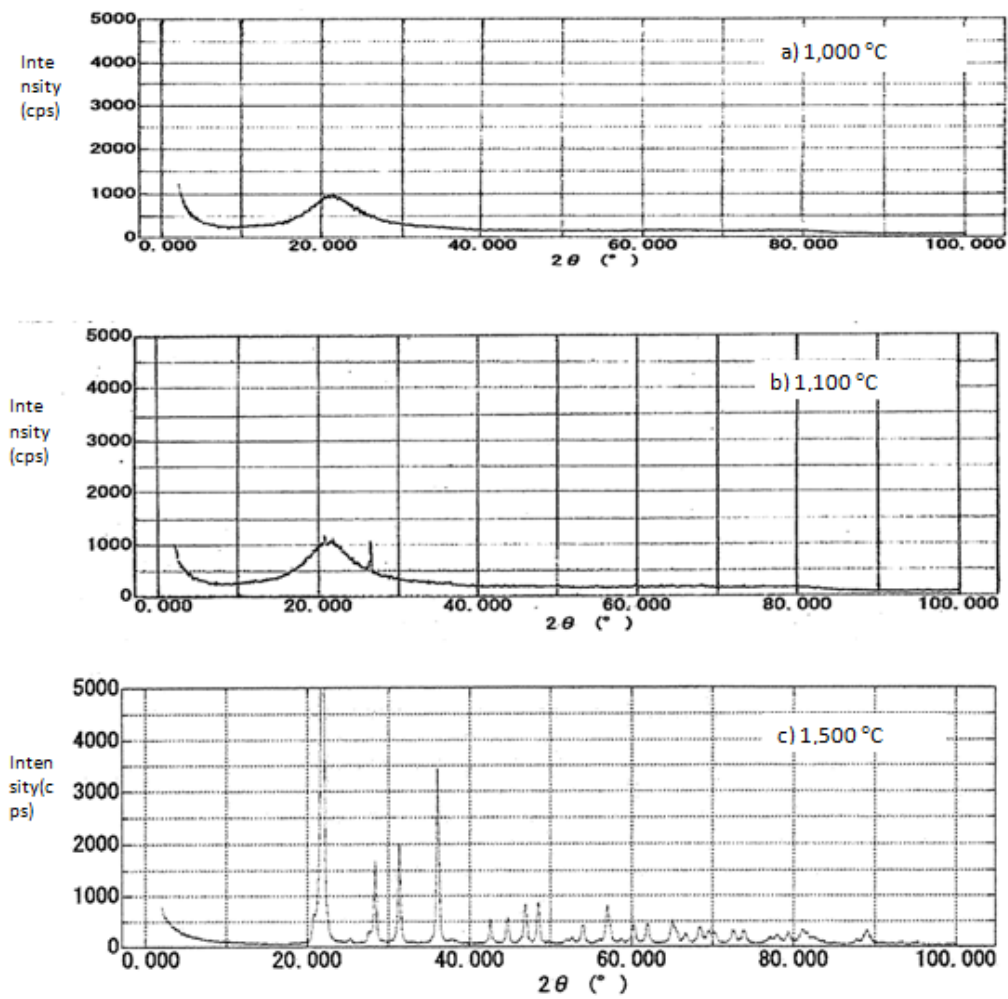
**Fig. 2-1-4. XRD curves at different calcination temperatures
a) 1,000 °C, b) 1,100 °C, c) 1,500 °C**

Surface Observation of Rice Husk Ash

Surface observations were performed at macro and micro scales using a handy zoom camera and a FE-SEM, respectively.

According to Fig. 2-1-5, rice husk ash burned at the lower temperatures, i.e., 500 and 600 °C, was broken into small pieces, indicating that the ash burned at those temperatures was fragile and easily broken. Ash burned at 700—1,500 °C held the rice husk shape, however, the shape seemed to shrink for samples burned at over 1,000 °C, i.e., 1,100 and 1,500 °C, because of the extremely high temperatures. This indicates that ash at 1,500 °C calcination became rounded and narrower in width in comparison to the samples burned at 700—1,000 °C. The close observation, but SEM, of rice husk ash has not been reported anywhere according to authors' knowledge.

Fig.2-1-6 shows surface observations at a micro scale for samples burned at 600 °C, 1,000 °C, 1,100 °C, and 1,500 °C, which were observation of the inner surface. As the samples at 500 °C and 600 °C and the samples at 700 °C through 1,000 °C had similar appearances, the 600 °C and 1,000 °C samples were selected as representative samples, respectively, for micro observation. There was no great morphological difference between the samples at 1,000 °C and 1,100 °C. The wall thickness of the pores seemed much thicker at 600 °C than at the higher temperatures of 1,000 °C and 1,100 °C. The surface of the sample burned at 1,500 °C had completely different morphology. It became very smooth, which could be the result of melting due to the extremely high temperature (1,500 °C). Nakata et al. (1989) have presented SEM photos in their paper. However, the rice husks used in their study were processed, that is, compressed and crushed before burning. Thus, a comparison between their work and the current study cannot be made because the ash contained pieces of broken rice husks. According to their results, the SEM photo at 500 °C is similar to the one at 600 °C in this study, and the SEM photo at 900 °C matches the one at 1500 °C in our study very closely.
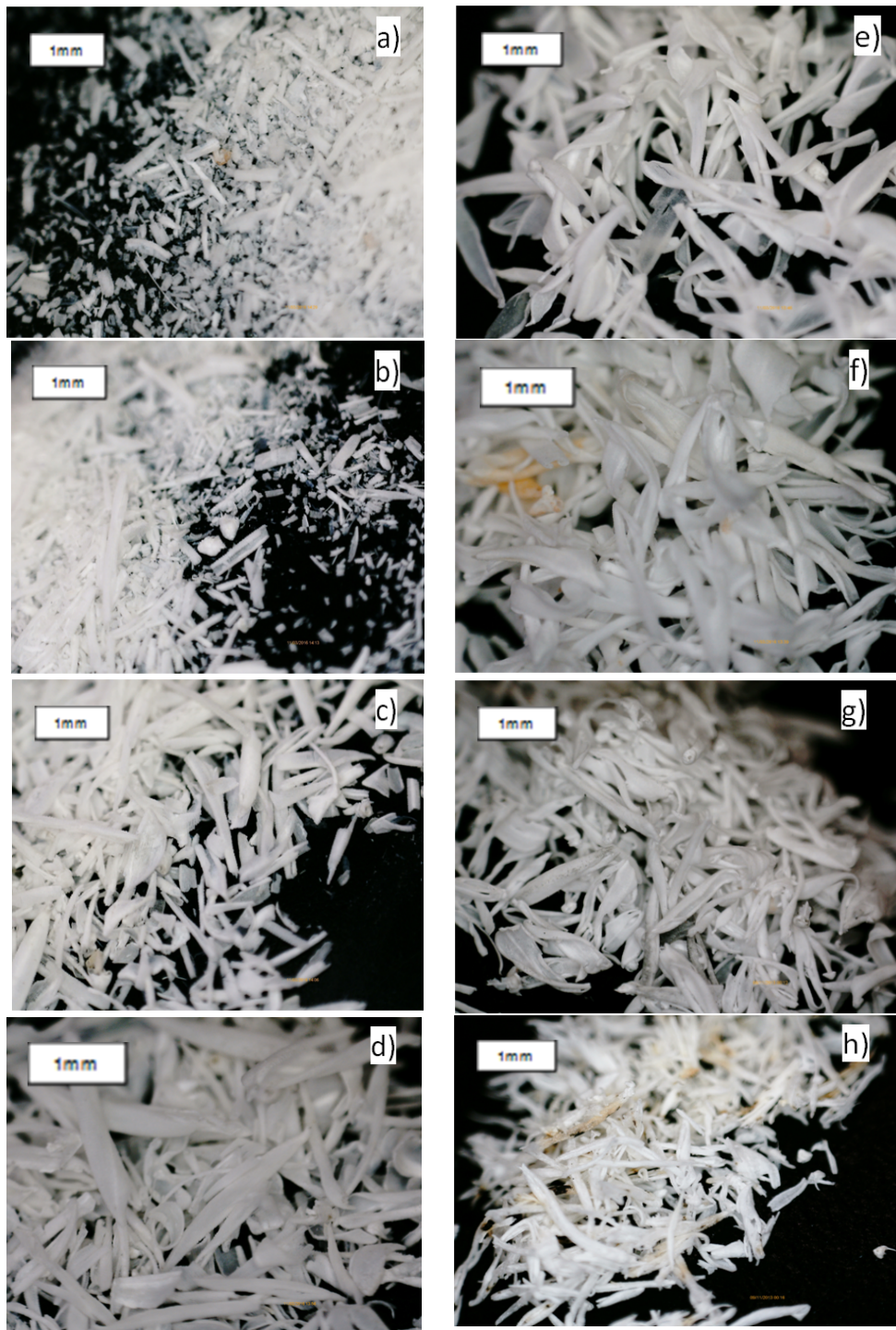
**Fig. 2-1-5. Close observations at macro scale of rice husk ash
at each calcination temperature**
a) 500 °C, b) 600 °C, c) 700 °C, d) 800 °C, e) 900 °C, f) 1,000 °C, g) 1,100 °C, h) 1,500 °C
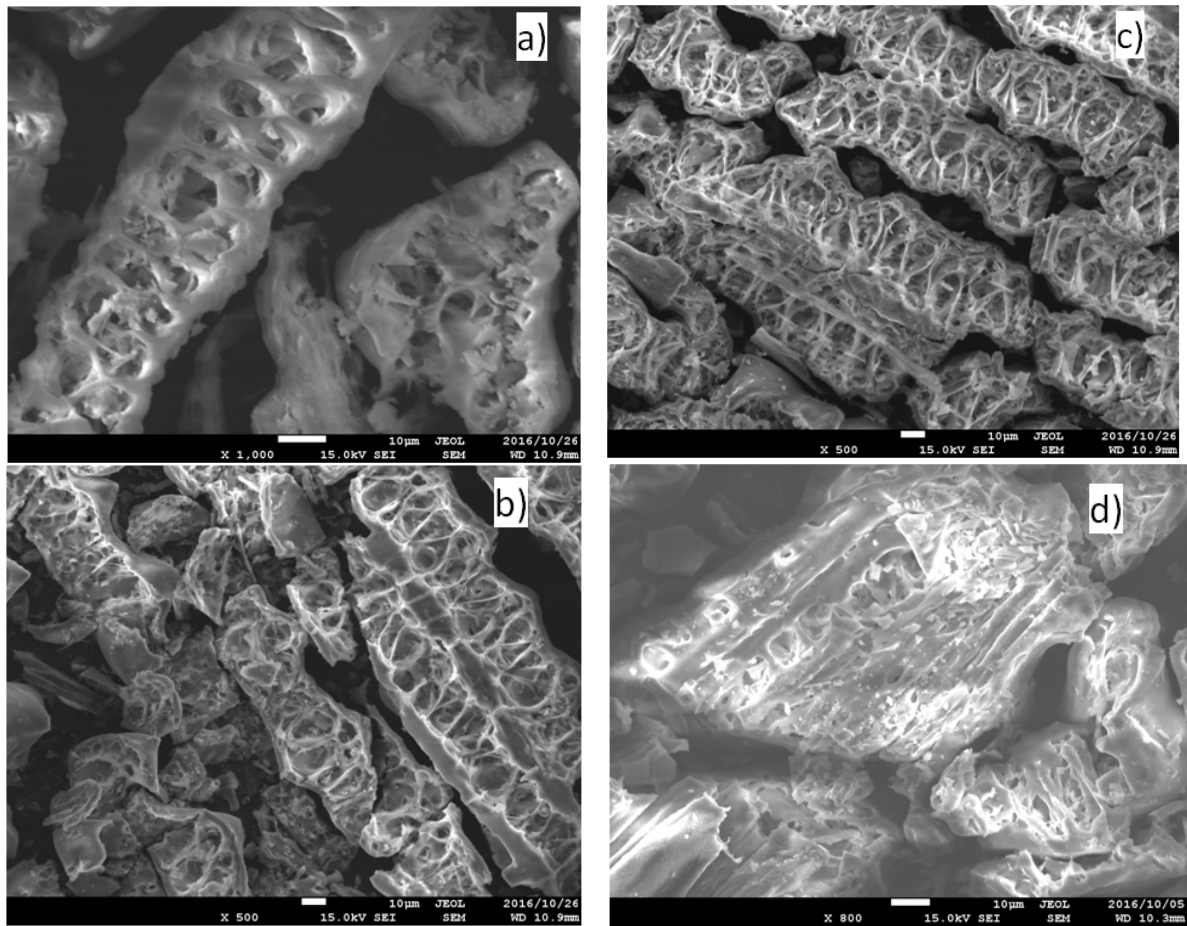
Fig. 2-1-6. FE-SEM results for the samples;
a) 600 °C, b) 1,000 °C, c) 1,100 °C, and d) 1,500 °C

DISCUSSION

Regarding Fig. 2-1-1, the solubility of the sample washed by citric acid decreased to only 83.1 % according to Tateda et al (2016b); in contrast, the solubility of the sample washed acetic acid in this study decreased to 35.3 %. Although it was not considered in this study, the effects of different washing solvents on the solubility of rice husk silica are interesting and should be studied. In addition to rice husks, the solubility of crystal, tridymite, and opal was measured, and their values were 0.4 %, 0.4 %, and 49.3 %, respectively. According to Fig. 2-1-1, silica under the 1,000 °C treatment could have a similar nature to opal, which is amorphous and not crystalized, according to Fig. 2-1-4, and showed low solubility. The silica at 1,500 °C, which had a solubility of 0.6 %, had the same solubility as crystallized crystal and tridymite, corresponding with the results of Fig. 2-1-4. As solubility was calculated by (measured soluble silica (g)/ sample taken at the beginning (g)) x 100, the solubility values can be directly applied to Fig. 2-1-3 due to the loss of carbon from the ash (Fig. 2-1-2).

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Considering measurement errors, S-silica constituted all the T-silica at 500 °C—800 °C. The differences in the occupational percentage of T-silica and S-silica at burning temperatures above 900 °C were approximately 5 points, 63 points, 95 points, and 97 points at 900 °C, 1,000 °C, 1,100 °C, and 1,500 °C, respectively. The silica in rice husk ash is usually expressed as T-silica, and the soluble portion is S-silica and amorphous. The remainder is non-S-silica, some of which are amorphous and crystallized.

From 500 °C to 800 °C, all of the T-silica was S-silica. At 900 °C, approximately 5 % of 99 % was non-S-silica, and the other 94 % was S-silica. At 1,000 °C, approximately 63 % of 98 % was non-S-silica, and 35 % was S-silica. At 1,100 °C, 95 % of 99 % was non-S-silica, and 4 % was S- silica. At 1,500 °C, 97 % of 98 % was non-S-silica, and 1 % was S-silica. As silica in rice husks is initially amorphous and soluble, T-silica is S-silica, and the silica burned at 500 °C to 800 °C shows this nature. The silica in rice husks changes its nature under high heat and begins to lose solubility, but it is still amorphous in nature, so, amorphous nature does not mean soluble. Under higher heat, the amorphous nature changes to crystalline; the change point was 1,100 °C, according to Fig. 2-1-1.

Impurities such as alkali metals, particularly potassium, strongly influenced the transformation of amorphous silica to crystalline in rice husks (Benassi et al 2015). The rice husks burned above 800 °C produced cristobalite (Inoue et al 1998), because the rice husks were burned without being washed so impurities remained on the surface of the rice husks. In contrast, rice husk silica in this study crystallized at temperatures over 1,000 °C, because impurities on these rice husks were low and did not affect the acceleration of crystallization.

Volatile matter in rice husks consisted of cellulose, lignin, pentosans, and other organic matter, in the order of high to low content (Chandrasekhar et al 2003). The calories of volatile matter in rice husks are usually low, and volatile matters that burn more easily or less easily have low and high calorie content, respectively (Shimizu et al 1978). As the analysis of volatile matter in Fig. 2-1-2 was not for rice husks, but for rice husk ash, the volatile portion observed in this figure would be those that were difficult to burn. The percentage of volatile matter decreased as calcination temperatures increased, and was non-existent in samples burned at temperatures over 800 °C. The volatile material trend was similar to that of water

content. The surface of the ash melted, became shiny, and entered glass-like states as calcination temperature increased, which is why water and volatile material could not remain on the surface of the ash, which diminished.

Ash morphology can be observed in Fig. 2-1-5. Rice husk ash was fragile when the rice husks were burned at 500 °C and 600 °C. Ash was easily broken down and became powder under those temperatures. Ash treated at temperatures over 700 °C became firm and kept the rice husk shape. The shape shrank as the temperatures increased, and it appeared to become thinner and firmer. According to Fig. 2-1-2, water content decreased as temperatures increased and was almost nonexistent at 1,100 °C and 1,500 °C. Bakar et al (2016) stated that silica produced at 600 °C burning was the best of silica burned between 500—900 °C, according to its surface area and particle size, which is consistent with the results from this study; it is implied that the fragile nature of ash burned at 500 °C and 600 °C is attributed to the largest and smallest values of surface area and particle size, respectively. Xiong et al (2009) stated that the densification of rice husk ash decreased with increasing calcination temperatures. Their results are consistent with the results of this study, according to Fig. 2-1-2.

More close observations at a micro scale were conducted by FE-SEM of the reverse surface of rice husks. The structures of rice husks are more noticeable as temperatures increased, however, at the highest temperatures the structures could not be clearly recognized due to the surface melting.

CONCLUSIONS

Under no influence of fixed carbon, the amorphous silica in rice husks transformed to crystalline silica at temperatures over a 1,000 °C burning temperature. The T-silica in the ash that burned at 500 °C—800 °C were almost entirely S-silica, and then over 900 °C, the non-S-silica portion increased in T-silica. Volatile matter was nonexistent after burning at 800 °C. The ash portion excluding T-silica was mainly composed of P, Ca, Fe, and K oxides. For morphological observations, at low temperatures the rice husk ash was fragile and did not hold its original shape; in contrast, rice husk ash held its original shape at higher temperatures. At extremely high temperatures, such as 1,000 °C and 1,500 °C, the original

shapes seemed to shrink by melting on the surface of the ash; this observation was supported by SEM analysis.

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2-2. Solubility and physical composition of rice husk ash as a function of calcination temperature and duration

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. 2-2-1(a) 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. 2-2-1(b) also successfully achieves heat recovery.

(a)

(b)
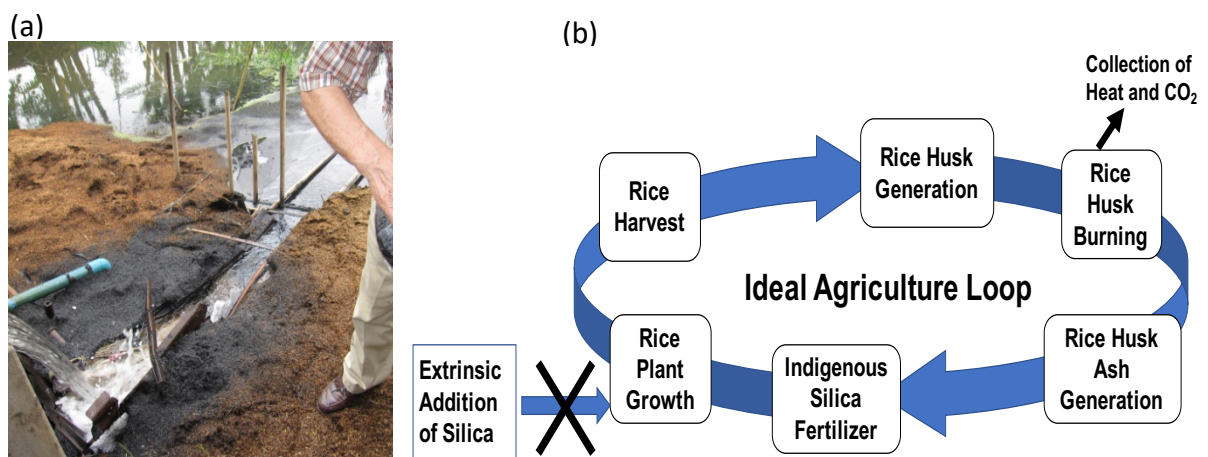
Fig. 2-2-1. (a) Discharged rice husks, (b) Ideal agriculture loop

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 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 rice husks.

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):

$$\text{Solubility (\%)} = VS \times C \times f \times \frac{V1}{V2} \times \frac{15.021}{W} \times \frac{100}{1000} \qquad (1)$$

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. 2-2-2 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) 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 ºC 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. 2-2-2, 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.

Fig. 2-2-2. Appearance of the rice husk ash after different calcination temperatures and durations

Solubility and Calcination Temperature

Fig. 2-2-3 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.
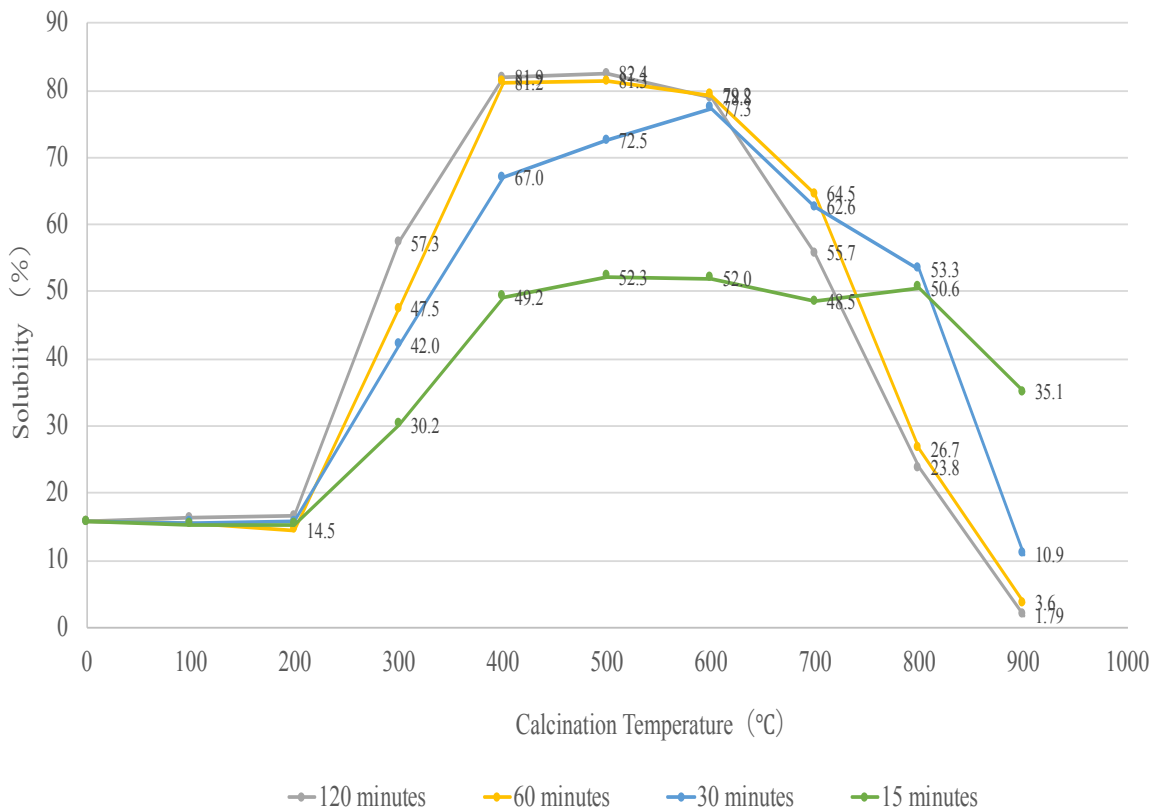
**Fig. 2-2-3. Solubility as a function of calcination temperature
for different calcination durations**

Solubility and Calcination Duration

Fig. 2-2-4 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.
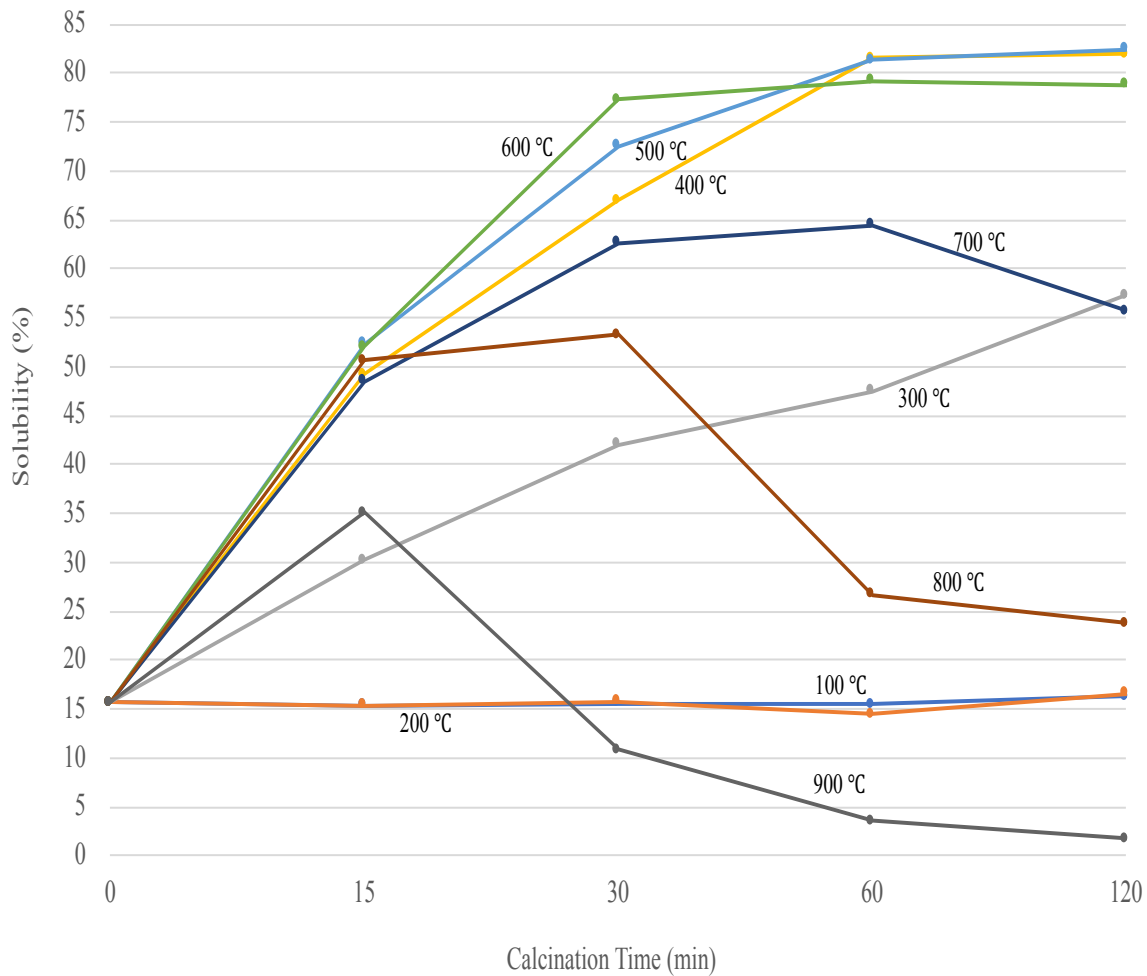
**Fig. 2-2-4. Solubility as a function of calcination duration
for different calcination temperatures**

Physical Composition of Rice Husk Ash As a Function of Calcination Conditions

Fig. 2-2-5 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.

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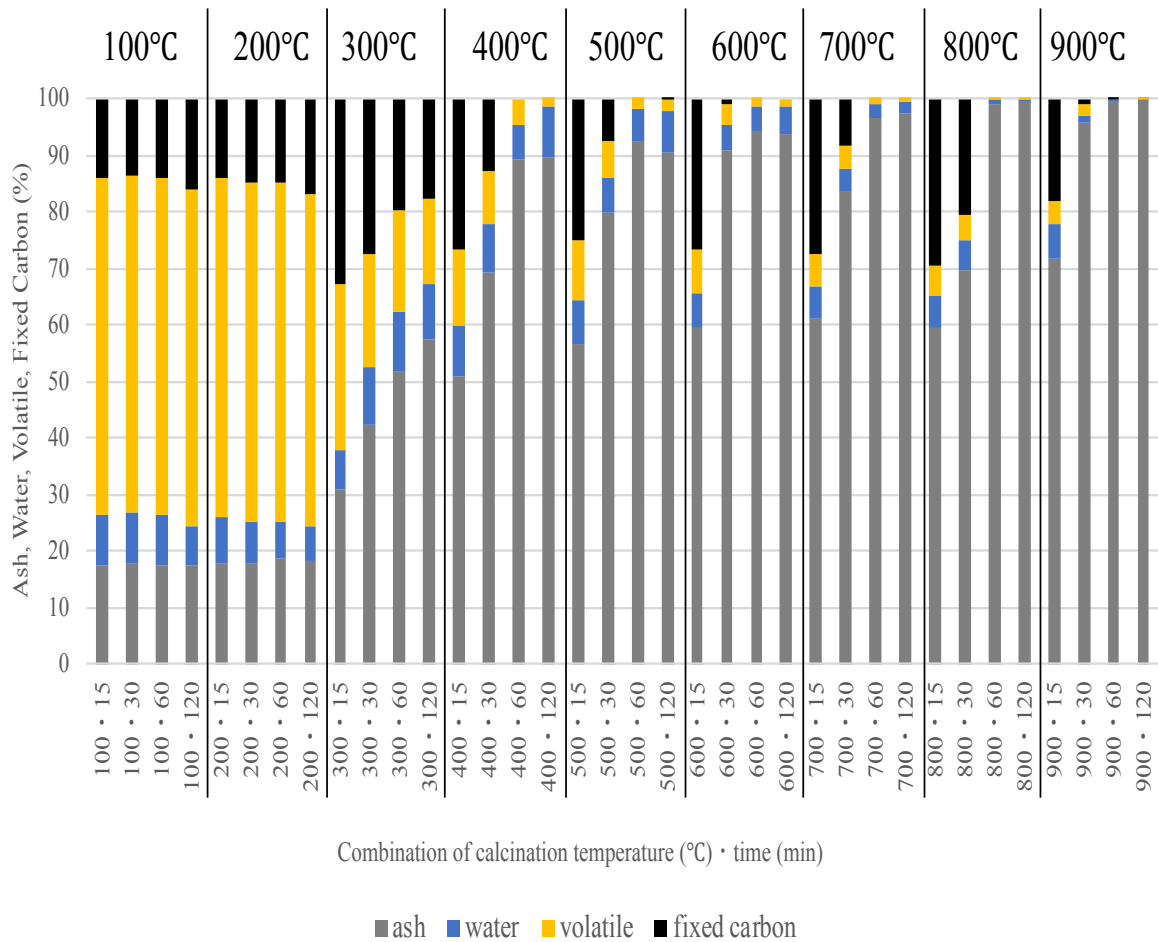
Fig. 2-2-5. Physical composition of rice husk ash samples subjected to different calcination conditions

Relationship between Appearance, Solubility, and Physical Composition

Fig. 2-2-6(a)–(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. 2-2-6(a) and (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. 2-2-6(c)), 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. 2-2-6(d)), 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. 2-2-6(e)), although the ash appeared whitest after 120 min of calcination at this temperature. At 600 °C, the solubility became stable after 30 min (Fig. 2-2-6(f)), and the ash became slightly black again after 120 min. Fig. 2-2-6(g) 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 maximum after 60 min of calcination and then decreased. At 800 °C, the solubility decreased by half after 30 min of calcination (Fig. 2-2-6(h)) 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. 2-2-6(i)) 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. 2-2-6(d)), at 700 °C for 120 min (Fig. 2-2-6(g)), and at 600 °C for 30–120 min (Fig. 2-2-6(f)). Therefore, rice husk ash with a whitish appearance does not always make a better fertilizer.
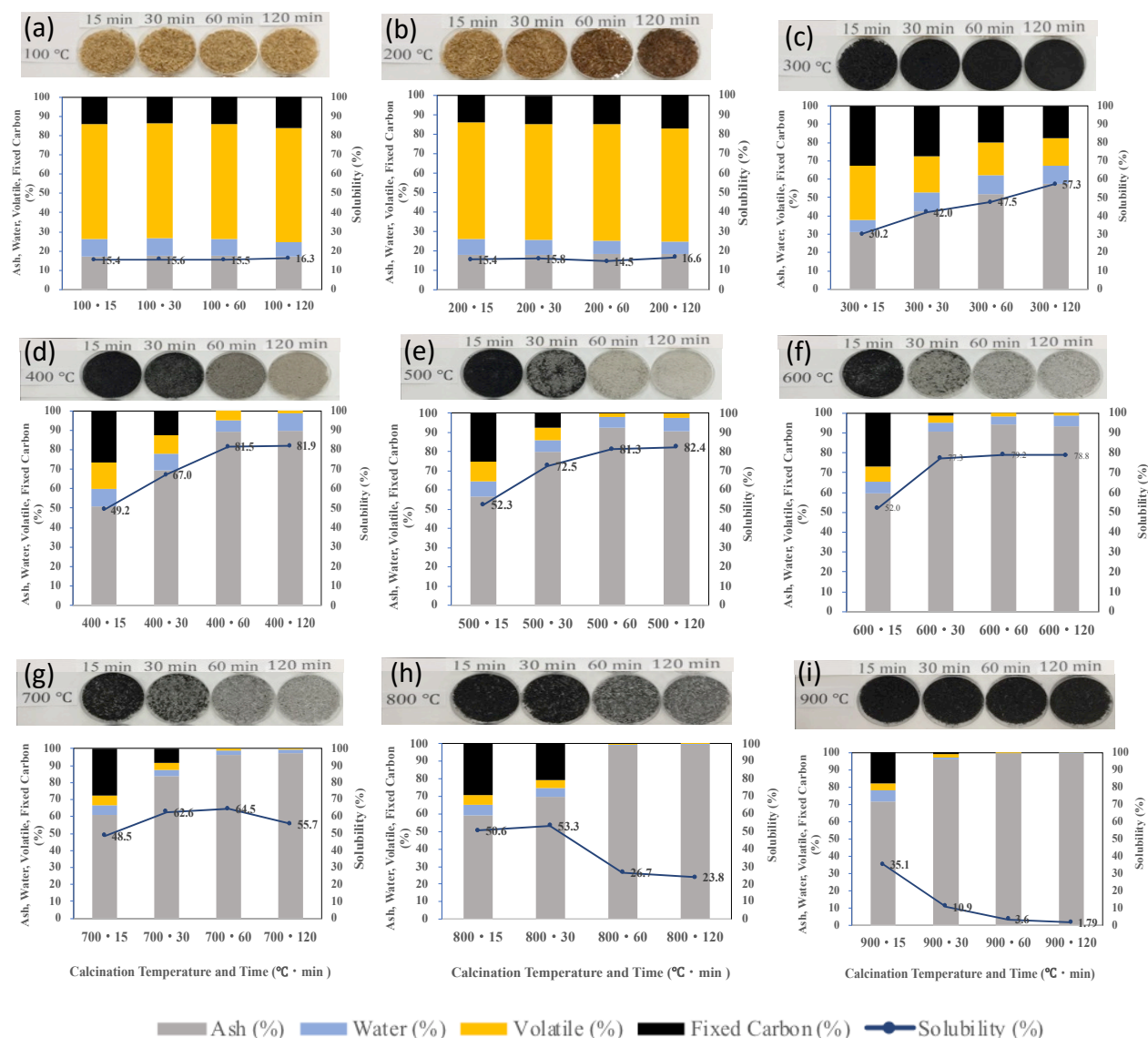
Fig. 2-2-6. Physical composition, solubility, and appearance of rice husk ash for different calcination conditions: (a) 100 ºC, (b) 200 ºC, (c) 300 ºC, (d) 400 ºC, (e) 500 ºC, (f) 600 ºC, (g) 700 ºC, (h) 800 ºC, and (i) 900 ºC

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. 2-2-6(a)–(e)). At calcination temperatures above 600 °C, a gap appeared between the ash portion and the soluble silica portion (Fig. 2-2-6(f)–(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 crystalized form. At 700 °C, the gap was much larger than that at 600 °C (Fig. 2-2-6(g)). 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. 2-2-6(h)). 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. 2-2-6(i)).

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. 2-2-7).
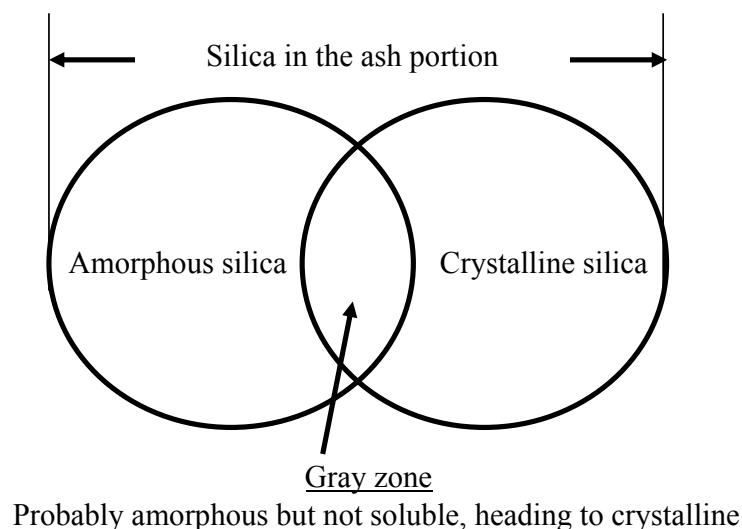
Fig. 2-2-7. Concept of the gray zone between amorphous and crystalline forms in the ash portion of silica derived from calcined rice husks

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,

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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. 2-2-6, 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. 2-2-8). 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. 2-2-8); 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. 2-2-7, 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. 2-2-8). 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.
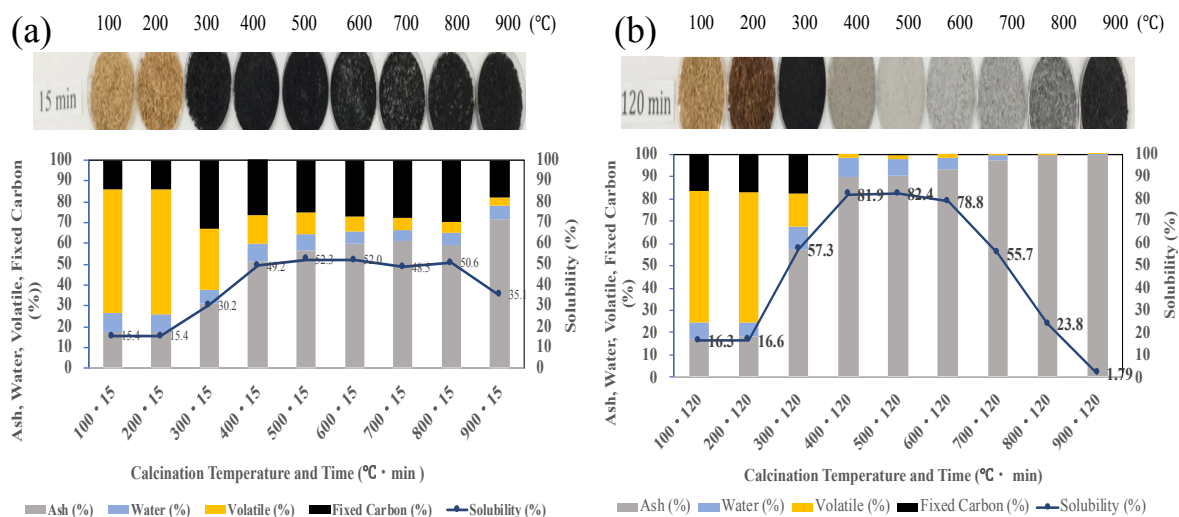
Fig. 2-2-8. Contrasting physical composition, solubility, and appearance of rice husk ash after (a) 15 min and (b) 120 min of calcination

CONCLUSIONS

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.

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Doi 10.9734/JSRR/2016/27239

Chapter III   Case Studies for Thermal Recovery of Rice Husk and Fertilization of Rice Husk Silica

3-1. Case study: Technical considerations to optimize rice husk burning in a boiler to retain a high solubility of the silica in rice husk ash

INTRODUCTION

Rice husks have been gaining much attention for their amorphous silica property, which has been referred to as "bio-ore of silica" (Tateda 2016a). Recently, not only the agricultural field but many other fields such as medicine have been focusing on the silica in rice husks (Athinarayanan et al 2015). However, rice husks are still generally viewed as a waste product that needs to be disposed of. As a result, an abundant amount of rice husks has been disposed of as a valueless material in many parts of the world. For a practical use of rice husks, the best method is to burn the husks and use the concentrated silica as an agricultural fertilizer. The carbohydrates that occupy a large proportion of rice husks by weight can be an effective biomass fuel to produce heat and the remaining silica in the rice husk ash can be used as an essential element for rice growth in healthy agricultural conditions (Datnoff et al 2007, Ma et al 2006). Several Southeast Asian countries have been producing energy for a long time by burning rice husks (Pode 2016). Tateda (2016b) reported on the establishment of a local energy system using rice husks to save on management costs of drying rice husks and running greenhouses during winter, and concluded that the system was practically sustainable. Burning rice husks is not a difficult task and individuals can obtain heat from the process. However, the silica would crystallize and no longer be a valuable resource if the rice husks are burned carelessly and without the proper consideration. There was a previous incident in Japan, in which a boiler blasted free because its stack was clogged with crystallized silica due to careless operation. Silica in the rice husk ash after burning must be amorphous; otherwise, crystalline silica is dangerous in operation, even to human health, and becomes useless as a resource.

Silica deposited in the cell walls (Byun et al 2011) of the rice husk, called "opal" (Richmond et al 2003, Kondo 2010), is amorphous; thus, an important consideration when burning rice husks is how high the solubility of silica in the rice husk ash can become as a result of burning. Amorphous silica can be dissolved in an alkali solution. The degree of amorphous silica can be evaluated by determining its solubility. The higher the solubility, the better the amorphous state of the silica in the rice husk ash; in other words, the better the quality of the ash, and vice versa.

An electric furnace is usually used to burn rice husks to extract precious silica from the husks (Ruangtaweep et al 2011, Sarangi et al 2011, Bakar et al 2016), which is referred to as "sintering" or "calcination," and it is generally accepted that a high quality of silica could be produced by the furnace, yet the costs to run the electric furnace are too high to burn a large amount of rice husks. Direct combustion of rice husks was introduced by several researchers (Pode 2016, Sun et al 2001), but very limited information, such as "combustion should be less than 800ºC for getting amorphous silica" (Sun et al 2001), has been made available; the research did not mention the quality of the silica in the rice husk ash after combustion. In this study, detailed steps to achieve the optimal operation of a boiler were described for stakeholders in this field. The best quality of silica, based on a solubility evaluation, in rice husk ash and heat could be obtained simultaneously through the optimal operation. Since the boiler used in this study was very simple and inexpensive, the best practices reported here can be transferred and applied to using rice husks as a resource in many parts of world, especially in Southeast Asian countries. This is the consecutive report of Tateda et al (2016b).

MATERIALS AND METHODS

Rice Husks

The rice husks from Koshihikari (*Oryza sativa L.*) used in this study were obtained from the local Imizuno Agricultural Association (IAA) in Imizu, Japan, where the Toyama Prefectural University is located. The rice harvested in the area is transferred to the large rice storage yard at the IAA before the rice is processed. This processing entails milling and cleaning the rice to produce a product suitable for sale. Most of the rice husks generated in this community are accumulated and stocked at the IAA, amounting to 600 tons of rice husks annually. Half of the stocked rice husks are used as flooring material for the housing of domestic animals and as water drainage systems in the paddy fields. However, such usage of rice husks is neither stable nor sustainable, and the entire amount of 600 tons/year will eventually reach the end of its useful life and have to be treated as waste. The density of rice husks is very low, at 0.1–0.2 ton/m^3, meaning that extremely large storage spaces would be necessary for disposal unless recycling methods are developed. Generation of rice husk does not directly connect to disposal, so waste rice husk is stored anyway somewhere before disposal. The husk is currently considered merely as waste and is therefore a burden on the rice producers in the area.

Boiler Used in This Study

In this study, the boiler shown in Fig. 3-1-1 was used to combust the rice husks. The boiler has an air blower system and the rice husks fed from the inlet is combusted in an oxygen-rich condition on moving fire grates, which are shown as a sloped surface in the figure. By the movement of the grates, rice husks could be moved forward during combustion. The combustion capacity of the boiler is 100 kg/h of rice husk, with a water content of approximately 10–13 %. Table 3-1-1 shows sampling ports for temperature measurement inside the boiler furnace, which correspond to the numbers in Fig. 3-1-1.
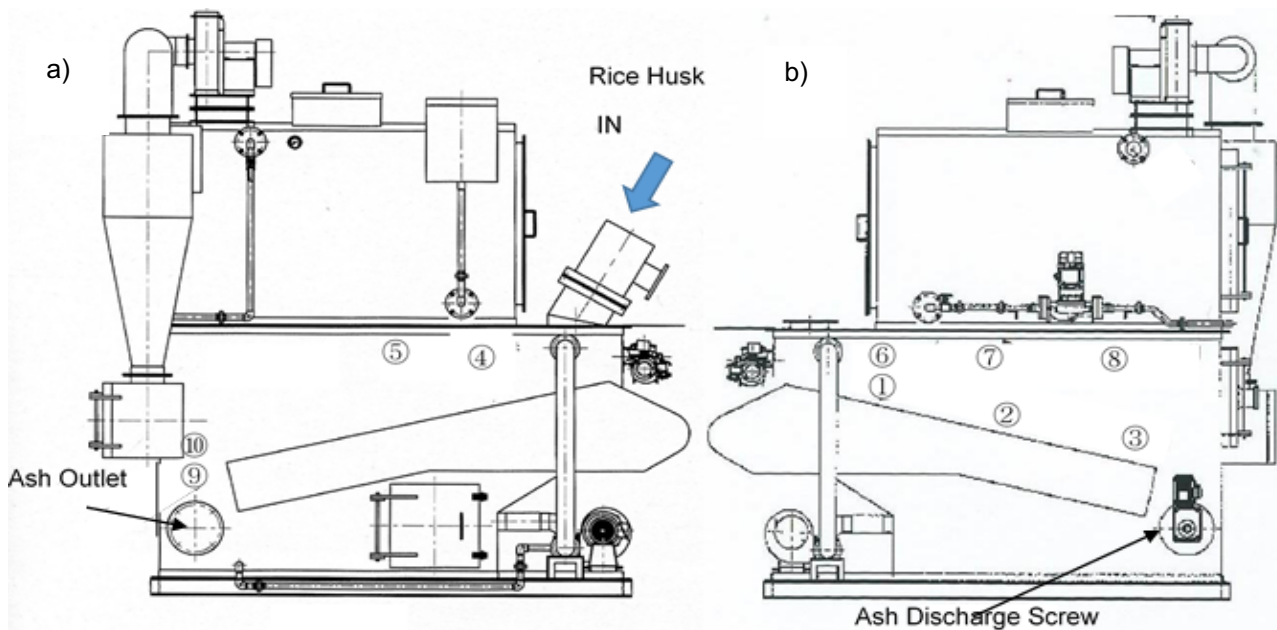
Fig. 3-1-1. Diagram of the boiler from a) the left side view and b) the right side view. The numbers indicate sampling ports for temperature measurement.

Table 3-1-1. Temperature sampling ports for thermocouples

Port Number	Location Details
1	Surface of upper part of fire grates
2	Surface of middle part of fire grates
3	Surface of lower part of fire grates. After installation of the sink, the ash accumulated in the front part of the sink.
4	Head space on the left side where the rice husks are fed in
5	Head space on the left side on the middle position of fire grates
6	Head space on the right side where rice husks are fed in
7	Head space on the right side on the middle position of fire grates
8	Head space on the right side on the lower position of fire grates
9	The lower position of ash deposition sink
10	The upper position of ash deposition sink
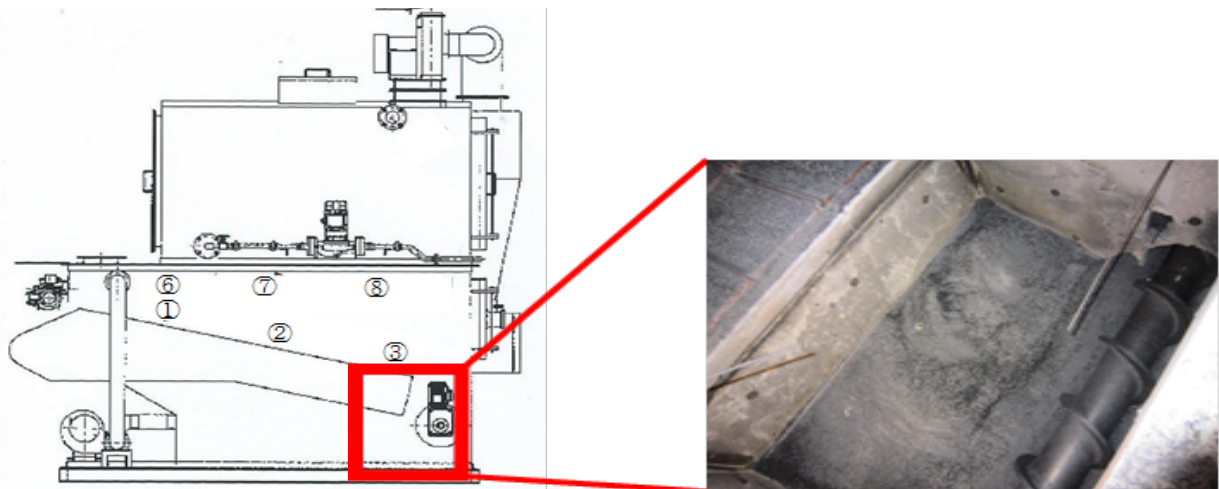
Fig. 3-1-2. Ash deposit sink in the furnace of the boiler

Fig. 3-1-2 shows the ash deposit sink used to keep ash at a high temperature. The sink was made by removing two lines of fire grates that were originally located there.

Ash Sample Collection and Temperature Measurement

Ash was sampled by discharging ash from the outlet by loosening with a screw (Figs. 3-1-1 and 3-1-2) at an early stage in the experiment. After installation of the sink, ash sampling was performed manually with a shovel by an operator. Ash sampling was conducted immediately after combustion was stopped (Time 0), one day after combustion was stopped (Time 1), two days after (Time 2), and three days after (Time 3). The temperature distribution in the furnace was measured with 10 thermocouples (Type K) and recorded for analysis by a data logger (Paperless Recorder GP10, Yokokawa).

Quantitative Measurement of Solubility

In this study, the sodium hydroxide (NaOH) method at an early stage and the Testing Method 4.4.1.c (Tateda et al 2016, FAMIC 2015) were employed to measure the solubility of the silica in the rice husk ash. The NaOH method is a simple method and the Testing Method 4.4.1.c is a more official method (not authorized by Japanese Government, however), and the former showed mostly higher values than the latter (Fig. 3-1-3).
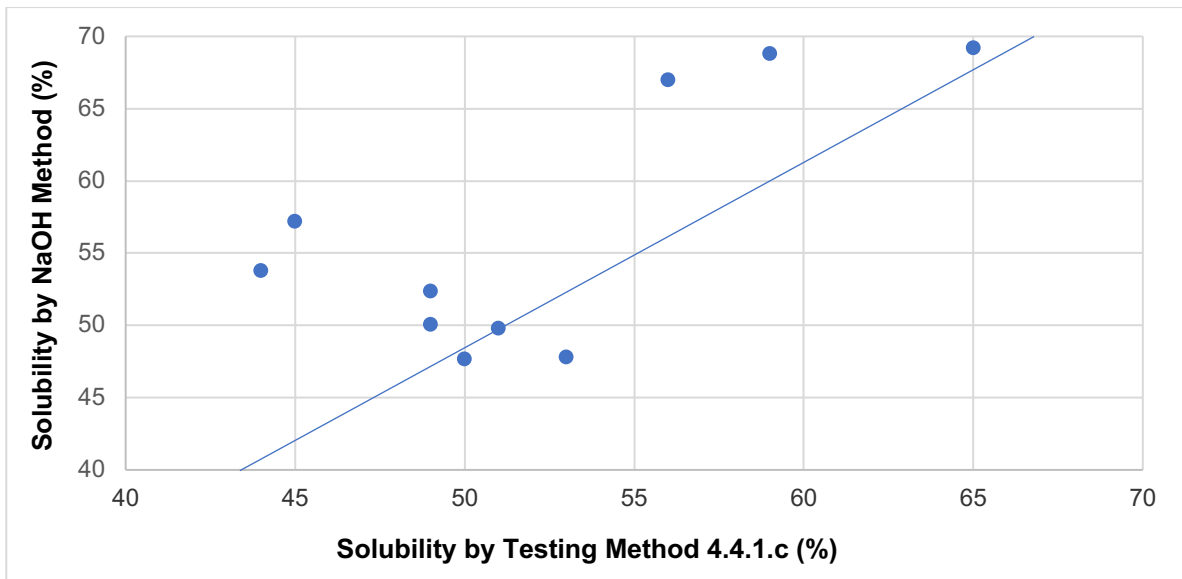
**Fig. 3-1-3. Solubility data comparison between the NaOH method
and testing method 4.4.1.c.**

The NaOH method can be described as follows: the ash sample (1 g) was placed in a 250 ml Erlenmeyer flask, and 150 ml of 0.5 M NaOH (Kanto Kagaku), heated at 60 °C, was poured into the flask, which was placed in a water bath at 60 °C. After one hour of stirring, the NaOH solution was quickly cooled to room temperature and purified water was added to a level of 250 ml. Subsequently, the 250 ml solution was filtered with one micro glass-fiber filter, after which an aliquot of the filtered sample was placed in a white porcelain dish and dried on the water bath. A few milliliters of hydrochloric acid (HCl, 1+1 [conc. HCl: purified water = 1:1 in volume]) was added to the white porcelain dish and it was dried in the water bath. The process of HCl addition and drying was repeated several times. Subsequently, the dish was placed in a drier and was dried completely at 110 °C. After cooling, 50 ml of HCl (1+4) was poured into the dish and the dish was heated to 90 °C. After the dissolution of the residue on the bottom of the dish was complete, the solution was filtered with one micro filter. The material on the filter was dissolved with HCl (1+10) and the procedure was repeated.

RESULTS AND DISCUSSION

Burning with and without a Set Maximum Temperature

Operation of the boiler was performed without setting a maximum temperature at the early stage of this experiment. Samples at only Time 0 were taken for a solubility measurement of this operation. Solubility during this period was measured by the NaOH method and the mean, median, and standard deviation were 49.4 %, 50.1 %, and 6.4 %, respectively. Next, the maximum temperature was set at 600 ˚C (port No. 8 in Fig. 3-1-1) and burning was conducted.

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It was found that some measuring ports detected temperatures exceeding 1,000 °C, which will make silica in rice husks crystallize, even when 600 ˚C was selected as the setting. Fig. 3-1-4 shows the representative temperature profile data of the boiler when the maximum temperature was set at 600 °C. The symbol "CH" in the figure corresponds to the temperature sampling ports in Fig. 3-1-1 and Table 3-1-1. Temperatures at sampling port Nos. 4 to 7 (CHs 4 to 7) exceeded 1,000 ˚C according to Fig. 3-1-4. Next, the maximum burning temperature was set at 500 ˚C. Measured temperatures almost never reached 1,000 ˚C. Solubility measured by Testing Method 4.4.1.c was 57.3 %, 59.0 %, and 5.3 % for the mean, median, and standard deviation, respectively. Comparing values of the operation without a set maximum temperature, it can be said that higher values (quality) of ash would be produced when the burning of rice husks was conducted under a controlled operation. Since the values of the NaOH method were always higher than those of the Testing Method 4.4.1.c, in the case of Fig. 3-1-3, the solubility values of burning without the temperature setting would be lower than the values shown in the case of Testing Method 4.4.1.c. Thus, a controlled operation is very important to improve the quality of ash. Rice husks have been used for energy recovery, especially in Southeast Asia (Pode 2016); however, the improvement of ash quality in the operation as discussed here has not yet been considered.
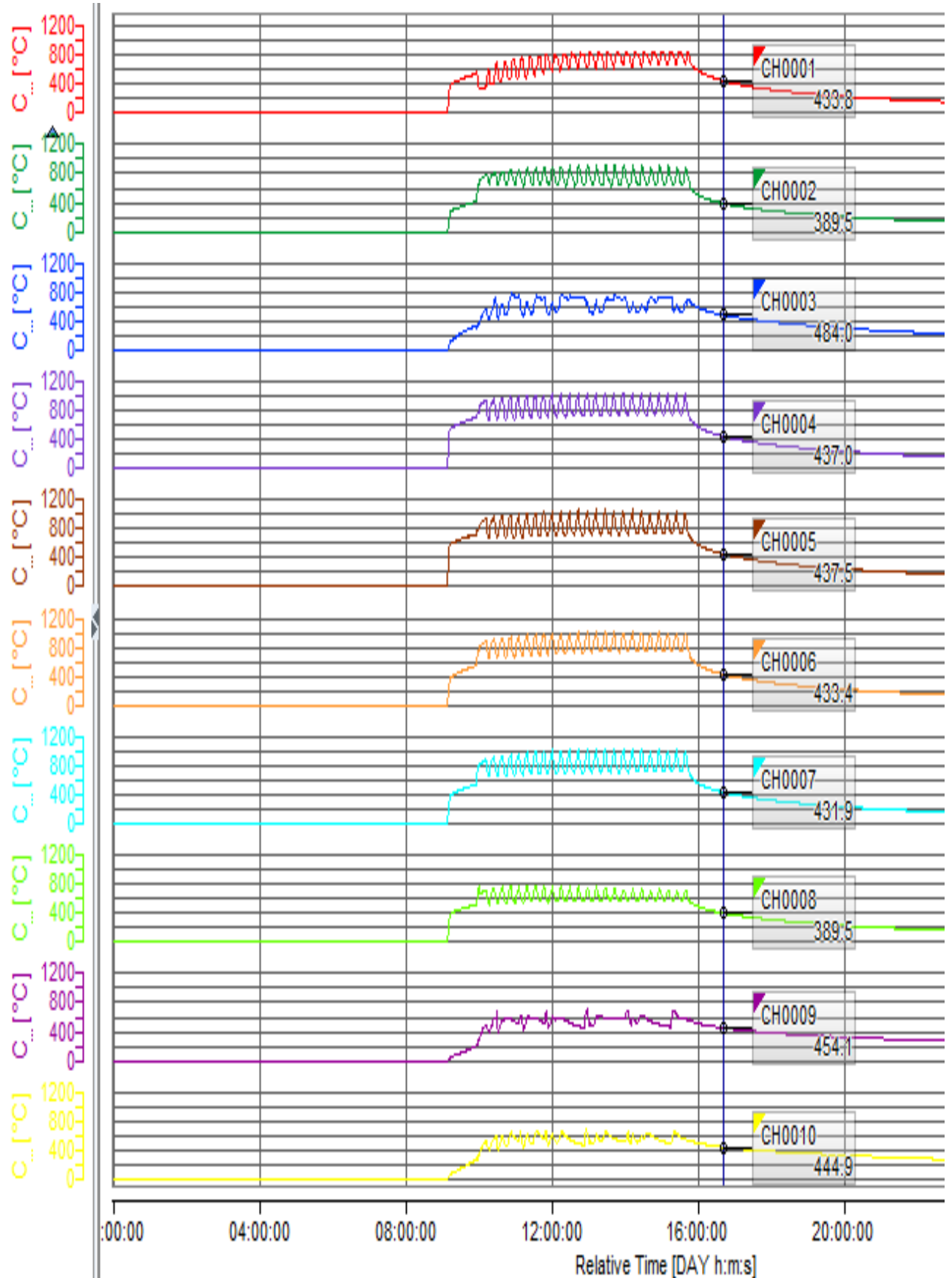
Fig. 3-1-4. Temperature distribution of boiler operation set at 600 ˚C for the Maximum Temperature

Establishing the Importance of Curing Time after Burning

After discovering that the solubility of the ash increased after a curing phase under a high temperature, the sink was installed in the boiler (Fig. 3-1-2). By taking out two lines of fire grates, approximately 200 L of free space was created to hold ash stock. It is similar to a composting process. For compost, the first phase is the degradation of organic material and the second is the curing phase. During the curing phase, the quality of the compost increases (Tateda et al 2002). To increase the quality of rice husk ash, two phases are required if an exothermal reaction, such as burning in a boiler, is taking place (Fig. 3-1-5). The first phase is for burning flammable materials such as cellulose, hemi-cellulose, and lignin, and the second phase is for burning nonflammable material, which is carbon. Energy recovery occurs in the first phase.

Raw Rice Husk → First Phase Exothermal Reaction → Second Phase Endothermic Reaction → High Quality Ash

-Burning flammable organics
-Recovering heat
-Resulting black ash

-Burning nonflammable organics
-Resulting white ash
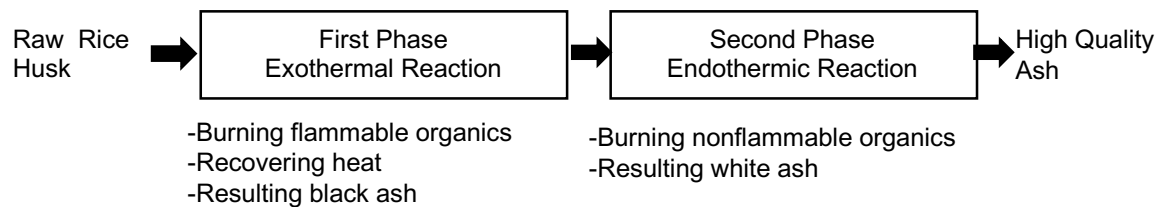
Fig. 3-1-5. Two phases for improving quality of ash during boiler burning

If ash is created only in the first phase, the color of the ash is black and its solubility is low, which means the quality of the ash is not good. In the second phase, akin to the curing phase in composting, the remaining unburned carbon on the surface of ash particles is burned and volatizes into air as CO_2. The ash becomes white at this point. The carbon on the surface of the ash particles can be burned if the carbon is in the proper environment, which would provide an endothermic reaction to the ash. Burning the remaining carbon on the surface of ash particles requires calories, so heat must be provided exogenously. When burning rice husks in an electric furnace, it is quite easy to obtain high solubility (high quality) ash because burning in an electric furnace is an endothermic reaction and ash receives a continuous energy supply. As seen in our study, a temperature of at least 400 ˚C is required for the second phase. Below 400 ˚C, the remaining carbon on the ash surface could not be volatized as CO_2. For an easy and inexpensive modification of the boiler and a minimal heat loss from ash, the sink was installed in the boiler to provide the second phase for the ash. Ash after the first phase falls into the sink, losing a minimal amount of heat, and automatically proceeds to the second phase. Fig. 3-1-6 shows the

representative solubility data for 8 consecutive operations. Solubility was measured with the Testing Method 4.4.1.c and the operation conditions were as outlined in Table 3-1-2.

Table 3-1-2. Boiler operation conditions

Factor	Condition	Explanation
Temperature Control	AUTO	Automatic and manual control options are available.
Maximum Temperature Setting	500 ˚C	According to result in Section "Burning with and without a Set Maximum Temperature".
Fire Grates Operation	Continuous	Normal operation. Rice husks are carried forward by the movement of fire grates.
Air Flow Capacity	30 Hz	It connects directly to the air flow amount sent into the furnace. Values of 10, 20, 30, 40, and 50 Hz can be chosen. The middle of 30 Hz was chosen.
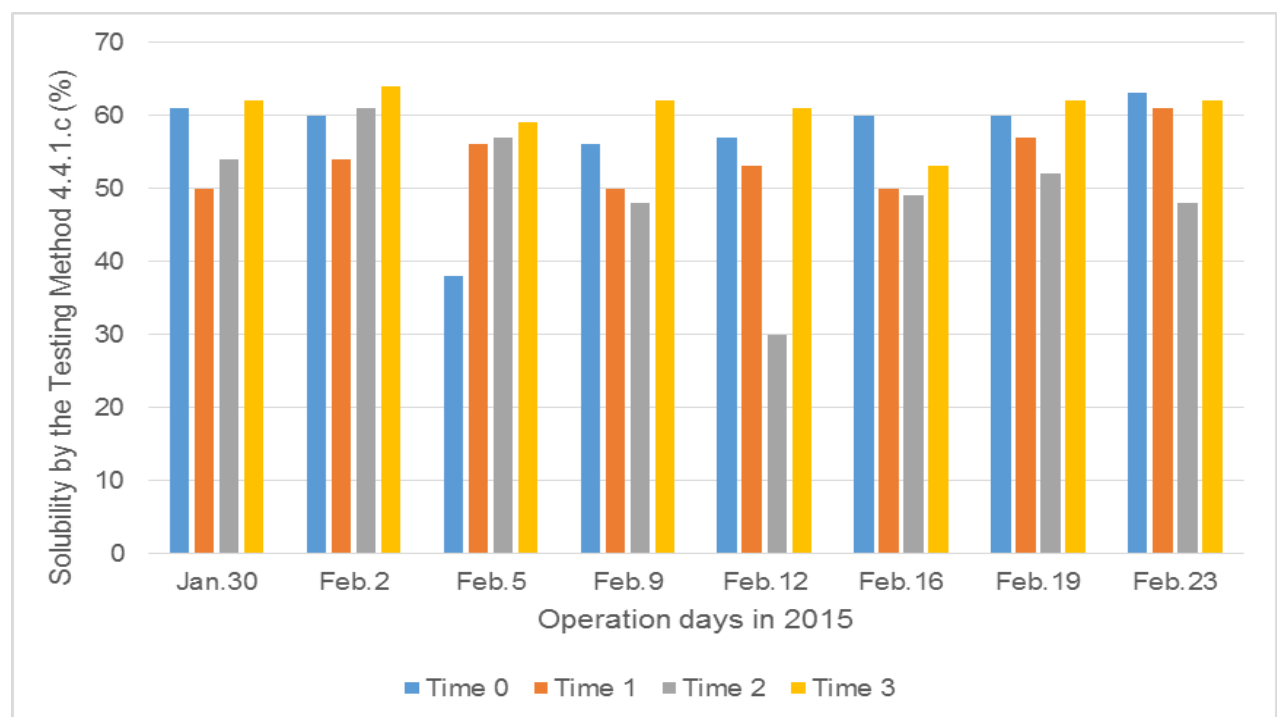
Fig. 3-1-6. Eight consecutive operations after installation of the sink

The fluctuation of solubility in the graph might be caused mainly by unreliability of the manual sampling method. The samplings at Times 0 to 3 were performed by an operator with a hand shovel by manually digging into the ash pile at the point near temperature measuring port No. 9, as seen in Fig. 3-1-1. Samples were taken by digging into the ash pile from the surface, which was at an extremely high temperature; thus, it was difficult to take a sample from the exact same spot each time. Moreover, ash in the sink is a solid, so its qualities are heterogeneously distributed in the pile and only a tiny amount (1 g) is used for the solubility measurement. Although such limitations existed, notable remarks on solubility trends were found. Solubility at Time 3 mostly increased as compared to Time 0. Solubility at Time 0 was higher than the

values recorded in the uncontrolled operation. This result was due to the maximum temperature being set and the ash being in the curing phase in the sink. According to the study results, it can be seen that the second phase plays a very important role in improving the quality of the ash. However, other data showed that an extended curing time (the second phase) up to Time 5 did not improve the quality of the ash (Fig. 3-1-7).
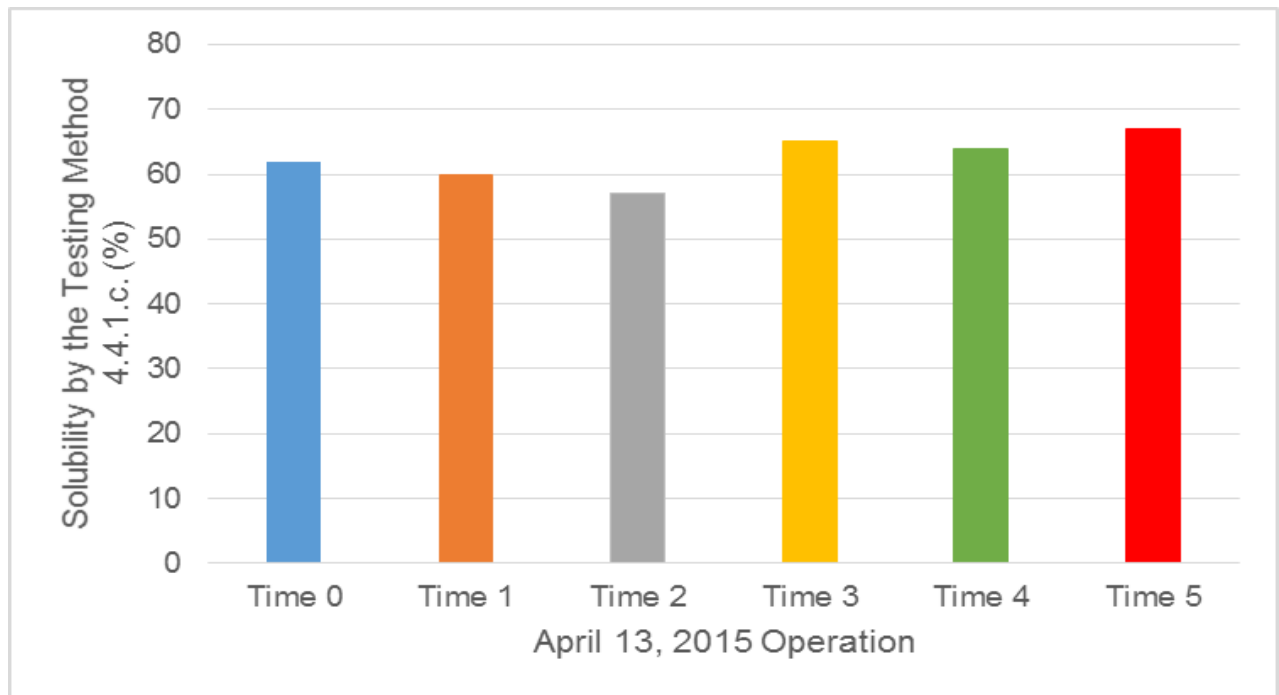
Fig. 3-1-7. Five consecutive data for solubility

Determining the Optimal Operation of the Boiler

By changing factors outlined in Table 3-1-2, the best combination for the optimal operation was investigated.

<u>**Air flow capacity**</u>

The best air flow capacity was investigated by changing the capacity from 10 to 50 Hz, as seen in Table 3-1-2, and the solubility at each Hz was evaluated. The results are shown in Fig. 3-1-8. The data were representative and showed clearly significant differences.
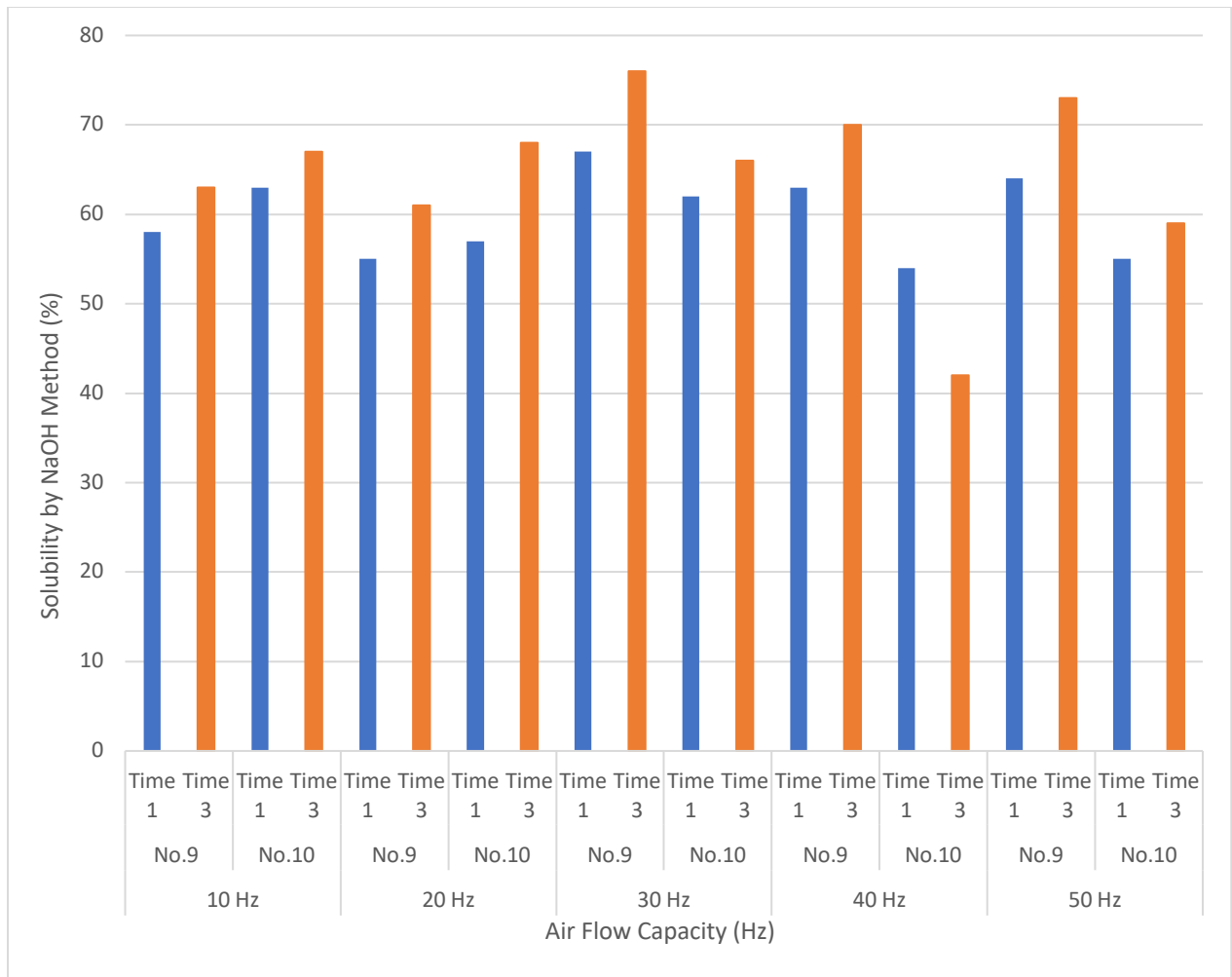
Fig. 3-1-8. Solubility measurements based on differences in Air Flow Capacity (Hz)

According to Fig. 3-1-8, the 30 Hz air flow capacity was best; thus, 30 Hz was selected for the optimal air flow capacity.

Fire grate operation

Rice husks were fed from the inlet and moved down through the surface of No. 1, 2, and 3 in Fig. 3-1-1 by the back and forth movement of the grates. Fire grates were basically operated continuously; however, their movement could be controlled. The grates were operated using a stop mode (intermittent operation) to determine the optimal operational conditions. For this experiment, the fire grate operation detailed in Table 3-1-2 was changed in a series of continuous and intermittent (3-3-6, 3-6-8, and 5-5-6) modes. "3-3-6," for example, means that the fire grates moved for 3 s and stopped for 3 s, and the rice husks were retained on the grates for 6 min. The results are included in Table 3-1-3. All data of Times 0 to 3 were used to obtain the mean, median, and standard deviations.

Table 3-1-3. Influence on quality of different fire grate operation settings

Fire Grate Operation	Solubility by the Testing Method 4.4.1.c (%)		
	Mean	Median	Standard Deviation
Continuous	54	56	7.8
3-3-6	61	60	3.3
3-6-8	56	56	5.0
5-5-6	60	60	2.3

According to the table, it can be seen that the 5-5-6 operation was best and the most stable quality (high solubility) can be achieved with this combination.

Temperature control

The factor of temperature control, as seen in Fig.3-1-2, was changed in this experiment. The maximum temperature was not changed but remained at 500 ˚C. Under the AUTO operational condition, the temperature in the inside of the furnace gradually increased to reach the maximum temperature of 500 ˚C at temperature sampling port No. 8, as seen in Fig. 3-1-1 and Table 3-1-1. It took time to reach 500 ˚C under the AUTO condition because the automatic feeder of rice husks often limited the feeding to prevent the temperature from exceeding 500 ˚C. Therefore, the boiler in this experiment was operated without using the AUTO control; rather, the manual setting was used from the starting period until the temperature at No. 8 reached 700 ˚C. At that point, the temperature control was switched to AUTO. Solubility data were 69 %, 70 %, and 3.9 % for the mean, median, and standard deviation, respectively. According to the results, operation without the AUTO setting at the beginning showed better data than the operation on full AUTO control. The representative temperature profile data of the boiler is shown in Fig. 3-1-9. Compared to Fig. 3-1-4, it is clear that the temperature distribution inside the furnace should be below 800 ˚C to produce high quality ash. This conclusion corresponds to the results of Sun et al. (2001). The representative solubility data is shown in Fig. 3-1-10. Solubility consistently increased from Time 0 to Time 3.
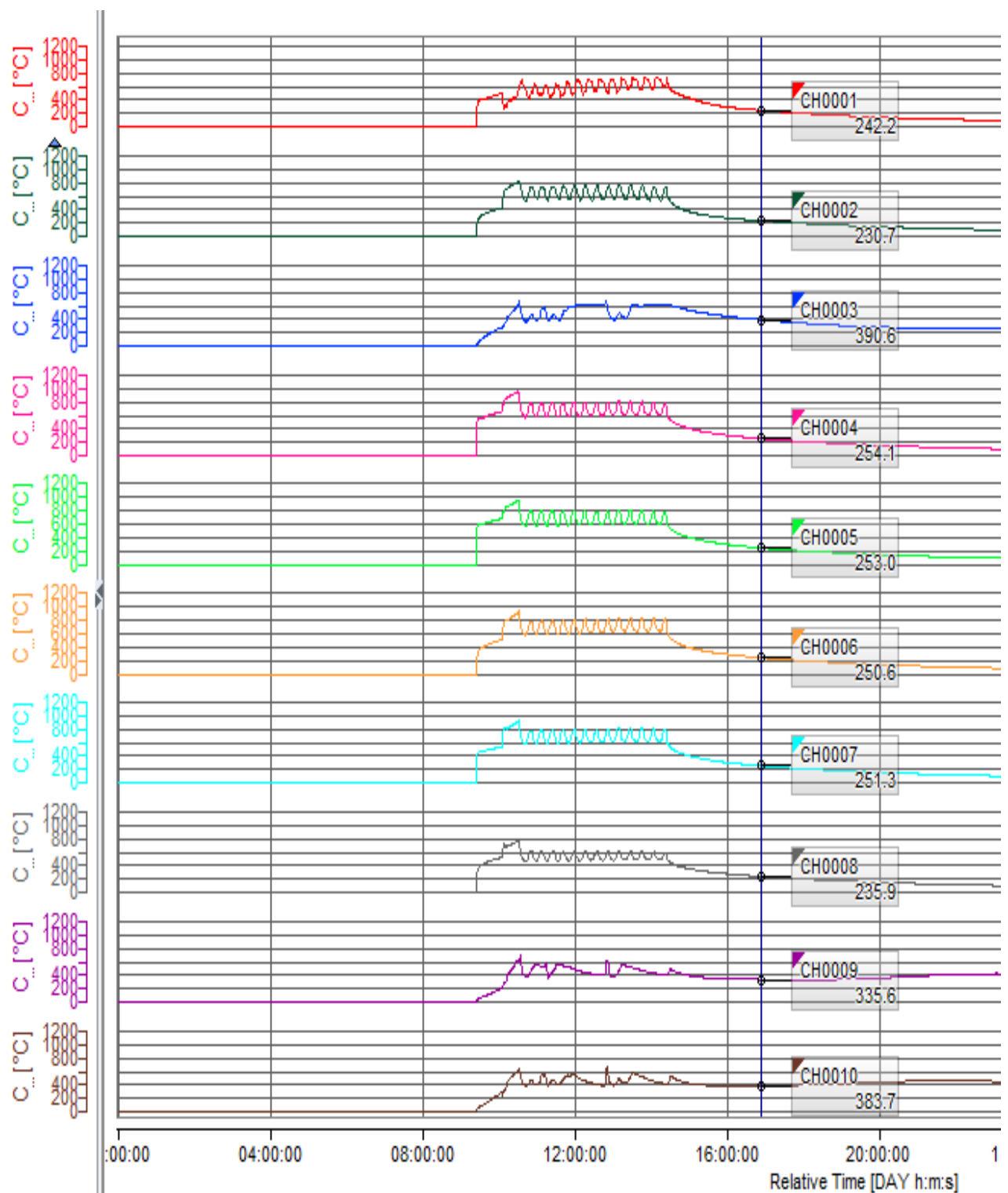
Fig. 3-1-9. Temperature distribution of boiler operation without AUTO setting at the beginning
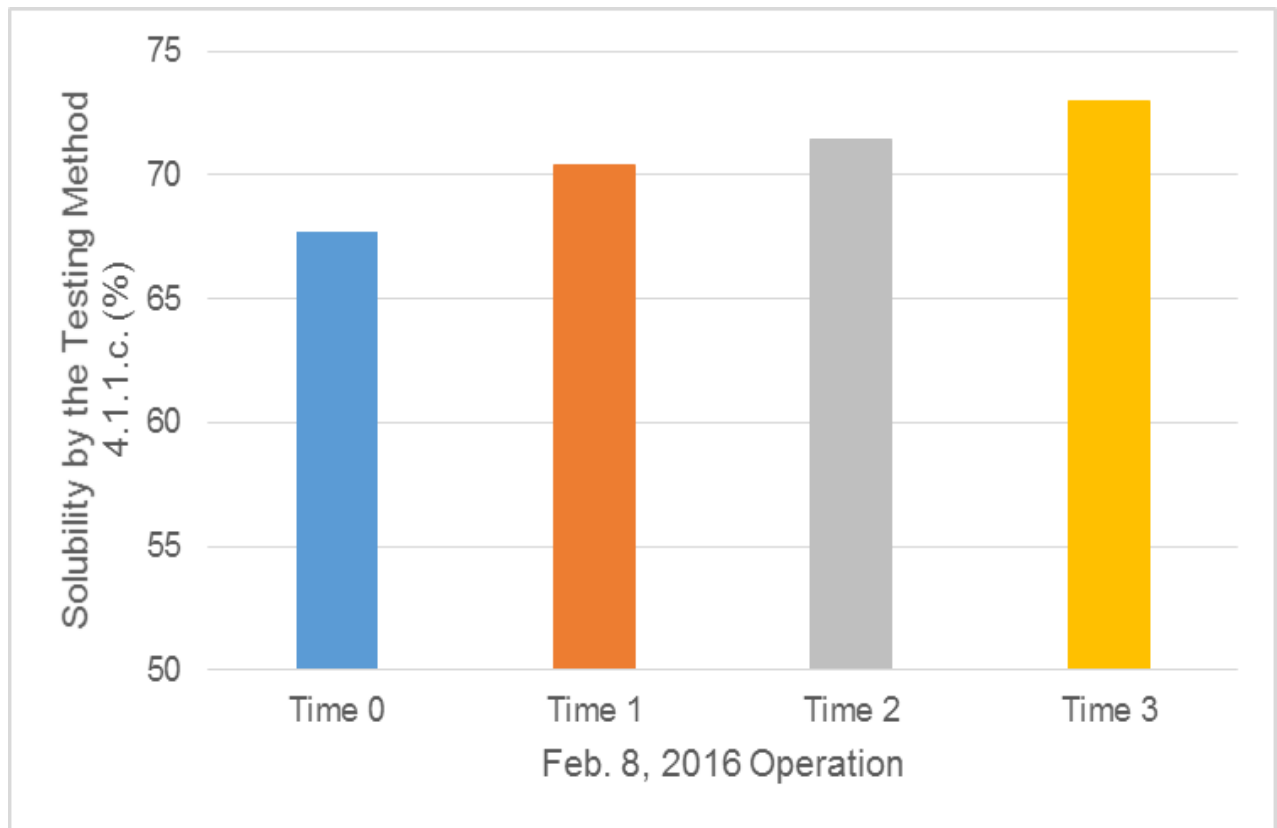
Fig. 3-1-10. Operation without AUTO control at the beginning

CONCLUSIONS

The optimal operation of a boiler to produce high quality or high solubility ash was investigated. From the results, the following conclusions were extracted:

- For boiler burning, or an exothermal reaction, two phases were needed: the exothermal reaction for the first phase and the endothermic reaction for the second phase;
- A maximum temperature setting was necessary; and
- The following specific settings were determined: No AUTO setting at the beginning and AUTO setting engaged after the boiler idling finished, 500 ˚C as the maximum temperature, 30 Hz for air flow capacity, and 5-5-6 for fire grate movement.

There could be additional factors that influence the operation, resulting in a better performance. Besides just generating heat by burning rice husks, the boiler operation should be more carefully considered to produce better quality ash. Then, the ash would be more valuable and bring larger profits to the local community.

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3-2. Comparison of processes for producing better rice husk silica produced from a field-scale incinerator

INTRODUCTION

A rice husk is "a bio-ore" for silicon because it contains approximately 20 % silica by weight (Tateda 2016a). A material can be a resource if it is accumulated in one place; however, a material cannot be a resource if it exists only in small amounts that cannot be easily gathered. Silicon is the second most abundant element in the Earth's crust; however, this is not a good resource as the silicon is widely scattered. A rice plant, on the other hand, accumulates silicon in one place: the husk of the rice, which is so rich in silica as to be called a bio-ore for silicon. A critical standard exists for using rice husks as a resource: that of amorphous silica.

Silica, the form of silicon present in rice husks, must be removed from the husks while the silica remains in an amorphous state. To remove the silica, the rice husks must be burned in order to separate organics such as cellulose, hemicellulose, and lignin from the silica. Burning rice husks is not an easy task if the silica must remain amorphous: unless rice husks are properly treated, the silica becomes crystalline, and therefore useless. Empirical evidence demonstrates that high-solubility ash cannot be obtained if rice husks are burned in an uncontrolled way; on the other hand, evidence shows that this desirable type of ash can be obtained when the ash is treated properly (Tateda 2016b, Tateda et al 2016a, Tateda et al 2016b). The meaning of "properly" was, however, ambiguous for a long time; and some ambiguity still remains. For example, an element of "properly" processing the ash could be its handling after burning, in the curing stage. This raises a number of questions: how should the curing be conducted? How should the ash be handled between burning and curing? Should an external heat source be provided? Should air be forcibly applied to the ash during the curing process?

The purpose of this study was to answer these questions using three rice husk ash treatment methods. Rice husk ash of the highest quality is usually produced from an electric furnace after acid or alkali washing (Chandrasekhar et al 2003, Bakar et al 2016); however, an actual field scale incinerator was used in this study. To the authors' knowledge, no previous studies have utilized a field scale incinerator for high-quality rice husk ash production to date.

MATERIALS AND METHODS
Rice Husks

Rice husks used in this study were obtained from Koshihikari (*Oryza sativa L.*), one of the main rice cultivars grown in the area where Toyama Prefectural University is located.

Incineration Furnace

An incineration furnace with a boiler system was used for this study. Although several types of rice husk incinerators were described in Soltani et al (2015), this study employed a furnace with a simple configuration consisting of moving grates and an air blower system (Fig. 3-2-1). The system was simple and cost-effective to make and operate. The combustion capacity of the furnace was 100 kg/h, with kilograms referring to the rice husks as were.
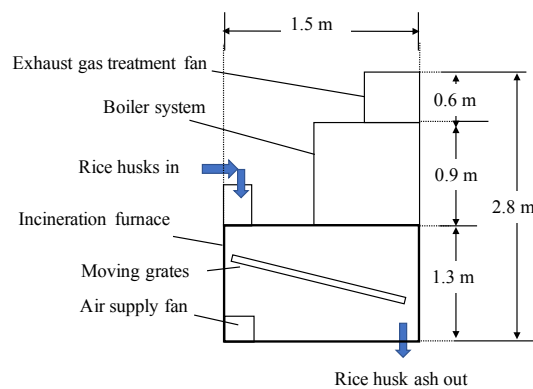
Fig. 3-2-1. A simple diagram of the incineration-furnace

Employed Methods after Burning

A summary of the processes used in this study is shown below in Table 3-2-1. Remained carbon in the rice husk ash is burned in curing stage so that air supply is an important function.

Table 3-2-1. Summary of the methods used in this study

	Heating drum	Insulating drums	Sink
Volume (L)	300	100	200
External heat	Yes	No	Yes
Source	Electricity		External heat from rice husk burning
Air supply	Yes (10 L/min)	Yes (10 L/min)	Yes (open air on top and 3 L/min in bottom)
Configurations	Fig. 3-2-2	Fig. 3-2-3	Fig. 3-2-4

<u>Heating drum</u>

The configuration of the heating drum can be seen in Fig. 3-2-2. External heat produced by electricity was introduced indirectly to the drum in order to keep the ash at the desired temperature. Air was taken directly from the outside environment and pumped into the drum.
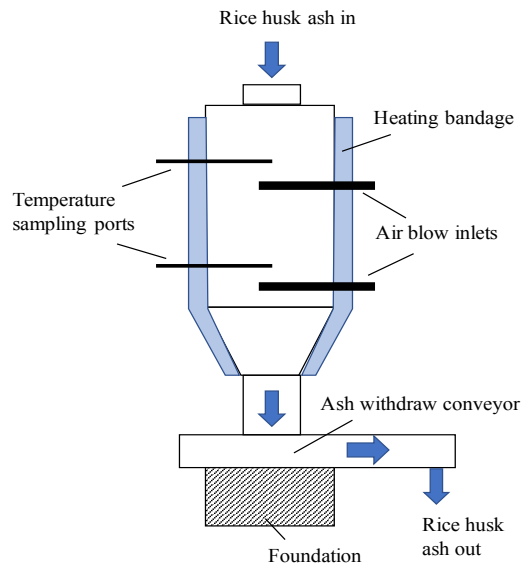
Fig. 3-2-2. Diagram of the heating drum

Insulating Drums

The insulating drums consisted of two drums, i.e., a 100 L drum and a 200 L one (Fig. 3-2-3). A 100 L drum was placed into the center of a 200 L drum, with the smaller drum placed such that the space between the two drums would be uniform all the way around, providing added insulation. Air was pumped directly in from the outside environment. No external heat source was applied; the only heat acting on the ash was residual heat from the previous burning stage. This idea came from composting process of organic solid waste (Tateda et al 2003). The considering disadvantage of this process is a large influence of ambient temperature. The pile temperature drastically decreases when the ambient temperature is quite low.
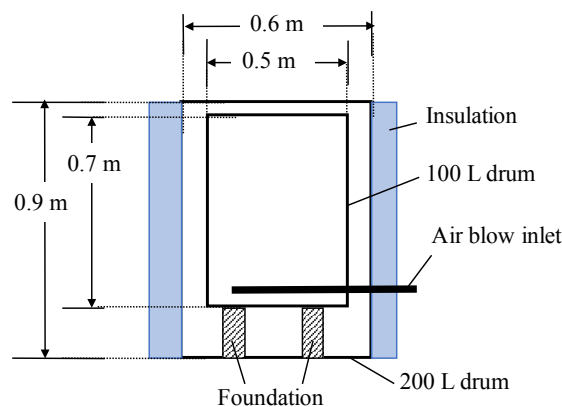
Fig. 3-2-3. Diagram of insulating drums

Sink

The sink was made by removing two lines of fire grates that were originally located at the bottom of the incinerator, and replacing these with a storage sink for the ash (Fig. 3-2-4). Air was pumped directly in from the outside environment. The ash in the sink was exposed to an external heat source, which was generated by burning rice husks in the previous step. The furnace was still burning new rice husks while the ash in the sink was curing.
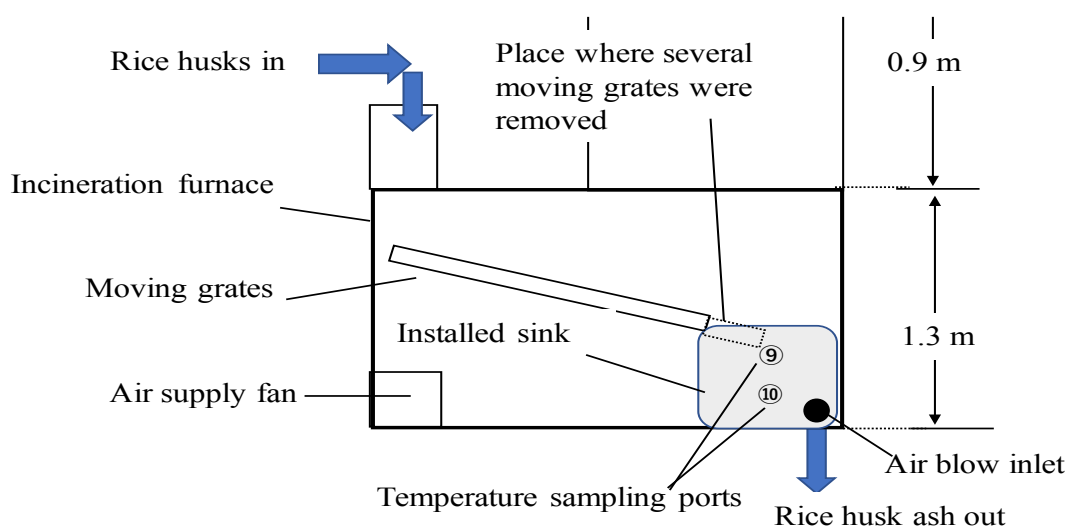
Fig. 3-2-4. Diagram of the sink

Analytical Methods

For the purposes of this study, the quality of rice husk ash was determined by solubility only. According to previous studies conducted by Tateda (2016b) and Tateda et al (2016a), high solubility values – for example, more than 40 % -indicate that ash in is an amorphous state. It can be said that the higher the solubility value of the ash, the better the quality of the ash. The solubility of rice husk silica was measured by two methods: the sodium hydroxide (NaOH) method and the Testing Method 4.4.1.c. Deshmukh et al (2012) used the former method as silica activity index. The latter has been accepted as a standard method while the former is a more simplified method. Solubility values were represented by a mean of triplicated measurements. Details of these methods can be found in Tateda et al (2016a). Values produced by the two methods were closely related (Tateda et al 2016b). Because of this, the two values were compared for evaluation of ash quality in this study. Mean values were used for

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representing solubility values. Thermocouples (Type K) were used for temperature monitoring and data were recorded in a data logger (Paperless Recorder GP10, Yokogawa).

Experimental Methods

The rice husks as were, which had a moisture content of 10–13 % before burning, were burned in the incineration furnace at 500–800 ˚C. Next, the resultant rice husk ash was put through the treatment processes in Table 3-2-1. One day after the introduction of the ash into each process, ash samples were taken at the 20 cm-depth from the surface of the ash pile, at its center. Temperatures were taken during operations at designated points in the ash pile.

RESULTS AND DISCUSSION

The solubility of the silica produced by each process is shown in Table 3-2-2. According to the table data, the solubility of the ash produced from the sink process was high in comparison to other curing methods. The solubility of ash from the heating drum was the lowest. Solubility values were strongly influenced by temperatures within the ash piles.

However, these results cannot be explained by pile temperatures alone, as the solubility values of ash from the sink were extremely high compared to those from the insulating drums, which reached close temperatures. The pile temperatures in the insulating drums with air reached 300 ˚C, which is similar to the temperature of the ash pile in the sink. Although those temperatures were close, solubility values in the two processes were quite different.

Usually, the processes such as a gasifier (Pode 2016), a fluidized bed combustor (Honma et al 1989, Fang et al 2004, Fernandes et al 2016), a moving grate (Fernandes et al 2016), and a suspension chamber (Fernandes et al 2016) have only a burning step. Burning and curing comprise two different steps (Tateda et al 2016b). From our long empirical experience with burning rice husks, we have found that not only burning rice husks but also curing them is extremely important in order to produce high solubility, i.e., high-quality ash. In the burning step, rice husks burn with no other heat source except for the start-up ignition, in this case, provided by kerosene. Cellulose, semi-cellulose and other compounds are burned during this step, creating excess heat that can be used to heat water or generate electricity. Moreover, carbon dioxide generated in this step could be provided to nearby greenhouses for agricultural uses. Rice husk ash is blackish because the ash is usually removed from the incineration system at this point. The second step, curing, is very important for producing high-quality ash. The main purpose of this step is to remove or burn out nonflammable carbon, i.e., fixed carbon,

from the surface of the ash. Based on the concept, the three processes above were proposed and performed in this study. The simplified total flows are shown in Figs. 3-2-5 – 3-2-7.

The incinerator in Figs. 3-2-5 – 3-2-7 played the role of the burning step in each process, and the heating drum, the insulating drums, and the sink were considered the curing step in each process. In the first two curing methods, represented in Figs. 3-2-5 and 3-2-6, the curing step - namely, the heating drum and the insulating drums - was outside of the incinerator system. The ash created in the incinerator was manually carried via bucket into the heating drum; on the other hand, the ash was sent into the insulating drums by a conveyor tube, as shown in Fig. 3-2-8.

The ash temperatures rapidly decreased upon removal from the incineration system. The period during transferring by bucket or sending by conveyer tube decreased the temperature due to low atmospheric temperatures in Japan, especially in winter. The conveyor tube, made of iron, became extremely cold in winter temperatures, and the ash that was sent from the incinerator cooled down to atmospheric temperatures as the metal of the conveyor removed heat from the ash (Figs. 3-2-5 and 3-2-6). However, the conveyor tube was gradually heated by this process, and much of the ash sent into the insulating drums remained at a high temperature. In the cases of the heating drum and the insulating drums, the removal of the ash from the incinerator system for transfer became a critical problem: the resultant rapid decrease of ash temperature made solubility low.

The strongest advantage of the sink process was that the sink existed within the incinerator system (Fig. 3-2-7). Rice husks were burned in the incinerator and the resulting ash was sent into the sink without exiting the incinerator system.

The idea of the sink process resulted from a long continuous operation of incineration. Initially, the incinerator was operated by continuously withdrawing the ash, with the removed ash then stocked in empty drums to await disposal, usually for use in soil conditioning materials. Typically in this process, no stock of ash would remain inside the incinerator. However, at several points during these continuous operations, empty drums were not available for removing the ash, and thus the ash remained in the incinerator. This is not part of the normal operation of the incinerator, but a small space exists to permit ash to remain in the incinerator in case the ash discharge screw is out of order. In these cases of ash accidentally remaining in

the incinerator, it was found that the solubility of the ash kept in the stock space showed high solubility characteristics. The stock space was then widened for this study in order to evaluate its effectiveness in promoting higher ash quality.

In this third curing method, the ash enters the curing step with its high incineration temperatures retained. Because the curing step involves an endothermic reaction, external heat should be provided, and in this case, the heat from the burning step provides the necessary heat for the ash in the curing step. Temperature monitoring in the sink is shown in Fig. 3-2-9. According to this figure, temperatures remained around 400 ˚C during the curing step in the sink treatment method. Observing the results in Table 3-2-2, temperatures in the sink need to remain around 400 ˚C in order to obtain ash with a high solubility. According to Moriizumi et al (2004), the temperature around 390-400 °C was the key for a drastic impact on organics. The temperature of 400 °C was kept in the process because the heat flowed continuously from the burning step to the curing step without interruption (Fig.3-2-7). From this observation, exiting the incineration system received a tremendous disadvantage.

Table 3-2-2. Data summary of three processes

	Heating drum	**Insulating drums**	**Sink**
	air (10 L/m)	air (10 L/m)	air (3 L/m)
Solubility (%) on average	25.5	41.0	70.4
Temperature (˚C) in ash pile	89-117	300	380-400
Time of sampling	1 day later	1 day later	1 day later
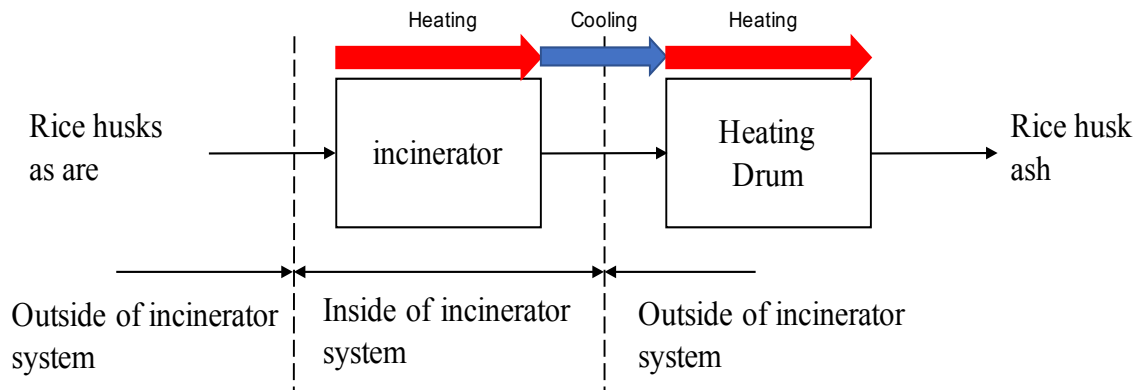
Fig. 3-2-5. The process flow of the heating drum
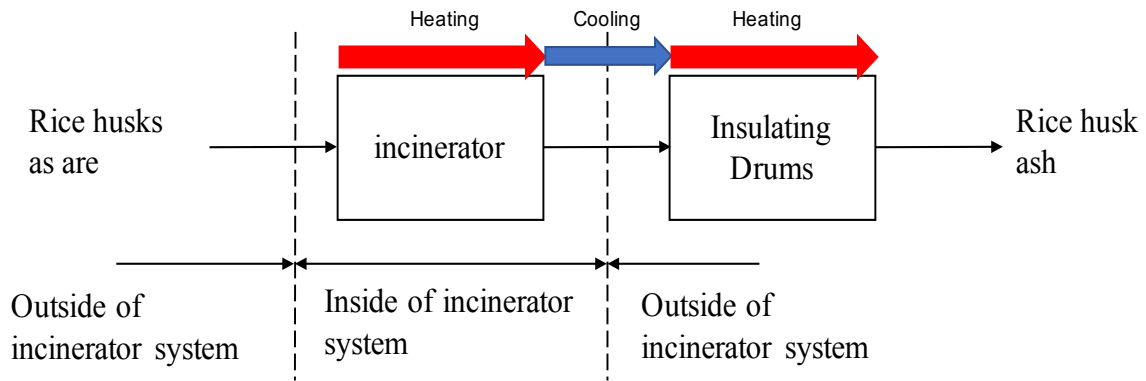
Fig. 3-2-6. The process flow of the insulating drums
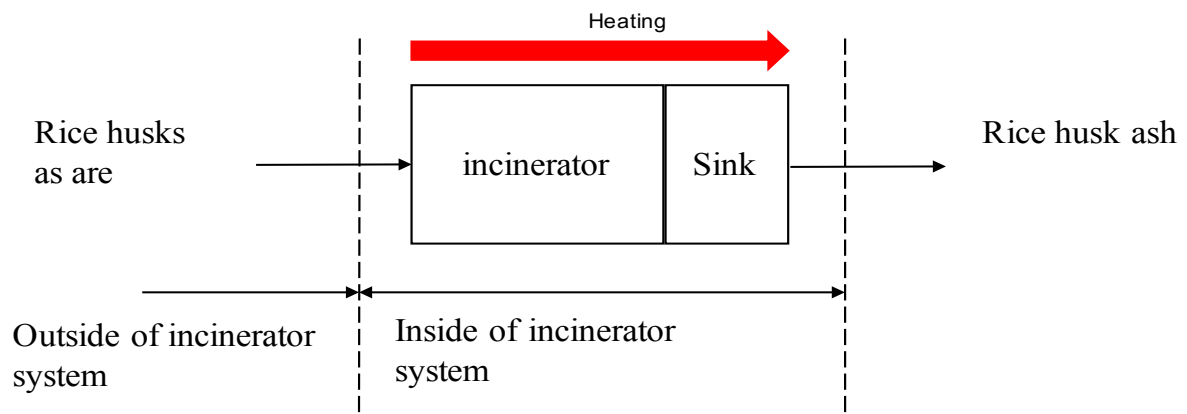
Fig. 3-2-7. The process flow of the sink
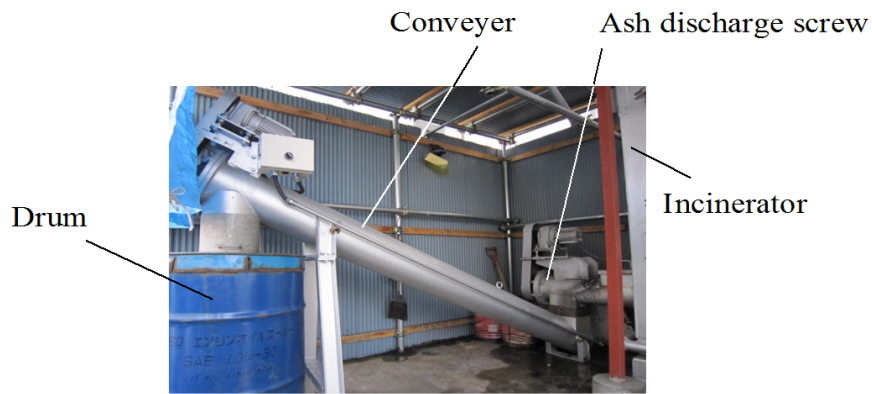
Fig. 3-2-8. The conveyor tube used for transferring the ash from the incinerator into the insulating drums
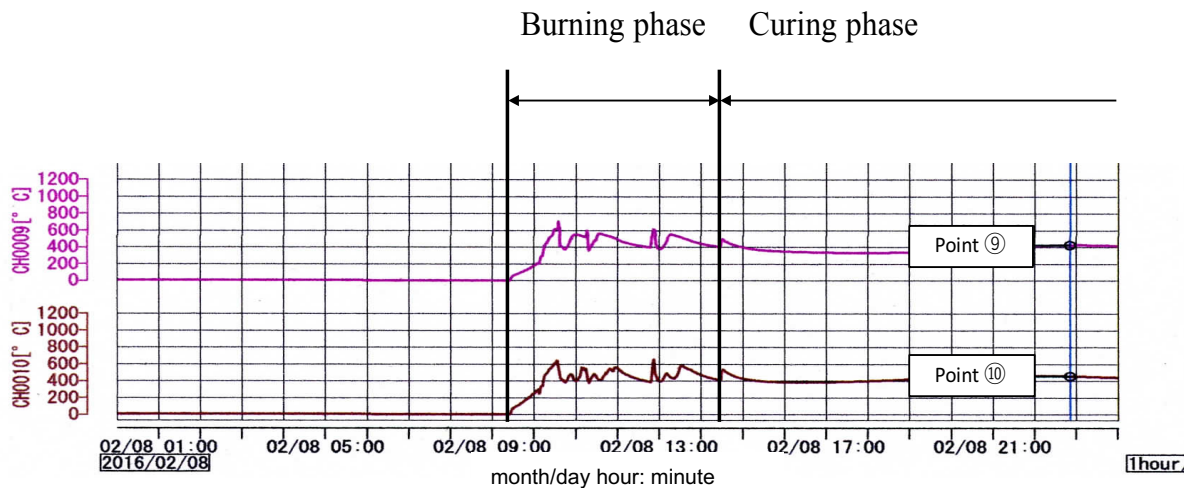
Fig. 3-2-9. Temperature profiles in the sink process

CONCLUSIONS

In light of the results obtained in this study, the following conclusions were reached.

- To obtain high solubility ash, the rice husks must be submitted to a two-step process, that of burning followed by curing;
- After undergoing these two steps, the ash can show high solubility, i.e., more than 70 %;
- The solubility of the ash increases when the ash is put through these two treatments within the same system, i.e., the incinerator, without being removed; and
- The sink process is easily made by modifying an incinerator which stakeholders currently own.

If rice husks are burned for heat alone, they are burned at high temperatures, creating less valuable ash because a high percentage of the silica in the ash is crystallized. The crystalline silica is also carcinogenic, creating an additional problem. If the ash burning is controlled and

conducted at low temperatures, much less heat is produced; however, the value of the ash will be much higher and could be sold at a high price. Whether a community chooses heat or high-quality ash depends on conditions within the community. The heat is needed if a community does not have electricity, but more valuable ash can be produced when rice husks are burned in a mass reduction treatment. The optimal choice, however, is to pursue both valuable ash and heat. With consideration for their specific situation, a community should handle rice husks as a resource, with the opportunity of bringing happiness and prosperity to its next generation.

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3-3. Study of the feasibility of a rice husk recycling scheme in Japan to produce silica fertilizer for rice plants

INTRODUCTION

Renewable energy is the key to creating a sustainable society. Biomass is one of many sources of renewable energy. In Japan, since 25 billion m^2 of land was covered by forest in 2017 (MAFF 2017), equivalent to 66 % of Japan's entire area, forest timber may be considered a suitable form of renewable energy. However, the long lifespan of trees seriously draws into question the idea of timber being an appropriate renewable energy source. Rice husks, on the other hand, are generated every year and are therefore a suitable form of renewable energy. On the other hand, using rice husks for energy comes with a major drawback. Rice plants accumulate silica, so that rice husks and straws are approximately 20 and 5 % silica, respectively. This implies that rice plants need silica to grow, which is why rice plants absorb amorphous silica that is dissolved in irrigation water. If enough silica is not available to rice plants, they do not grow well and fail to stand straight up in paddy fields. This leads to invasion by insects or causes water from the rice to evaporate during the growing period; in either case, the plants do not produce good rice (Ma et al 2002, Ma et al 2006). Rice plants need silica to grow healthily. The ash content of a rice husk is about 20 % by weight, which is extremely high compared to other biomass such as poplar (1.0 %) and cedar (0.2 %) (The Japan Institute of Energy 2002). Approximately 20 tons of ash will remain when 100 tons of rice husk are burned for heat recovery.

Dealing with the large amount of remaining ash is extremely difficult and stressful for stakeholders. Therefore, they have preferentially used timber for heat recovery, with rice husks as their last choice. To use rice husks as a renewable energy source, it is essential to find a way to economically recycle the ash generated from burning rice husks (Tateda 2016). Rice husks can be sustainably used as a fuel for energy recovery only when their ash is used as a resource. The ash is mostly made up of silica, which, if amorphous, has many industrial applications. An optimal conditions to produce effectively amorphous silica was investigated in a field-scale furnace (Tateda et al 2016a). Given that rice plants in Japan require additional silica to grow healthily, silica fertilizer must be applied to paddy fields. Currently, the fertilizer used in Japan is produced by materials from other industries. Fig. 3-3-1 shows the main sources of silica fertilizers that have been used for rice production (AAFS 2013, AAFS 2017). Slag from the steel industry has mainly been used for this purpose. The main goal of this research is to return

silica in rice husks to the original paddy field as a fertilizer, in order to make rice production more environmentally and economically sound. The purpose of this study was to evaluate the feasibility of rice production based on rice husk ash recycling by comparing two schemes: heat recovery and silica fertilizer production. The study was based on a questionnaire method.

	2007	2008	2009	2010	2011	2012	2013	2014
■ Silica hydrogel	0.167	0.163	0.184	0.126	0.109	0.139	0.103	0.057
■ Silica gel	0.82	0.683	0.135	0.056	0.057	0.063	0.062	0.057
■ Autoclaved lightweight concrete	7	6	5	4	5	0.812	6	4
■ Slag from steel industry	184	181	171	174	172	174	177	164
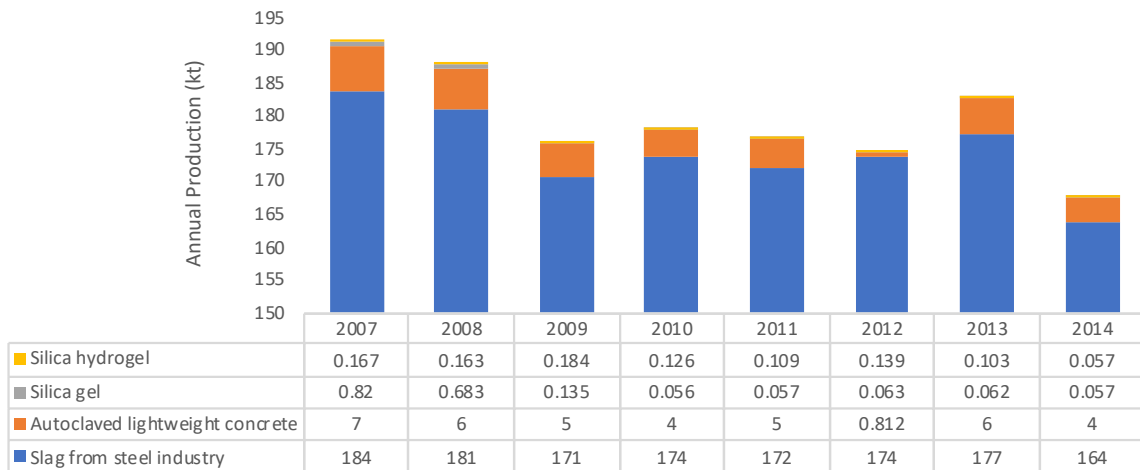
Fig. 3-3-1. Annual production of authorized silica fertilizers

Rice Plants and Silica

Rice plants need silica for healthy, continuous growth (Meena et al 2014). Although it may not be essential (Ma et al 2006, Guntzer et al 2012), a shortage of silica has a tremendous negative effect on rice plants, and its presence benefits the plants. Silica provides rice plants with disease control (Ma et al 2002, Guntzer et al 2012, Jeer et al 2018), resistance to drought (Ma et al 2002, Zhu et al 2014) and salt (Ma et al 2002, Abel-Haliem et al 2017), and metal toxicity control (Ma et al 2002, Guntzer et al 2012, Li et al 2009).

In Japan, the study of the effects of silica on rice plants began in the late 1930s (Takahashi 2007). The study was conducted in a hydroponic culture and showed that silica was needed to improve crop yields and resistance to pest invasion. However, the results were not confirmed in actual fields because people thought that rice plants would not face a silica deficit there due to the existing abundance of silica in soil. Since continuous cultivation of rice is possible in paddy fields but not in dry-fields, Japan prefers paddy field cultivation for rice because it is a staple crop for Japanese people. Moreover, Japan is a small island and has limited areas for rice production. However, a large volume of irrigation water passes through paddy fields, which flushes away dissolved silica. Moreover, silica is reduced in anaerobic conditions in paddy fields and dissolves into water, where it is also flushed away. Consequently, silica

availability became low, causing rice plants to sometimes lose condition and became affected by pests in fall. This phenomenon, called "the fallen condition in fall," became the one of the main topics of agricultural studies in the 1950s, when the Japanese government wanted to increase rice production during the era of food shortage that followed World War II.

The silica taken up by rice plants is amorphous and in a colloidal state in water. The silica in rice husks is therefore also amorphous. To use rice husk ash for fertilizer, it is critical that the silica is in an amorphous state. It is impossible to distinguish amorphous and crystalline silica by visual observation; X-ray diffraction (XRD) analysis is required. The solubility of silica into 1 N NaOH is a reliable indicator of the state of silica in the ash (Tateda et al 2016b). Generally, it can be said that the higher the percentage of solubility is (more than 50 %), the better quality the silica is. Solubility is also expressed by the Silica Activity Index (Deshmukh et al 2012). Many studies have been conducted on how to produce better ash, including how to burn rice husks (Chandrasekhar et al 2003, Xiong et al 2009, Martinez et al 2011, Fernandes et al 2016). These studies mainly focused on combustion temperature. Other studies focused on energy recovery from rice husk burning concentrating only on energy production and did not consider the quality of ash (Chungsangunsit et al 2005, Ramirez et al 2007, Prasara-A et al 2011, Lim et al 2012, Bhattacharyya 2014). A further study investigated using different types of incinerators such as fluidized bed, cyclonic furnace, and rotary kiln to burn rice husks (Soltani et al 2015). To make better ash, the formation of carbon black particles in the ash was investigated with the goal of reducing the amount of carbon black particles produced (Krishnarao 2001). In the 1980s, researchers assessed the growth of crystalline silica in rice husk ash (Ibrahim et al 1981) and the thermal decomposition characteristics of rice husks (James et al 1986). Rice husks have many industrial applications including insulators (Soltani et al 2015, Pode 2016, Sekifuji et al 2017a), lithium battery anodes (Pode 2016, Liu et al 2013), fuels (Soltani et al 2015, Pode 2016, Shimizu et al 1978), cement and concrete (Soltani et al 2015, Rukzon et al 2009), wastewater adsorbents (Pode 2016, Kumar et al 2015, Mor et al 2016), and fertilizer and soil amendment (Tateda 2016, Pode 2016).

MATERIALS AND METHODS
Research Site
The Local Agriculture Association Imizuno (LAAI) in City Imizu (approximate population: 90,000) in Toyama Prefecture, Japan, was chosen for the study. LAAI sells agricultural products that the members of the association grow under a contract, instead of the members

selling their products by themselves. Rice is one of the products sold by LAAI, so rice from various paddies was brought to LAAI for milling. LAAI has three milling facilities: a, b, and c. Facility "a" (LAAIa) was chosen for conducting this research. The LAAI has been spending a high tipping fee for rice husk disposal annually and purchasing silica fertilizers, and spending a high cost for kerosene use for greenhouse operation. The basic concept in this research was that the recycling of rice husks would solve those problems.

Questionnaire on Use of Rice Husk Ash as Silica Fertilizer

To understand users' expectation of silica fertilizer from rice husks and produce a better silica fertilizer product for users, several questionnaires were sent to the members of LAAI. The questions were as follows: what kinds of effects do you expect silica fertilizer made from rice husks to have on to rice plants? What factors influence your purchase of a silica fertilizer? What states of fertilizer do you prefer? What do you expect from silica fertilizer made from rice husks? How much silica fertilizer would you apply to 100,000 m^2? How much would you be willing to pay for silica fertilizer made from rice husks for an area of 100,000 m^2?

Comparing the Processes of Heat Recovery from Rice Husks

For energy recovery, two schemes were compared: heat recovery from hot water and electricity generation. The comparison was made in scaled-up model based on data obtained from the current small-scale model.

Measurement and Analysis

Furnace

A small-scale furnace, with moving grates and an air blower system, was used to burn the rice husks as shown in Fig. 3-3-2 (Sekifuji et al 2017b). The hourly combustion capacity was 100 kg of rice husks.

Determination of amorphous state

XRD analysis was done by Smart Lab (Rigaku) with the conditions of 9 kW, Cu-Kα, and 2θ: 5–80°.
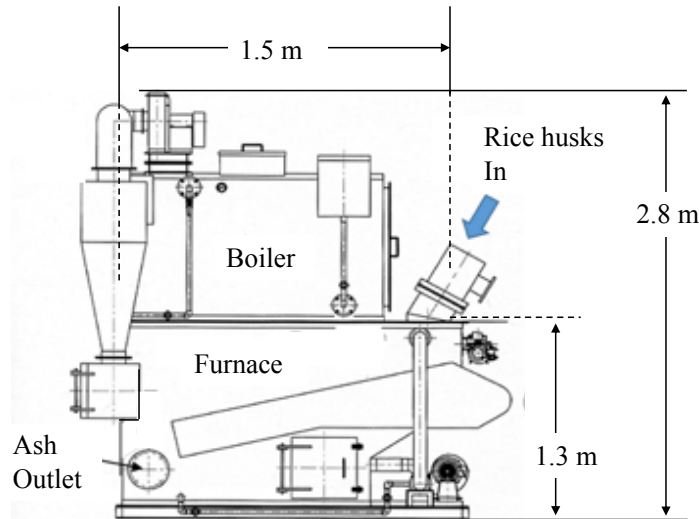
Fig. 3-3-2. The Boiler used in this study (Tateda et al 2016a)

RESULTS AND DISCUSSION

Research Site

Approximately 1.5 kt of rice husks are annually generated at LAAI facilities a–c. The water content of these husks is about 12 %. Fig. 3-3-3 shows the stages of use of a cultivated rice plant and the product division, by weight, at each step (RCA 2012). According to the figure, the 1.5 kt of rice husks that come from the LAAI facilities may be the result of over 8 kt of production from the paddies. In Japan, 2 Mt of rice husks are generated annually and used for different purposes (Fig. 3-3-4). Floor bedding for domestic animals, compost, and unknown purposes each account for over 20 % of the overall use of rice husks (over 60 % all together). At the LAAI, half of the annual 1.5 kt is used for floor bedding for domestic animals and materials for underdrain in paddy fields, but several hundred thousand USD are also spent to dispose of rice husks. The facility at which this research was conducted annually generates approximately 0.6 kt of rice husks. Although half of those are used for other purposes, such as floor bedding and underdrain materials, those usages are very unstable because the recycling is to some extent forcibly conducted. Therefore, it would be ideal to use all 0.6 kt of rice husks for a more sustainable purpose.

Harvested rice plants
20 Mt

Paddies
11 Mt

Straws and leaves
9 Mt

Brown rice
9 Mt

Rice husks
2 Mt

White rice
8.1 Mt

Brans
0.9 Mt
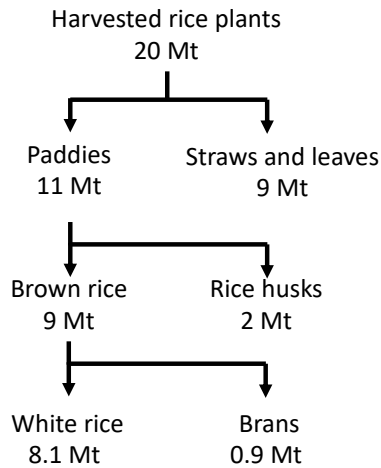
Fig. 3-3-3. Distribution of rice plants at each step post-harvest (numbers shown are approximate actual tons)
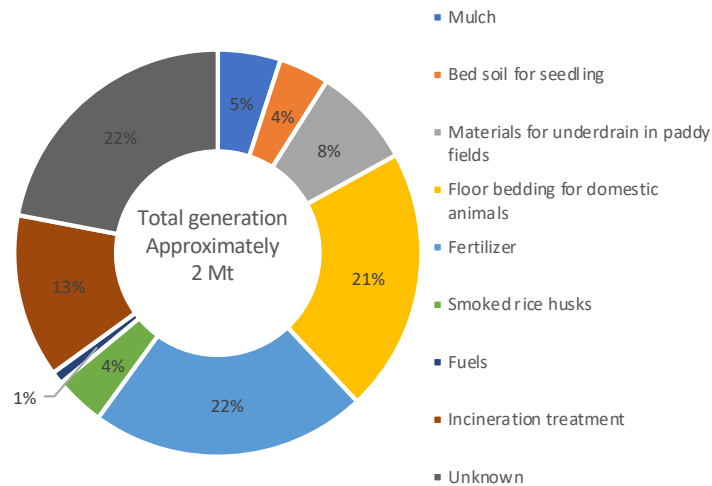
Fig. 3-3-4. Current usages of rice husks in Japan

Questionnaire on Use of Rice Husk Ash as Silica Fertilizer

A questionnaire was distributed to the members of the LAAI. The questionnaire was sent to 94 members; 90 were returned (collection percentage: 95.7 %). The results are shown in Fig. 3-3-5a – 3-3-5f. According to the results, member farmers expect the silica fertilizer to increase the strength of the rice plants' straw, so that the plants will not be easily bent over by wind (Fig. 3-3-5a). Recommendation by a local agricultural association, price, and distribution history mostly influence the members' purchase of silica fertilizer (Fig. 3-3-5b). Pellets were the preferred state of silica fertilizer (Fig. 3-3-5c) because it can easily be handled, which was very important to the farmers. Powder, on the other hand, was considered very difficult to handle.

Farmers' expectations of silica fertilizer made from rice husks were mostly centered on its beneficial effects for rice plants and its price (Fig. 3-3-5d). The estimated amount of silica fertilizer required for 100,000 m^2 was 80–100 kg (Fig. 3-3-5e). The price that the farmers could pay for silica fertilizer for 100,000 m^2 was 30–60 USD (Fig. 3-3-5f).

(a)

What kinds of effects do you expect silica fertilizer made from rice husks to have on to rice plants?

- Resistance against bugs 6%
- Notihng specially expect 12%
- Amendment of acid soil 14%
- Construction of strong straw 40%
- Quality and quantity of rice production 28%

(b)

What factors influence your purchase of a silica fertilizer?

- Price 26%
- Recommendation of local agricultural association 28%
- Brouchure 19%
- Distribution history 27%

(c)

What states of fertilizer do you prefer?

- Others 4%
- Powder 3%
- Sandy 13%
- Pellets 80%

(d)

What do you expect from silica fertilizer made from rice husks?

- Others 4%
- Eco-friendly 21%
- Good effects 38%
- Price 37%

(e)

How much silica fertilizer would you apply to 100,000 m^2?

- 100–140 kg 7%
- 20–40 kg 10%
- 80–100 kg 36%
- 40–60 kg 25%
- 60–80 kg 22%

(f)

How much would you be willing to pay for silica fertilizer made from rice husks for an area of 100,000 m^2?

- 75–90 USD 2%
- 60–75 USD 13%
- 15–30 USD 13%
- 45–60 USD 38%
- 30–45 USD 34%

Fig. 3-3-5. Results of questionnaire about rice husk silica fertilizers
(a) What kinds of effects do you expect silica fertilizer made from rice husks to have on to rice plants? (b) What factors influence your purchase of a silica fertilizer? (c) What states of fertilizer do you prefer? (d) What do you expect from silica fertilizer made from rice husks? (e) How much silica fertilizer would you apply to 100,000 m^2? and (f) How much would you be willing to pay for silica fertilizer made from rice husks for an area of 100,000 m^2?
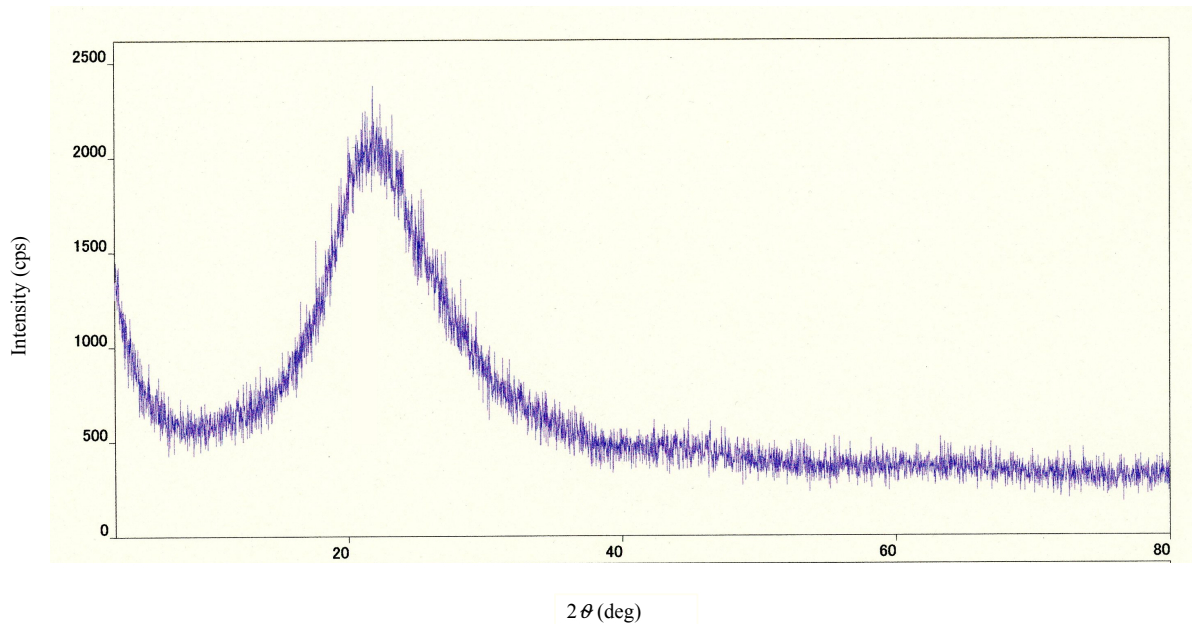
Fig. 3-3-6.   An X-Ray Diffraction chart of amorphous silica made from rice husks

Comparing the Processes of Heat Recovery from Rice Husks

The essential condition for heat recovery is that the silica in rice husk ash must be amorphous. Silica exists in two phases at ambient temperature and pressure: amorphous and crystalline. The former is safe, while the latter is a carcinogen and highly hazardous. Originally, the silica in rice husks is amorphous. Because rice plants need silica for healthy growth, they absorb silica from the irrigation water, which is amorphous and dissolved in the water in a colloidal state. Fig. 3-3-6 shows the result of our XRD analysis. The XRD diagram proves that the silica in rice husk ash from the furnace was not crystallized, but amorphous. This amorphous state means that the silica from rice husk ash could be used for other purposes.

The following operating conditions were utilized. The annual rice husk generation was 0.6 kt at LAAIa, half of which is recycled. The current recycling methods, however, are not stable. We anticipate that the amount of recycling will shrink in the future; therefore, the amount used for incineration is flexible and can be estimated to be much larger. Hence, a burning rate of 250 kg/h was set as the standard burning rate of rice husks. It was also reported that 250 kg/h rate is an economically feasible capacity (Jain et al 1994). Assuming six working hours per day and 220 d per year, the amount of husks produced overall would equate to a burning rate of 250 kg/h. Because rice husks have a calorific value of 12.5 MJ/kg, normal burning at 250 kg/h leads to 3.13 GJ/h of energy. Fig. 3-3-7 shows the process flows from inputting rice husks into

the furnace to the heat recovery stages. The hot water available after the boiler was either consumed by the greenhouse or used to produce electricity for on-site use.
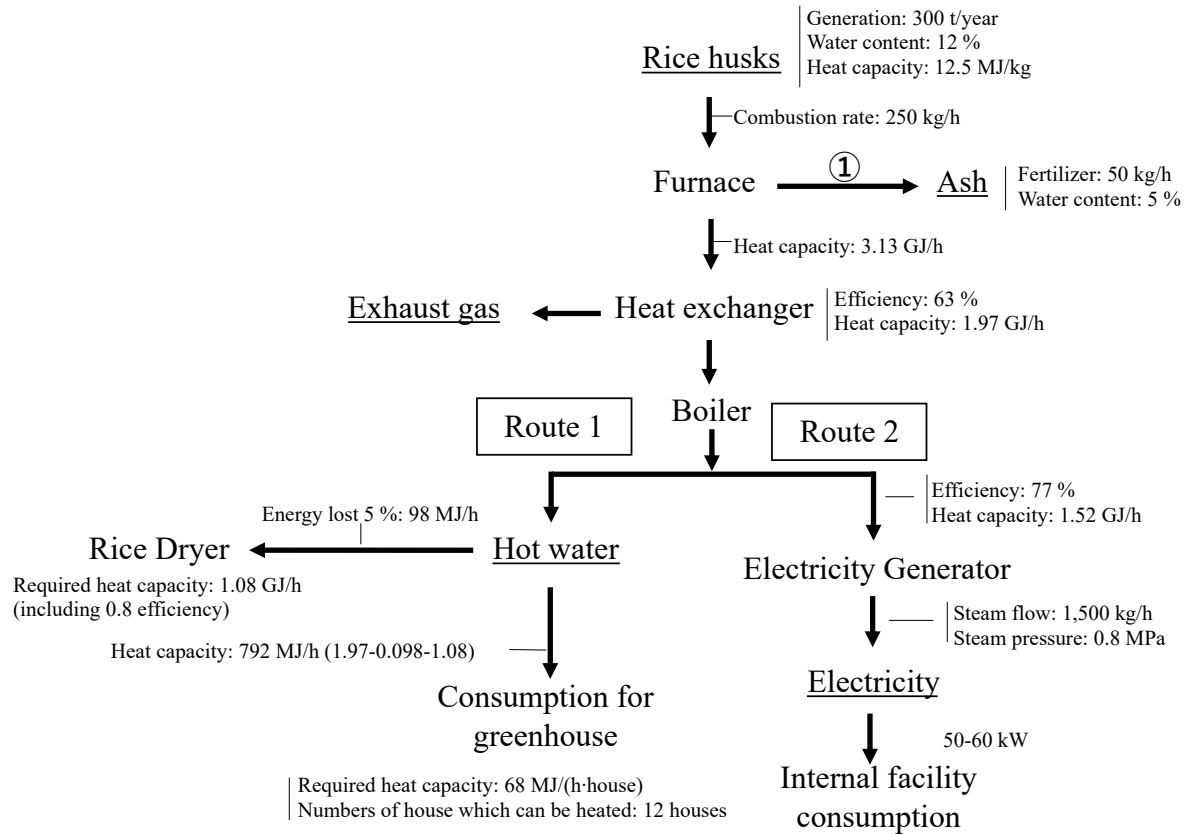
Fig. 3-3-7.   **Two energy recovery schemes based on rice husks**

After the rice husks were burned, the ash was generated. This point is indicated by the number ① in Fig. 3-3-7. The ash generated was approximately 20 % of the weight of the rice husks, or 50 kg/h. Solubility is an indicator of the quality of the silica in rice husk ash (Chandrasekhar et al 2003). Higher solubility indicates better quality ash, while lower solubility indicates more crystalline silica. Heat capacity of 3.13 GJ/h was sent to the heat exchanger, which has 63 % efficiency according to its operating history. From there, 1.97 GJ/h of heat was sent to the boiler. From the boiler, two routes were compared in this study.

In Route 1, hot water produced from the boiler was used directly for two processes: as a heat source for drying rice and to distribute heat to greenhouses. Based on kerosene consumption, which is how heat is currently supplied, the rice dryer required a heat capacity of 1.08 GJ/h, and each greenhouse required 68 MJ/h (Tateda 2016). The required heat to dry rice was

calculated based on 25 L/h of kerosene consumption. The amount for the greenhouse was obtained using the coefficient of 22.8 KJ/(h·°C·m^2), assuming the presence of curtains or insulators (35.5 KJ/(h·°C·m^2) without curtains or insulators). This coefficient was derived from the equation described in the previous report (Tateda 2016). The heat capacity sent to the greenhouses after the rice dryer would be 792 MJ/h, meaning that 12 greenhouses could be heated.

In Route 2, hot water produced from the boiler was used to generate electricity. The heat capacity was 1.52 GJ/h with a turbine efficiency of 77 %. Assuming a steam flow and steam pressure of 1,500 kg/h and 0.8 MPa, respectively, 50–60 kW of electricity would be generated. The electricity was consumed by the facility.

To evaluate the sustainability and feasibility of the two routes (Routes 1 and 2), their operating costs were compared. The two processes both produce ash; using this ash for silica fertilizer is the basic concept of rice husk recycling, and according to the results shown in Fig. 3-3-5c, the ash must be pelletized. The cost for pelletizing ash is shown in Table 3-3-1. Expenses for operating the boiler used in Route 1 are shown in Table 3-3-2, while the expenses for the boiler in Route 2 are in Table 3-3-3.

Table 3-3-1.   Cost of the ash pelletizing process

Items	Annual costs (USD*)	Notes
Pelletizer	20,000	200,000 USD/10 depreciation years
Running cost	12,000	1,000 USD/month
Maintenance cost	12,000	1,000 USD/month
Labor cost	17,500	0.5 person (35,000 USD/person)
Total	61,500	

*1 USD = 100 yen

Table 3-3-2. Cost of the boiler in Route 1

Items	Annual costs (USD*)	Notes
Boiler for hot water	25,000	200,000 USD/8 depreciation years
Running cost	12,000	1,000 USD/month
Maintenance cost	9,600	800 USD/month
Labor cost	35,000	One person
Total	81,600	

*1 USD = 100 yen

Table 3-3-3. Cost of the boiler in Route 2

Items	Annual costs (USD*)	Notes
Boiler for hot water	25,000	200,000 USD/8 depreciation years
Electric generator	5,700	80,000 USD/14 depreciation years
Running cost	14,400	1,200 USD/month
Maintenance cost	15,000	1,250 USD/month
Labor cost	35,000	One person
Total	95,100	

*1 USD = 100 yen

To evaluate the feasibility and sustainability of these methods, we compared the savings from reducing the currently energy sources with the cost of the proposed method. In Route 1, the costs saved would result from reducing kerosene consumption in the rice drying process and greenhouses; this is summarized in Table 3-3-4. In Route 2, savings would come from reducing the amount of electricity that the facility was required to purchase (Table 3-3-5). The advantage of this recycling scheme is that it allows the ash generated from burning rice husks to be sold as fertilizer. As shown in Fig. 3-3-7, since the combustion rate was 250 kg/h, ash would be generated at a rate of 50 kg/h (20 % of rice husks by weight would become ash). However, the price of the fertilizer produced must meet farmers' expectations. According to Figs. 3-3-5e and 3-3-4f, farmers expected to use 80–100 kg of fertilizer for a 10,000 m^2 paddy field, for which they would pay $45–60 USD. Therefore, the price of the silica fertilizer would be set at $0.70 USD/kg, which is 80 % of the price of the silica fertilizer that is currently used. The sale of the fertilizer was guaranteed in this case because farmers were members of the LAAI. Table 3-3-6 shows revenue from sale of the fertilizer.

Table 3-3-4. Cost savings from reducing kerosene consumption in Route 1

Processes	Cost saved (USD)	Notes
For rice drying	61,875 = 25 L/h·12.5 h/d·220 d/yr·$0.9/L	25 L/h: kerosene consumption 12.5 h/d: dairy operation hours 220 d/yr: yearly operation day 0.9 USD/L: kerosene price
For greenhouses	32,076 = 11 L/(m^2 yr)·3,240 m^2·$0.9/L	Heating period: November–March 11 L/(m^2 ·yr): kerosene consumption 3,240 m^2:12 greenhouses (270 m^2/house) 0.90 USD/L: kerosene price

Table 3-3-5. Cost savings from reducing electricity consumption in Route 2

Processes	Cost saved (USD)	Remarks
For internal facility use	9,438 = 55 kW·6 h/day ·220 d/yr·0.13 USD/kWh	55 kW: mean electricity generation 6 h: rice husk burning dairy operation 220 day/year: yearly operation day 0.13 USD/kWh

Table 3-3-6. Revenue from the sale of silica fertilizer

Item	Income (USD)	Remarks
Ash fertilizer sale	46,200 USD = 50 kg/h·6 h/day ·220 day/year·0.7 USD/kg	50 kg/h: effective silica 6 h/day: dairy operation 220 day/yr: yearly operation 0.7 USD/kg: fertilizer price

Table 3-3-7. Expenses and costs saved in Routes 1 and 2 (USD)

	Items	Route 1	Route 2
Expenses	Pelletizing ash	61,500	61,500
	Boiler operation	81,600	95,100
Costs saved	Rice drying	61,875	-
	Greenhouse heating	32,076	-
	Electricity consumption	-	9,438
	Fertilizer sale	46,200	46,200
	Profits	-2,949	-100,962
		(61,875 + 32,076 + 46,200) - (61,500 + 81,600)	(9,438 + 46,200) - (61,500 + 95,100)

The expenses and savings for Routes 1 and 2 are summarized in Table 3-3-7. For Route 1, the profit was negative, making the system unsustainable. However, a negative balance can easily become positive if more rice husks are burned each year, thereby increasing fertilizer sales. If 350 t/yr were burned, instead of 300, the net profit becomes -177 USD; however, if 375 or 400 t were burned annually, the net profit jumps to 2,595 and 6,845 USD, respectively. Increasing the quantity of husks burned is feasible, because, as mentioned earlier, other methods to recycle rice husks – such as mulching and floor bedding – are not stable pathways. Hence, Route 1 can be evaluated as a sustainable, feasible scheme for recycling rice husks. On the other hand, Route 2 incurred a net profit of -119,442 USD. This sizable deficit would be impossible to fill

with other income sources. Even if all 600 t of rice husks were burned to produce silica fertilizer, the expected income of 84,000 USD would still result in a 35,442 USD deficit.

CONCLUSIONS

In this study, we evaluated physicochemical and economic feasibility of improving agricultural processes by recycling rice husks, which contain amorphous silica. Amorphous silica effectively promotes the healthy growth of rice plants. We found that using the heat from burning rice husks to heat water was sustainable and feasible. On the other hand, burning rice husks to generate electricity was not sustainable; its high operational costs and the low sales price of electricity meant that this pathway was not economically viable. However, we only examined a Japanese case study. For villages in developing countries without electricity and with rice as a main agricultural product, generating electricity by burning rice husks is an excellent option. Sustainability and feasibility evaluations must therefore be conducted on a place-by-place basis. Rice husks are no longer waste but are a sustainable resource. Our findings may mean that rice husk ash is listed as an authorized silica fertilizer by the Ministry of Agriculture, Forestry and Fisheries.

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Chapter IV   Studies on Effects of Fertilization of Rice Husk Silica for Rice Taste and Growth of Vegetable

4-1. Taste evaluation of rice grown in soil treated with commercial silica and recycled rice husk silica

INTRODUCTION

Rice plants require silicon for their growth. They endure severe damages under silicon deficient conditions, such as insect attack and fungal infection (Ma et al 2016). It has been observed, especially in Japan that the development of rice blast is closely related to low level of silica (Takahashi 2007). At the start of the 20th century, the level of silica in the environment was low. The effect of silica on rice plants was studied extensively in the mid-1900s (Okuda 1958), because rice is the most important crop in Japan. In Japan, rice is cultivated by a special method known as repeated cultivation in paddy field. This leads to a gradual decrease in the available silica in paddy fields, therefore extrinsic addition of silica to the soil is important for the healthy growth of rice plants (Takahashi 2007). In Japan, silica (excluding rice husk silica) is officially designated as a fertilizer. Slag from iron industry was formally designated as one of the silica fertilizers. Currently, in Japan, rice is cultivated using the silica in slag. The objective of the present study was to use indigenous silica for cultivating rice, because the silica in the slag is of extrinsic nature to the rice plants. Furthermore, the rice husk silica might be more suitable for the rice plants than the slag, which comes from a completely different sector. Studies on the effect of silica on the growth in rice plant are scarce. To the best of our knowledge, the present study and study conducted by Abdel-Haliem et al. (2017) are the only studies on the role of silicon extracted from rice straw in rice plants. Tateda (2016) has proposed an ideal agriculture system, where the silica in rice husk is returned to the paddy field via recycling (Fig. 4-1-1).

Rice husk is generated while harvesting paddy annually. The husk generated is mostly used as a fuel in boilers. In the boiler, the rice husk is burned to produce heat, which is used to generate either hot water or electricity. The ash, residue of combustion, produced during the process is returned to paddy fields. The subsequent year, the rice plants cultivated use the silica in the ash for their growth. This cycle is repeated every year. Therefore, the rice husk generated is used to produce heat and silica fertilizer, which is a recycled source of silica to produce rice sustainably— an ideal agriculture system. However, there is a concern related to the taste of

rice. The recycling process is good in terms of resource recycling, however if the taste of rice decreases because of this, it would negatively affect the economy.

In the present study, the evaluation and comparison of taste of rice grown in soil treated with officially approved, commercial, best-quality silica fertilizer and rice husk silica were conducted. In this well-fed era of Japan, obtaining food is not difficult, however obtaining tasty food is of concern. The key aspect here is not about achieving better taste, but it is about not altering the taste of rice by following the usual production process.
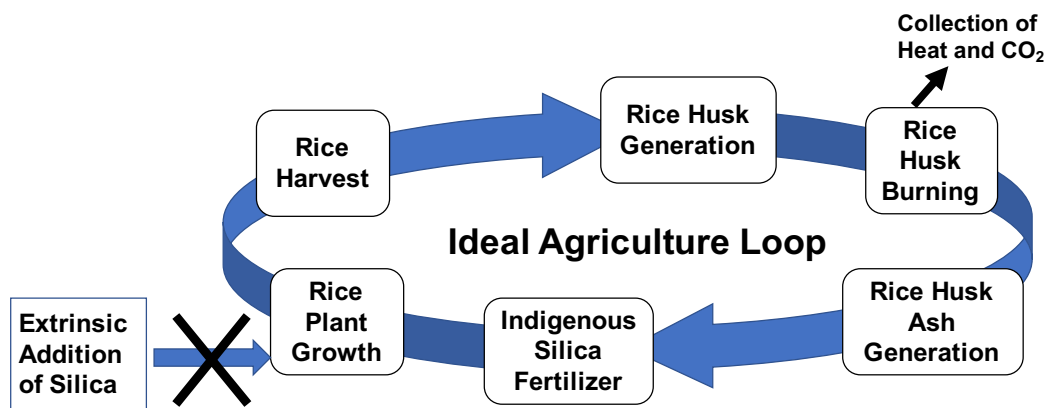
Fig. 4-1-1. Ideal agriculture loop

MATERIALS AND METHODS

Rice Plants and Husks Used

The rice variety Koshihikari (*Oryza sativa L.*) was used in the present study. The rice husk was burned in a boiler system (capacity: 100 kg/h) as described by Tateda et al. (2016a). Tateda (2016), based on the sodium hydroxide method, reported that silica content in rice husk ash is 90 % and the solubility of the silica in the ash is 50 %.

Chemical Fertilizer

The rice plants grown on soil treated with silica-gel fertilizer (Super Energy, Fuji Silysia, Japan) were used for a comparative study. The silica-gel fertilizer used is the best silica fertilizer available, however it is very expensive (> 100 USD/10 kg, silica content: 90 %). This fertilizer was used to observe the effects of silica on rice plants. Further, slag silica fertilizer was not used in the present study. According to Japan Standard Methods for measuring the

solubility of silica in fertilizer (4.4.1. a–c), the solubility of silica-gel fertilizer is 90 % (Tateda et al., 2016b).

Analysis of Growth and Production of Rice Plant

The following were measured to evaluate the growth of rice plant: fine brown rice weight, number of ears, number of grains per ear, percent of ripened grains, and percent of cracked rice. To evaluate silica sorption, amount of silica in leaf blades, leaf sheath, and ear during sprouting and maturity seasons were measured.

Analysis of Rice Husk Ash

Rice husk ash was analyzed for its chemical and physical properties. To evaluate the chemical property, the following were measured and presented as percent: alkali content (Standard Method 4.5.4), total potassium, citric acid soluble potassium, water soluble potassium (Standard Method 4.3), total phosphoric acid, citric acid soluble phosphoric acid, water soluble phosphoric acid (Standard Method 4.2), and sodium hydroxide soluble silica (Standard Method 4.4) according to Japan Standard Testing Method for fertilizer (FAMIC, 2015). To evaluate the physical property, contents of fixed carbon, volatiles, water, and ash were measured according to Japan Industrial Standard (JIS, 2016).

Analysis of Rice Taste

Although the taste of rice is an important parameter, it is difficult to evaluate (Ishibushi et al 1994). There are several ways to evaluate the taste of rice. In the present study, quality of brown rice was evaluated by quality evaluation value (QEV), which is a self-evaluation indicator employed by rice producers. The evaluation is based on the contents of protein (%), water (%), amylase (%), and fatty acid (mg KOH) in rice determined using an automatic analyzer (VPA-5500X-ES-TM, Shizuoka Seiki, Japan). The QEV is automatically obtained from the analyzer. The relevant equation for obtaining QEV has not opened to the public. Each analyzer machine has its own calculation mothed. The weak point of QEV is that QEV values are different among analyzers although it is the commonly used value to evaluate the taste of rice in Japan. Because of the weak point, Tanaka et al (1999) proposed that the taste of rice should be evaluated by protein content. The full score is 100 points and it can be said that rice with more than 85 points is excellent, 80–85: very good, 75–80: good, 70–75: fair, 65–70: poor, and less than 60: no good.

Cultivation of Rice Plants

Two paddy fields —A and B—were selected in Imizu city where Toyama Prefectural University is located. The types of soil were alluvial sandy soil and alluvial clay in paddy fields A and B, respectively. Water from river and spring was used for irrigating paddy field A, and only river water was used for irrigating paddy field B. Each paddy field was divided into three large areas (test, comparison, and control) by constructing ridges between areas, each area was subdivided into four smaller areas. The test areas 1 and 2 were treated with 10 and 30 kg/100 m^2 rice husk ash, respectively. The comparison areas 1 and 2 were treated with 5.5 and 16.6 kg/100 m^2 silica-gel fertilizer, respectively. The control area was not treated with silica. The amount of rice husk ash and silica-gel was deduced from silica content and solubility. The divisions of paddy fields have been represented in Figs. 4-1-2 and 4-1-3. The divisions with similar soil conditions have been shown as one division.
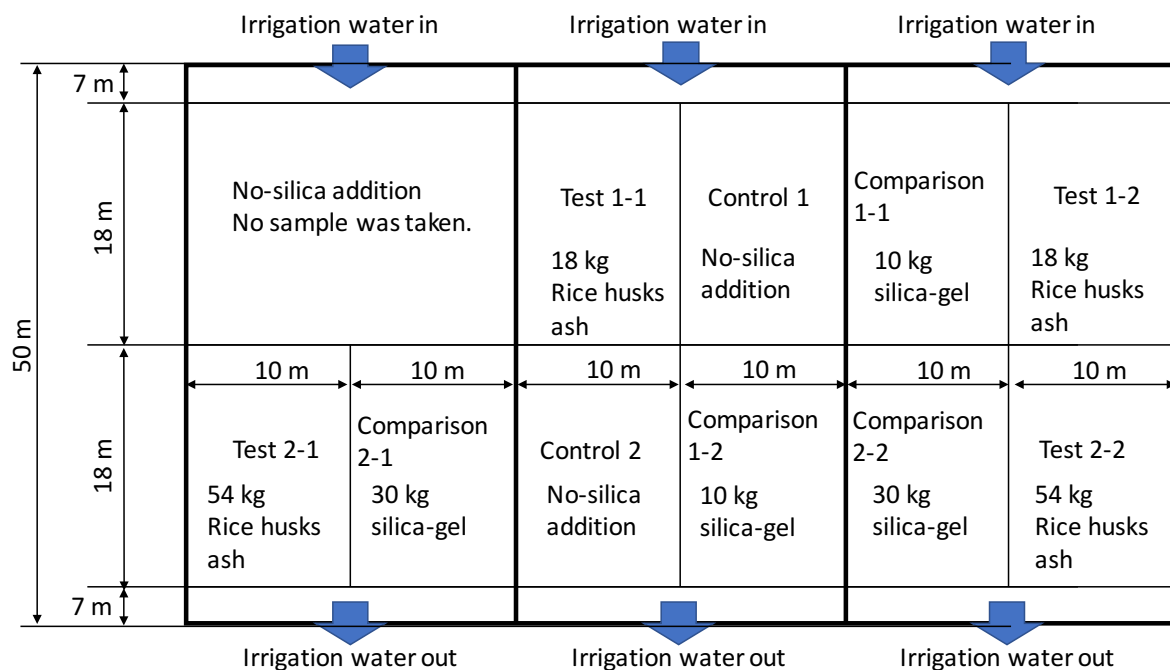
Fig. 4-1-2. Divisions of paddy field A
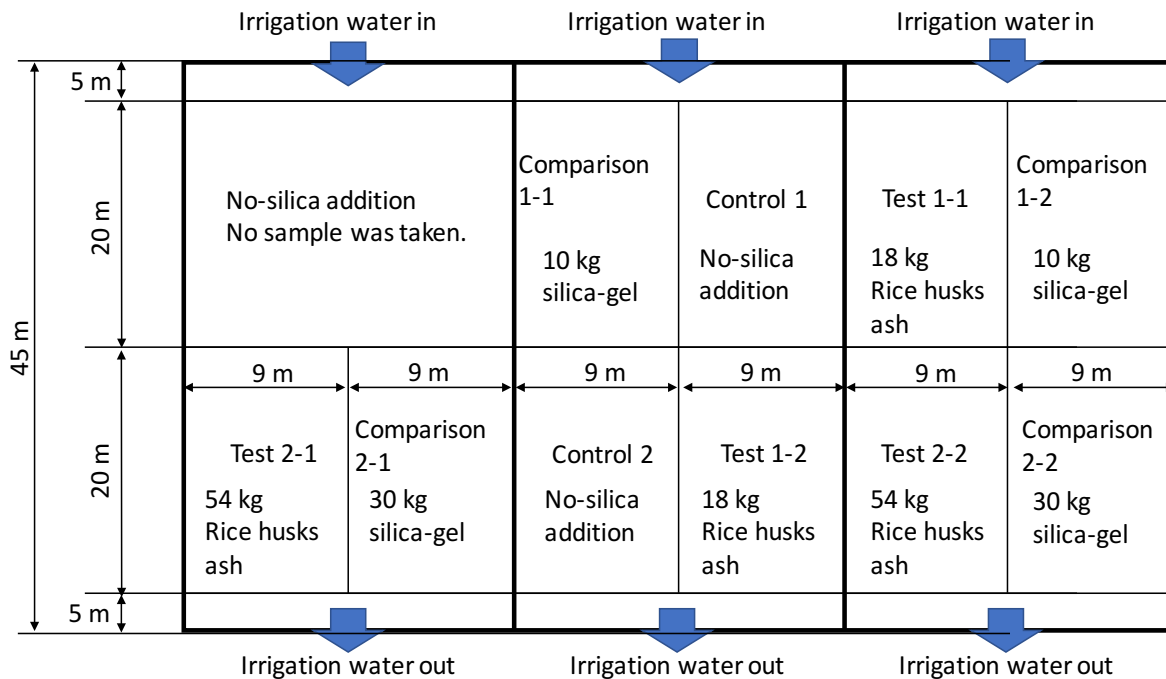
Fig. 4-1-3. Divisions of paddy field B

RESULTS

Experimental data obtained were of multiple trials; means of the data were used for analysis.

Chemical and Physical Properties of Rice Husk Ash

The chemical and physical properties of rice husk ash have been presented in Table 4-1-1. Rice husk mainly consists of carbohydrates, silica, and elements, such as phosphorus, calcium, ferrous, and potassium (Sekifuji et al 2017). Potassium is usually present in rice husk, and its level depends on the fertilizer used. Because of the potassium, the pH of rice husk ash is high (about 11). In the present study, when the rice husk was burned without pre-washing treatment, fixed carbon or unburned carbon remained on the surface of the rice husk ash. The fixed carbon content was found to be 6.5 %, therefore the color of the ash was black (Table 4-1-1).

Growth of Rice Plant

The growth analysis results have been shown in Tables 4-1-2 and 4-1-3. The growth of rice plants did not differ significantly among the divisions of paddy field. However, silica sorption by plants exhibited differences among the divisions. In paddy field A, silica sorption

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by rice plants was relatively high in the silica-treated divisions. A relatively low silica sorption by the plants was observed in test 1, which was lower than that of control.

Table 4-1-1. Chemical and physical properties of rice husk ash

	Variables	Percent (%)
Chemical property	Alkali content	0.4 ± 0.1
	Total potassium	2.0 ± 0.14
	Citric acid soluble potassium	1.9 ± 0.21
	Water soluble potassium	0.5 ± 0.1
	Total phosphoric acid	0.3 ± 0.1
	Citric acid soluble phosphoric acid	0.1 ± 0.0
	Water soluble phosphoric acid	0.1 ± 0.0
	Sodium hydroxide soluble silica	57 ± 2.9
Physical property	Fixed carbon	6.5 ± 5.2
	Volatiles	4.9 ± 1.2
	Water	1.0 ± 0.21
	Ash	87.8 ± 6.51

Table 4-1-2. Growth of rice plant and silica sorption by rice plant in paddy field A

	Divisions	Test 1	Test 2	Comparison 1	Comparison 2	Control
Growth of rice plant	Fine brown rice weight (kg/100 m^2)	63	68	70	63	65
	Number of ears (ear/m^2)	343	387	367	334	358
	Number of grains per ear	80	90	84	96	89
	Percent of ripened grains (%)	89.2	87.9	89.2	88.9	87.2
	Percent of cracked rice (%)	9.8	7.7	9.5	4.2	10.8
Silica sorption (g/m^2)	Sprouting season — Leaf blades	7.9	17.9	14.6	18.9	12.0
	Sprouting season — Leaf sheath	15.0	42.5	24.9	45.1	25.1
	Sprouting season — Ear	4.2	9.1	5.8	8.0	5.5
	Sprouting season — Total	27.1	69.5	45.4	72.0	42.6
	Maturity season — Leaf blades	10.8	19.2	17.3	20.1	13.1
	Maturity season — Leaf sheath	20.2	37.0	30.7	39.5	22.1
	Maturity season — Ear	18.8	27.8	21.2	27.8	16.4
	Maturity season — Total	49.8	83.9	69.2	87.3	51.6

Table 4-1-3. Growth of rice plant and silica sorption by rice plant in paddy field B

	Divisions	Test 1	Test 2	Comparison 1	Comparison 2	Control
	Fine brown rice weight (kg/100 m^2)	59	59	61	63	60
Growth of rice plant	Number of ears (ear/m^2)	434	414	434	410	383
	Number of grains per ear	70	76	71	71	75
	Percent of ripened grains (%)	86.8	88.6	81.0	87.8	88.5
	Percent of cracked rice (%)	3.9	2.6	2.8	2.8	2.8
Silica sorption (g/m^2)	Sprouting season — Leaf blade	21.2	23.5	25.9	31.0	18.5
	Leaf sheath	41.9	46.1	45.3	58.7	37.1
	Ear	8.7	10.5	9.8	9.5	9.0
	Total	71.8	80.2	81.0	99.2	64.6
	Maturity season — Leaf blade	26.3	32.6	26.9	35.7	23.1
	Leaf sheath	47.3	60.2	58.3	73.1	45.8
	Ear	22.8	30.6	29.1	30.3	24.7
	Total	96.5	123.5	114.4	139.1	93.6

The highest silica sorption was recorded in comparison 2. In paddy field B, a similar trend was observed. That is higher the silica application, higher the silica sorption by plants. In paddy field B, a relatively low silica sorption by plants was observed in control, while the highest silica sorption by plants was recorded in comparison 2. In both the fields, the plants of comparison 2 exhibited relatively high silica sorption.

Taste of Rice

The taste analysis results have been shown in Figs. 4-1-4 and 4-1-5. There was no significant difference in the taste of rice among the plants from different divisions of the paddy field. In paddy field A, the ranges of protein, water, amylose, fatty acid, and QEV were 6.3 %–6.5 %, 13.8 %–13.9 %, 18.9 %–19.0 %, 16.8–17.2 mg KOH, and 72–73, respectively. In paddy field B, the ranges of protein, water, amylose, fatty acid, and QEV were 6.1 %–6.2 %, 13.9 %–14.0 %, 18.9 %–19.0 %, 17.1–17.7 mg KOH, and 73–74, respectively.
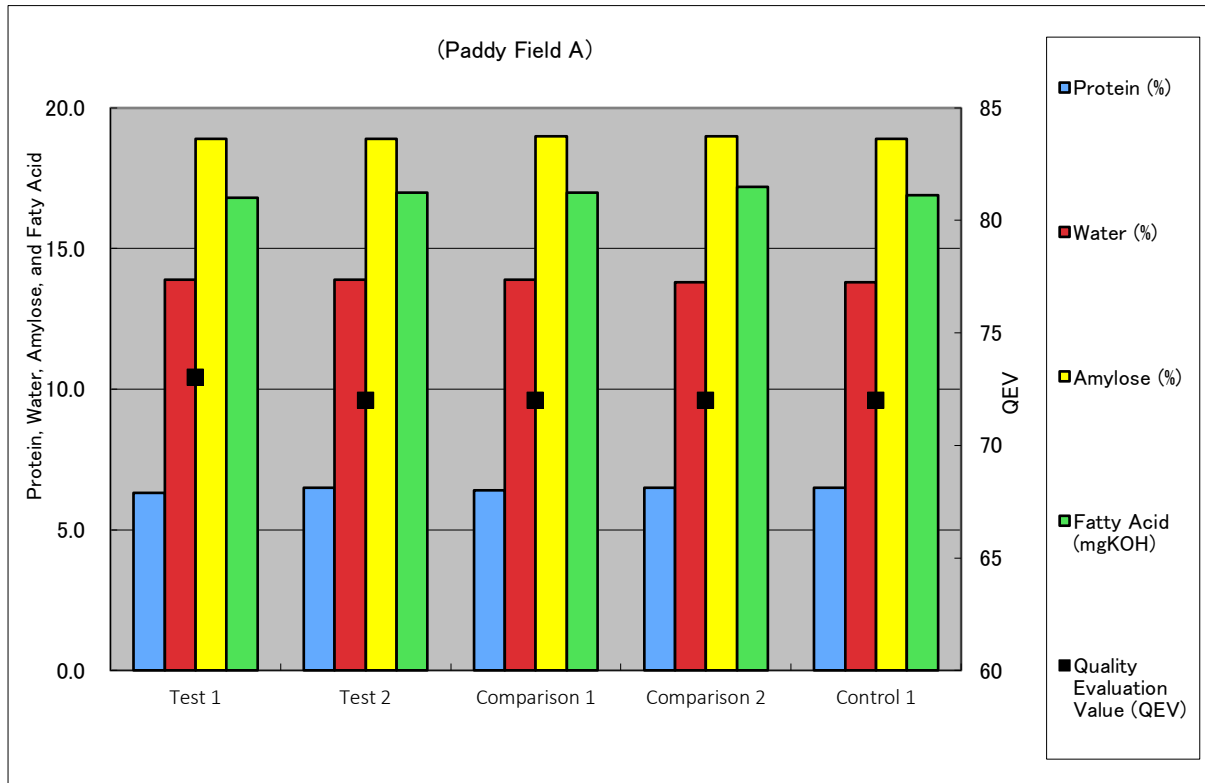
Fig. 4-1-4. Taste of rice in paddy field A
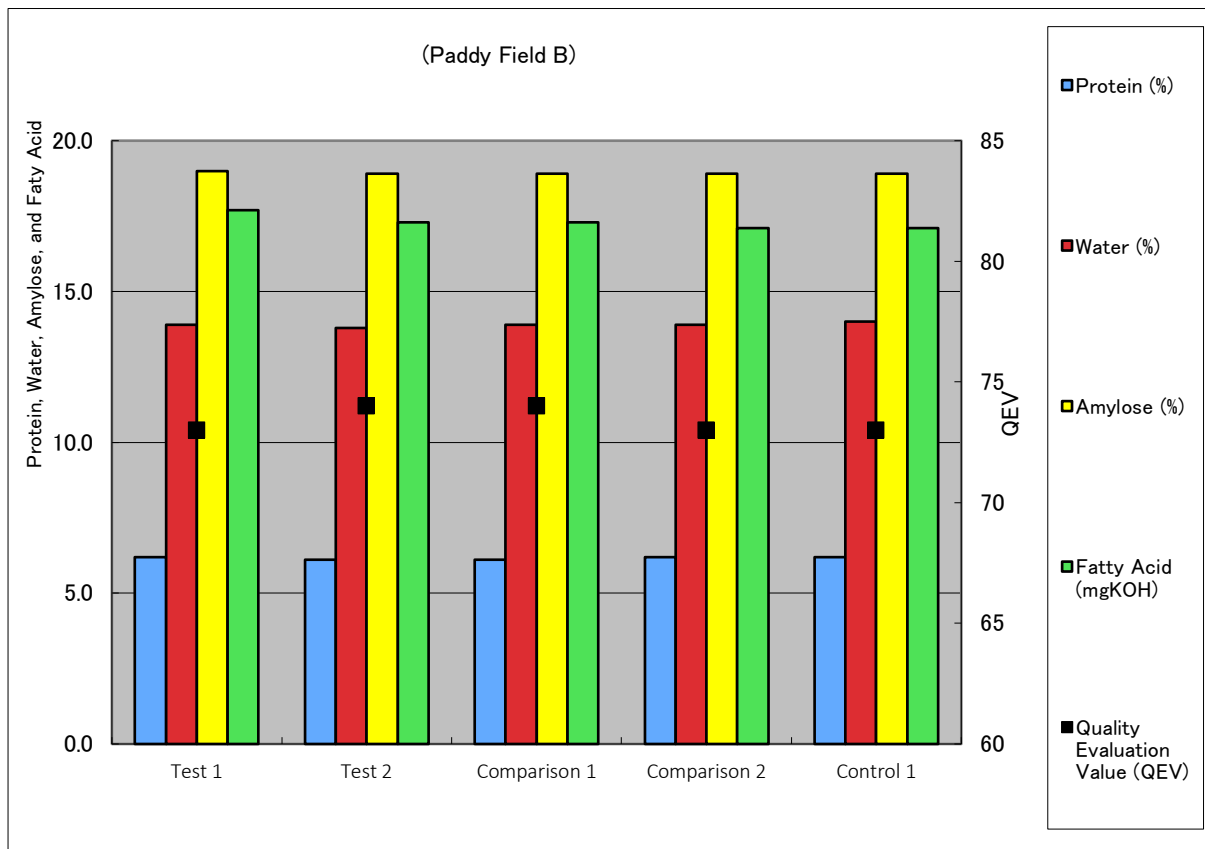
Fig. 4-1-5. Taste of rice in paddy field B

DISCUSSION

The two paddy fields used for the study had divisions of similar size (Figs. 4-1-2 and 4-1-3). The divisions were designed such that the silica applied to one division does not affect the silica concentration of other divisions—minimal influence.

In both the fields, there was no difference in the growth of rice plant between divisions. However, there was significant difference in silica sorption by plants between divisions. The plants of comparison 2 and test 1 exhibited relatively high and low silica sorption, respectively, in paddy field A. In paddy field B, the plants of comparison 2 and control showed relatively high and low silica sorption, respectively. The difference between the two paddy fields might be attributed to the difference in the soil type. The soil of paddy field A was alluvial sandy soil and that of B was alluvial clay. To assess the growth of rice plants, graphs were obtained for each factor to identify trends.

The results revealed that the weight of rice in paddy field A was higher than that of paddy field B (Fig. 4-1-6). The number of ears was higher in paddy field B when compared with that of paddy field A (Fig. 4-1-7). Further, the number grains per ear was higher in paddy field A than that of paddy field B (Fig. 4-1-8). Further, the percent of ripened grains observed in Comparison 1B was relatively low (Fig. 4-1-9). It was also observed that the number of cracked rice in paddy field A was higher than that in paddy field B (Fig. 4-1-10). The results indicated that the rice produced in paddy field B was better than that of paddy field A.
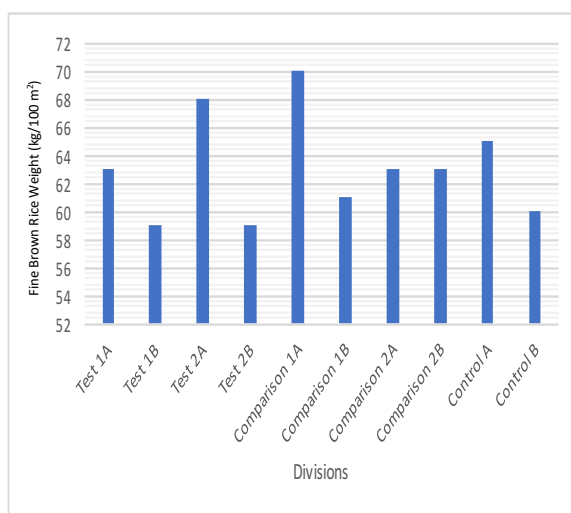
Fig. 4-1-6. Fine brown rice weight
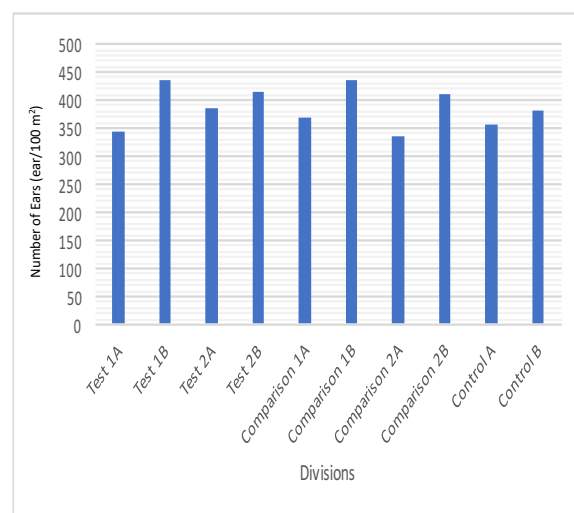
Fig. 4-1-7. Number of ears
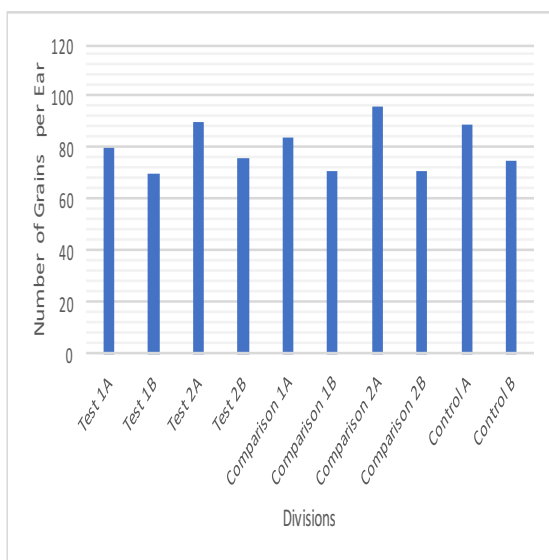
Fig. 4-1-8. Number of grains per ear
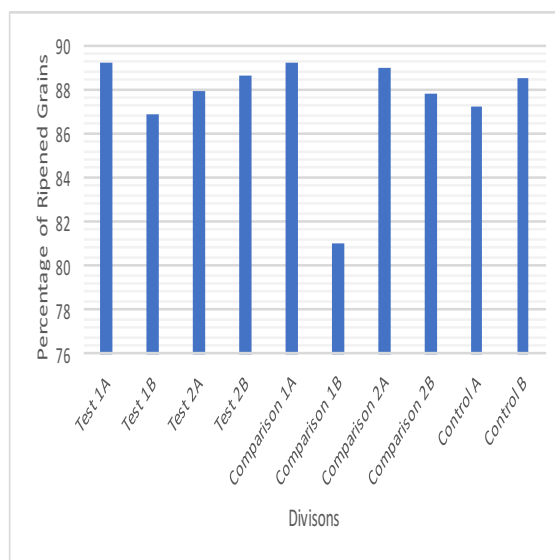
Fig. 4-1-9. Percent of ripened grains
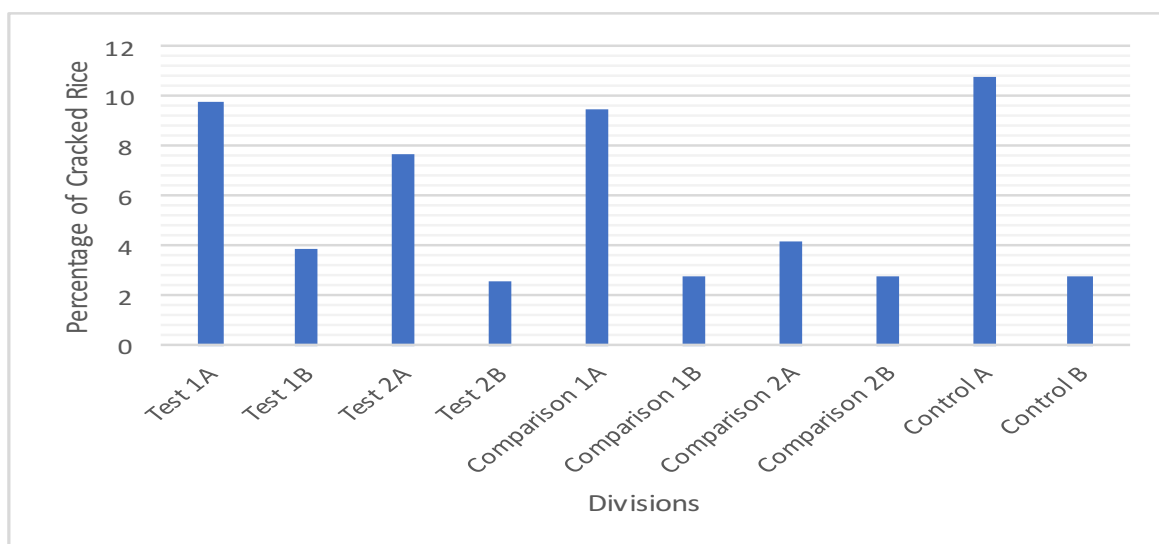
Fig. 4-1-10. Percent of cracked rice

The taste of rice was evaluated based on four parameters: protein, water, amylose, and fatty acid contents, which were used to obtain the QEV. Analysis of the four factors indicated the following (Fukui Kome Dot-Com 2017). Since proteins block water, it interferes with the absorption of water by rice. Rice loses its stickiness if the content of protein is high. However, in Japan, rice with low protein content is preferred, because it increases the stickiness of rice. In general, the average protein content of rice is 6.8 % in Japan. According to the official standard, the water content of brown rice can be up to 16 %. Furthermore, high water content is not desirable while storing rice, because it favors the growth of molds on the rice. However, if the water content is less than 14 %, it results in poor taste of the rice. Therefore, the optimal

water content of rice might be around 15 %. Low amylose content results in sticky rice, which is preferred in Japan. The amylose content of sticky rice is generally 16 %–18 %, while that of dry rice is 22 %–24 %. The fatty acid content in rice increases with time; less the fatty acid content, fresher the rice. The fatty acid content of fresh rice is generally 10–20 mg KOH. The Figs. 4-1-4 and 4-1-5 indicate that the four parameters—protein, water, amylose, and fatty acid contents— of the plants from both the paddy fields were almost similar to the standard values. Furthermore, there was no significant difference in relation to the four parameters among the divisions and also between the paddy fields. This suggested that the application of rice husk silica did not affect the taste of rice when compared with that of the rice grown in soil treated with commercial silica fertilizer.

CONCLUSIONS

Rice husk ash contains silica, which can be recycled as a silica fertilizer. Silica fertilizer is an inevitable part of rice production, because it is essential for the healthy growth of plants. Currently, an extrinsic silica material—slag from iron production processes—is being used in rice cultivation. To pursue the ideal sustainable agriculture, recycling rice husk ash after burning the rice husk to obtain heat is essential. However, the application of rice husk silica for plant growth should not affect the taste of the rice. In this milieu, the present study was conducted, where the rice plants were grown in soil treated with rice husk silica, obtained as a part of resource recovery, for sustainable agriculture. The taste of rice was evaluated using four parameters. The results revealed that the taste of rice grown in soil treated with rice husk silica was not significantly different from that of the rice grown in soil treated with commercial silica fertilizer. Therefore, rice husk silica can be used as a silica fertilizer. Further, this would reduce the problem associated with the disposal of rice husk, as it used to obtain heat, and also used as a silica fertilizer simultaneously. Thus, the rice growing countries can benefit from it.

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4-2. Investigation of negative effects of rice husk silica on komatsuna growth using three experiments

INTRODUCTION

Rice husks are one of the most trusted forms of biomass because of their sustainable generation and abundance. Rice husks are valuable sustainable resources for two purposes: energy recovery and material recovery. Their energy content is approximately 12 MJ/kg and they are a good source of fuel for producing hot water and steam. Rice husks contain silica, which can be a useful fertilizer for rice plants. This means that an ideal complete recycling scheme can be pursued (Fig.4-2-1). Rice straw, which is generated along with rice husks, does not cause any problems in Japan because it is plowed into the soil; although, several recent researches have studied the recycling of rice straw (Kaur et al. 2019; Kadian et al. 2019).
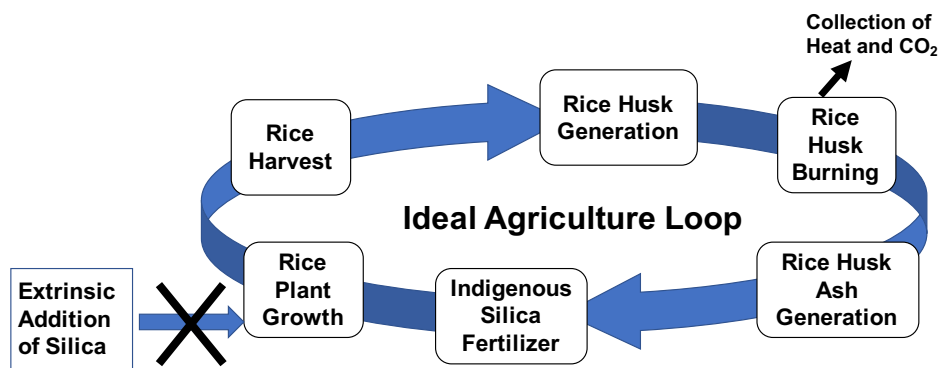
Fig. 4-2-1. Ideal agriculture loop based on rice husk recycling

The silica in rice husk is very useful and many researchers have reported its varied applications. Besides its numerous industrial applications, silica is quite beneficial for plants. Multiple researchers have reported the benefits of silica in rice husks, leading to the healthy growth of plants. Raven (1982) reported a comprehensive study on the total energy of silicon transport and its function in plants. Foy (1992) concluded that silicon causes an increase in phosphorus (P) efficiency, leaf size and chlorophyll content, and alleviation of aluminum (Al), iron (Fe), and manganese (Mn) in plants. The effect of silicon on the physical strength of plants, such as in their cell walls, was discussed by Guerriero et al. (2016). Most recently, silicon's role in tropical forest soils (Schaller et al. 2018) and its influence on numerous plants, such as maize, lettuce, wheat, carrot, and pea have been reported (Greger et al. 2018). Silicon fertilizers show improvements in crops, such as improved tolerance of biotic and abiotic stresses, and higher

yields (Vasanthi et al. 2014). Effects of silica on specific plants have been investigated. Henriet et al. (2006) investigated the effect of silica on banana plants, and Dorneles et al. (2018) investigated its effect on potato plants. Silicon was found to play an important role in these crops. Silicon has also been reported to have good effects on humans; it improves bone health and accelerates healing (Henstock et al. 2015) as well as improves the immune response and tissue health (Farroq and Dietz 2015). Since 1950s, there have been numerous researches on how silicon affects rice production (Yoshida et al. 1959; Yoshida et al. 1962; Krishnarao and Godkhindi 1992; Savant et al. 1996; Klotzbücher et al. 2015; Ito et al. 2015; Siregar et al. 2016; Waseem et al. 2016; Song et al. 2017).

The purpose of this study is to investigate the negative effects of silica in rice husk ash on the komatsuna plant using three different experiments. Komatsuna is a standard plant used in the evaluation of negative effects on plants in Japan. Kato et al. (2008) studied nitrate concentrations in komatsuna in an andisol. Furthermore, the flux of N_2O from komatsuna influenced by slag fertilizers has been investigated (Singla and Inubushi 2015). The uptake of tellurium and cesium from the soil by komatsuna plants has also been reported (Fujiwara et al. 2017).

Sekifuji and Tateda (2017) investigated the negative effect of silica in rice husks on the taste of rice and found that no such effect was evident when using silica as a fertilizer. This was done to confirm that there is no negative effect of the rice husk silica on plants; thereby promoting various applications of silica, especially recycling of rice husk silica. Moreover, rice husks could then be regarded not as waste but as a resource, which would help to promote a greener society in rice-producing countries.

MATERIALS AND METHODS

Rice husks of Koshihikari (*Oryza sativa* L.) were used for the following experiments. Rice husk ash was obtained by burning the husks in a field-scale boiler system (incineration capacity: 100 kg rice husks/h) (Fig. 4-2-2).
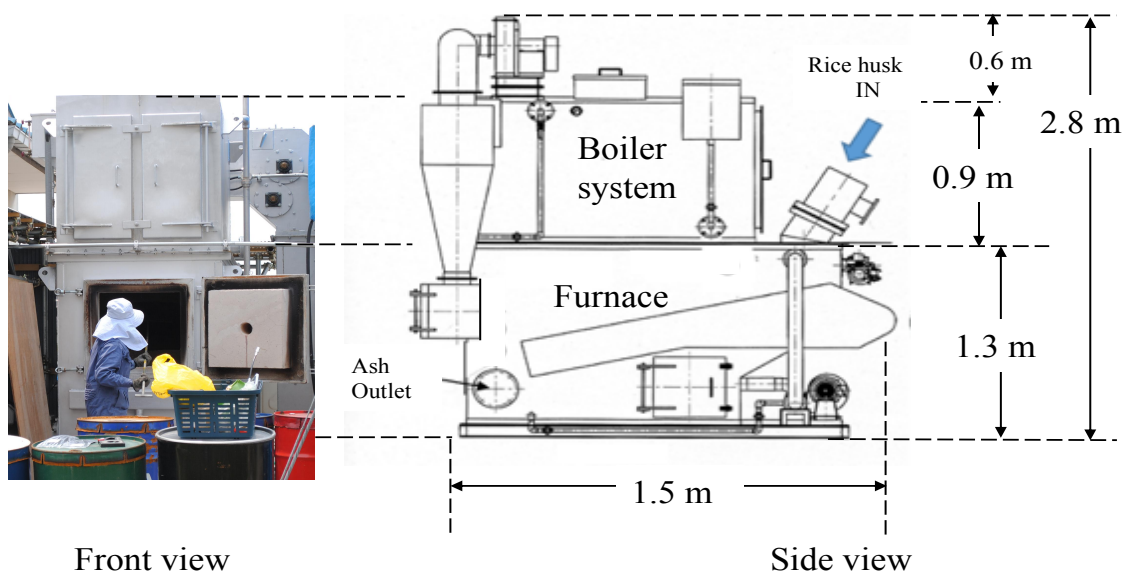
Fig. 4-2-2. Diagram of the boiler

The details of the boiler system are described by Tateda et al. (2016b). The silica in the ash was confirmed as amorphous using an X-ray diffraction analysis (XRD). The solubility of the silica was more than 50 %, thereby indicating its amorphous state. The solubility percentage of silica is an official indicator, which is highly correlated with the amorphous state of silica. Higher the solubility percentage, the more amorphous the state will be. Details of the solubility measurements are described by Tateda et al. (2016a). Komatsuna (*Brassica rapa* var. *perviridis*), a Japanese mustard spinach, was used for all the experiments. Possible contamination by radioactive cesium in the rice husk ash was also analyzed, because all the experiments were conducted after a severe incident involving an explosion at a nuclear power plant that had been damaged by the strong earthquake, which hit the northern area of Japan on March 11th, 2011. Levels of radioactive cesium (Cs-134 and Cs-137) were measured using the standard method for measuring radioactive cesium in fertilizers (MAFF 2011).

Pot Experiment for Comparison with Different Individual Fertilizers

The purpose of this experiment was to investigate the negative effects of rice husk ash as a fertilizer for komatsuna, compared to other common fertilizers and compost, using cultivation pots. The experimental procedure followed the standard method for solubility tests of silica (MAFF 2007). Neubauer pots (10^{-6} ha; inner diameter 11.3 cm × height 6.5 cm) were used for the experiment. Diluvium was used as the base soil, and its characteristics are shown in Table 4-2-1. For comparison, a dried cell fertilizer and farm compost were used, and their

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characteristics are shown in Table 4-2-2. Because nitrogen content was less than 2 % for SF and CF2, an application of 5 g (dry base) was set as the standard. For CF1, 100 mg of nitrogen was set as the standard because the nitrogen content was more than 2 % (dry base). The experimental design of the fertilizer and compost applications are shown in Table 4-2-3. The cultivation was conducted in a glass room and the room temperature was kept above 15 °C, with germination and growth observations conducted on day 5 and 9, and on day 14 and 21, respectively.

Table 4-2-1. Physical characteristics of the base soil (Diluvium)

Type of soil	Values
pH (soil:water = 1:2.5)	6.3
Exchangeable acidity	0.3
Electric conductivity (mS/cm)	0.15
Cation exchange capacity (mol_c /kg)	19.1
Phosphate adsorption coefficient (g/kg)	28.6
Air-dried fine soil volume weight (g/500 ml)	413
Maximum water holding capacity (g/kg)	1100

Table 4-2-2. Characteristics of fertilizers used

Short name	Name	Materials	Fertilizer effective components (%)				
			Water content	N	P_2O_5	K_2O	C/N
SF	Sample Fertilizer	Rice husk ash	6.1	0.11 (0.12)	0.19 (0.20)	1.92 (2.05)	112
CF1	Comparison Fertilizer 2	Dried cell fertilizer	7.1	5.08 (5.47)	2.27 (2.44)	0.19 (0.20)	6
CF2	Comparison Fertilizer 1	Farm compost	45.4	1.00 (1.82)	1.32 (2.42)	1.53 (2.81)	17

Note: Values in parentheses indicate the percentage in dry base.

Table 4-2-3. Design of fertilizers

Short name		Application design	Application amount (g/pot)	Fertilizer effective components (mg/pot)		
				N	P_2O_3	K_2O
SF	SFS	Standard	5.3	6 (25)	10 (50)	102 (25)
	SFD	Double	10.7	12 (25)	20 (50)	205 (25)
	SFT	Triple	16.0	18 (25)	30 (50)	307 (25)
	SFQ	Quadruple	21.3	23 (25)	41 (50)	409 (25)
CF1	CF1S	Standard	2.0	100 (25)	45 (50)	4 (25)
	CF1D	Double	3.9	200 (25)	89 (50)	7 (25)
	CF1T	Triple	5.9	300 (25)	134 (50)	11 (25)
	CF1Q	Quadruple	7.9	400 (25)	179 (50)	15 (25)
CF2	CF2S	Standard	9.2	92 (25)	121 (50)	140 (25)
	CF2D	Double	18.3	183 (25)	242 (50)	280 (25)
	CF2T	Triple	27.5	275 (25)	363 (50)	420 (25)
	CF2Q	Quadruple	36.6	366 (25)	484 (50)	561 (25)
		Control		25	50	25

Note: Values in parentheses indicate the amounts of ammonium sulfate, superphosphate, and potassium chloride used for N, P_2O_3, and K_2O, respectively.

Pot Experiment for Comparison with Different Mixtures of Fertilizers

The purpose of this experiment was to investigate the negative effects of rice husk ash mixed with compost on komatsuna using cultivation pots. The experimental procedure followed the standard method for solubility tests of silica (MAFF 2007). Neubauer pots (10^{-6} ha; inner diameter 11.3 cm × height 6.5 cm) were used for the experiment. Komatsuna was cultivated in a glass room at an average room temperature of 25 °C. Compost produced by mixing bark, poultry manure, tea dregs, pruned branches and/or leaves, and urea was used for making the bed materials for komatsuna growth. Tea dregs consisted of leaves left over from brewing tea,

which is one of the most popular drinks in Japan. The experimental design is summarized in Table 4-2-4. Bed materials A, B, and C are compost products that are commercially available. Volcanic ash subsoil was used as the base soil. 150 ml of the bed materials was added to the base soil (350 ml), which was 71 g, 70 g, 45 g, 61 g, 50 g, 49 g, 57 g, 51 g, and 45 g for pots #1, 2, 3, 5, 6, 7, 8, and 9, respectively. 360 g of base soil was used for the control.

Table 4-2-4. Experimental design and physical states

Pot		Components of Bed materials	Mixing percentage by weight (%)		Physical states		
#	Name		Bed material	Rice husk ash	Water content (%)	pH	Electric Conductivity (mS/cm)
1	A10	A: -Bark 94.0 %, -Poultry manure 5.0 % -Urea 1.0 %	90	10	51.8	8.4	1.3
2	A30		70	30	52.5	8.8	0.9
3	A50		50	50	35.6	9.0	2.0
4	B10	B: -Bark 52.3 %, -Tea dregs 22.5 % -Pruned branches and leaves 22.5 % -Poultry manure 2.2 % -Urea 0.5 %	90	10	53.4	7.8	1.4
5	B30		70	30	53.8	8.6	1.6
6	B50		50	50	46.9	9.0	1.7
7	C10	C: -Tea dregs 50.0 % -Pruned branches and leaves 50.0 %	90	10	53.4	6.2	1.7
8	C30		70	30	51.2	6.6	1.7
9	C50		50	50	45.4	7.6	2.0
	Control		-	-	132[a]	6.6[b]	0.07[c]

Note: Values of a, b, and c are from Saito et al. (1987). a: maximum water holding capacity

Field Experiment with Different Quantities of Silica

The purpose of this experiment was to investigate the negative effects of rice husk ash on komatsuna in field cultivation. Two greenhouses were used for the experiments. The configuration of the greenhouses and the experimental design are shown in Fig. 4-2-3.

Greenhouse A:
Field with no rice husk ash applied.

30 m	
5.5 m	No rice husk ash
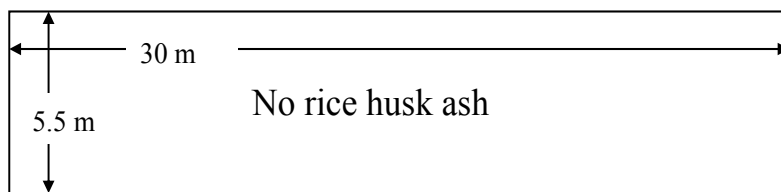
Greenhouse B:
Field with rice husk ash applied.

20 kg/100 m²	15 kg/100 m²	10 kg/100 m²	5 kg/100 m²
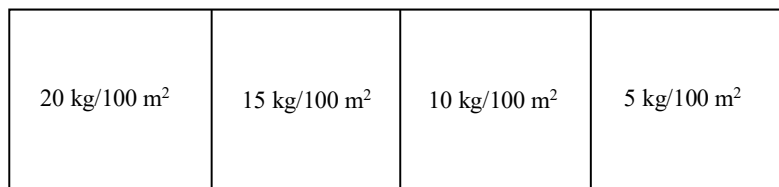
Fig. 4-2-3. Configuration of the experimental sections in the fields

Elemental components of the base soil in Greenhouses A and B, and the pH of each section are shown in Tables 4-2-5 and 4-2-6. The pH of the soil in each section (Table 4-2-6) was measured by dissolving the soil in tap water (pH 7.31) at ratio of 2:1 (soil:water) by weight. Resistance values to lodging were also obtained in order to evaluate the negative effects of the rice husk ash on komatsuna (Fig. 4-2-4). Seeding was conducted at the end of November 2013 and harvesting was conducted at the beginning of February 2014.

Table 4-2-5. Soil analysis (%)

Elements	Soil in Greenhouse A	Soil in Greenhouse B
Fe	43.2	43.1
Si	33.8	33.5
Ca	8.1	9.1
K	7.5	6.5
Ti	2.8	3.1
Ba	2.1	0.7
Mn	0.6	0.9
Zn	0.4	0.4
Sr	0.4	0.3
Zr	0.4	-
Cr	0.2	0.2
Rb	0.2	0.2
Ag	0.2	-
Y	0.1	-
S	-	1.9

Table 4-2-6. pH of the soil in each section

Soil	pH
Soil in Greenhouse A	5.17
Soil in Greenhouse B	5.38
Soil in the section of 5 kg/100 m²	5.12
Soil in the section of 10 kg/100 m²	5.40
Soil in the section of 15 kg/100 m²	5.28
Soil in the section of 20 kg/100 m²	5.48

Fig. 4-2-4. Resistance values test (leaf stem)

RESULTS AND DISCUSSION

Pot Experiment for Comparison with Mixed Single Fertilizer (Experiment 1)

Germination occurred in all the application designs, and showed equal or much better results, as compared to the control (data not shown). Abnormalities were not seen in any of the application designs. Growth observations on the 21st day are graphed in Fig. 4-2-5. The fresh weight index shows the proportion of fresh weight for each sample, taking the value of control (6.9 g) as 100. For both leaf length and fresh weight, all the application designs showed larger values than the control. In the case of leaf length, SF and CF2 showed an increase with increasing application of ash, though the values were almost the same for CF1. For fresh weight, CF2 showed an increase with increasing application of ash, and the increase was significant. In the case of SF, the standard and quadruple applications showed minimum values. A similar trend was seen in CF1. The status of growth of komatsuna is shown in Fig. 4-2-6; CF2 had grown significantly compared to SF and CF1 by the 21st day. Fig. 4-2-7 shows that the sample CF2 had significant growth in terms of fresh weight, because its N, P_2O_3, and K_2O were very high compared with the other samples. SF and CF1 contained small amounts of N, P_2O_3, and K_2O, which might be a reason that they did not grow as much as CF2 did.
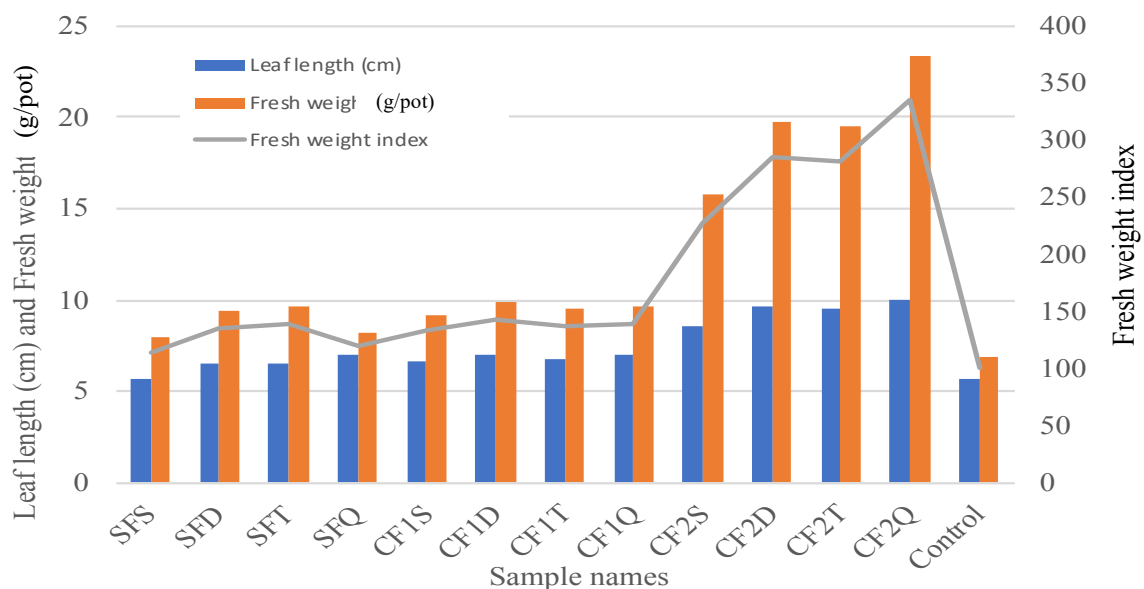
Fig. 4-2-5. Leaf length, fresh weight, and fresh weight index observed on the 21st day
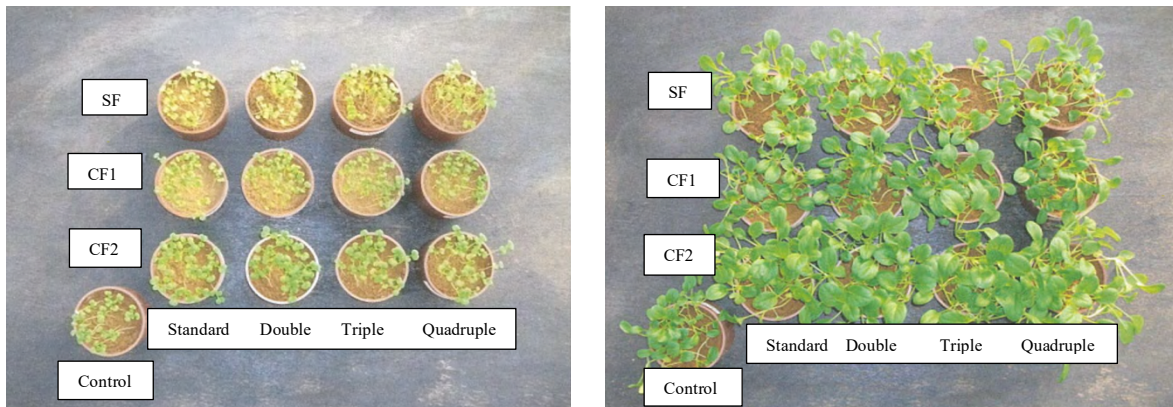
Fig. 4-2-6. Growth observation; left: germination on the 9th day; right: growth on the 21st day
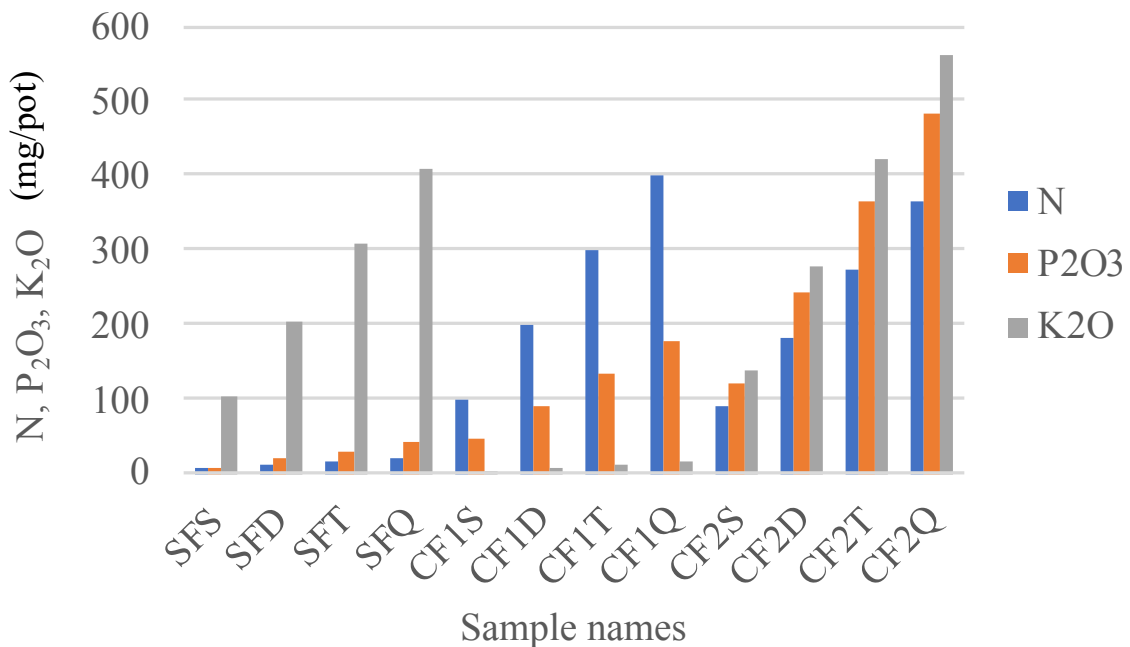
Fig. 4-2-7. Nutrient contents for each sample

Pot Experiment for Comparison with Mixed Multiple Fertilizers (Experiment 2)

The growth tests for abnormality revealed no abnormality in any of the pots (results not shown). In all the pots, normal growth of komatsuna was confirmed throughout the experiments, and 100 % germination was observed for all applications, which was better than the control (Fig. 4-2-10). Leaf length, fresh weight, and fresh weight index are graphed in Fig. 4-2-8, and the chlorophyll content in the leaves was measured as SPAD (Fig. 4-2-9). The fresh weight index shows the proportional fresh weight for each sample, taking the value of control (2.8 g) as 100.

Bed material A had a greater influence than bed materials B and C; however, all three produced far better growth than the control (Fig. 4-2-8). In bed material A, Sample A30 had the highest fresh weight, and A50 decreased substantially to become the smallest in Group A. Group A showed the highest fresh weight, followed by Group B; the least fresh weight was seen in Group C. In Groups B and C, no significant difference was observed among the samples. It can be said that fresh weight was influenced by the types of fertilizer. Fig. 4-2-10 shows the status of growth for all pots; the control grew less than the other pots. The SPAD values of control were the highest (Fig. 4-2-9), which may be attributed to the fact that its leaves remained small, hence the chlorophyll content showed a higher value.
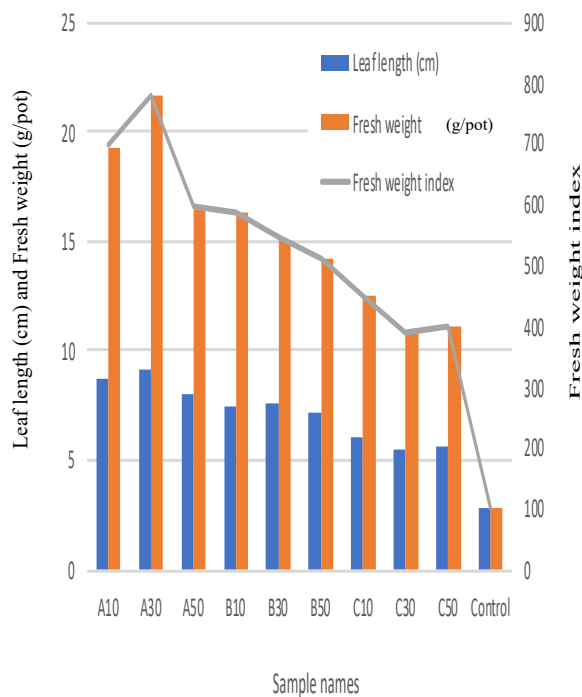
Fig. 4-2-8. Leaf length, fresh weight, and fresh weight index observed on the 21st day
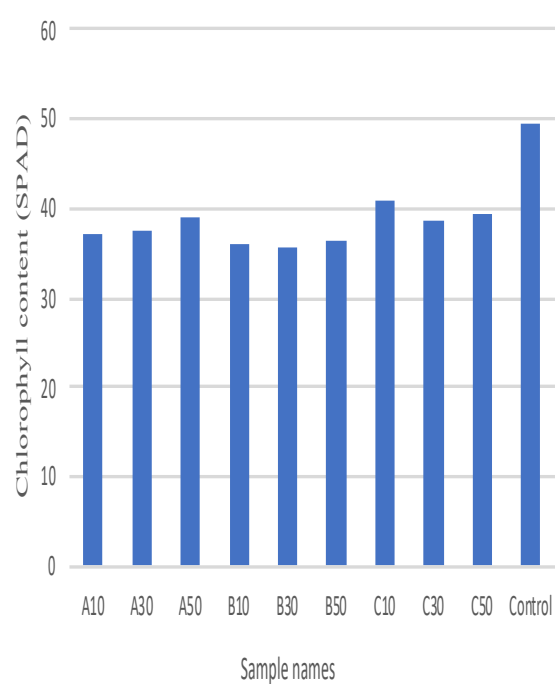
Fig. 4-2-9. Chlorophyll content of the leaves

	Pot A10	Pot A30	Pot A50

After 9 days

After 21 days

	Pot B10	Pot B30	Pot B50

After 9 days

After 21 days

	Pot C10	Pot C30	Pot C50

After 9 days

After 21 days

Fig. 4-2-10. Growth observation of each pot after the 9th and 21st day

Field Experiment with Different Quantities of Silica (Experiment 3)

Fig. 4-2-11 shows that there were no significant negative effects caused by use of rice husk ash, compared with the control sample. There were also no significant positive effects from the application of ash, compared to the control sample. The addition of 20 kg per 100 m^2 of ash might reduce the total sellable weight of komatsuna. In Fig. 4-2-5, SF is the sample with only rice husk ash addition; comparing the fresh weight of SF in Fig. 4-2-5 with the total weight in Fig. 4-2-11, the same trend of the samples with 1×, 2×, 3×, and 4× ash can be seen. The values increased with increasing ash amount, but decreased in the sample with 4× the ash, although the controls for each showed different trends. In the field experiment, control showed a better performance in all parameters compared to the other samples (Fig. 4-2-11); but in the pot experiments, control showed the least amount of growth, compared to all the samples (Fig. 4-2-5). The resistance values of the leaves were not significant for all samples; however, for the leaf stems, the sample with 10 kg ash application showed the highest value (Fig. 4-2-12). The results imply that the addition of ash to the soil did not cause weakening of the leaves or leaf stems of komatsuna.
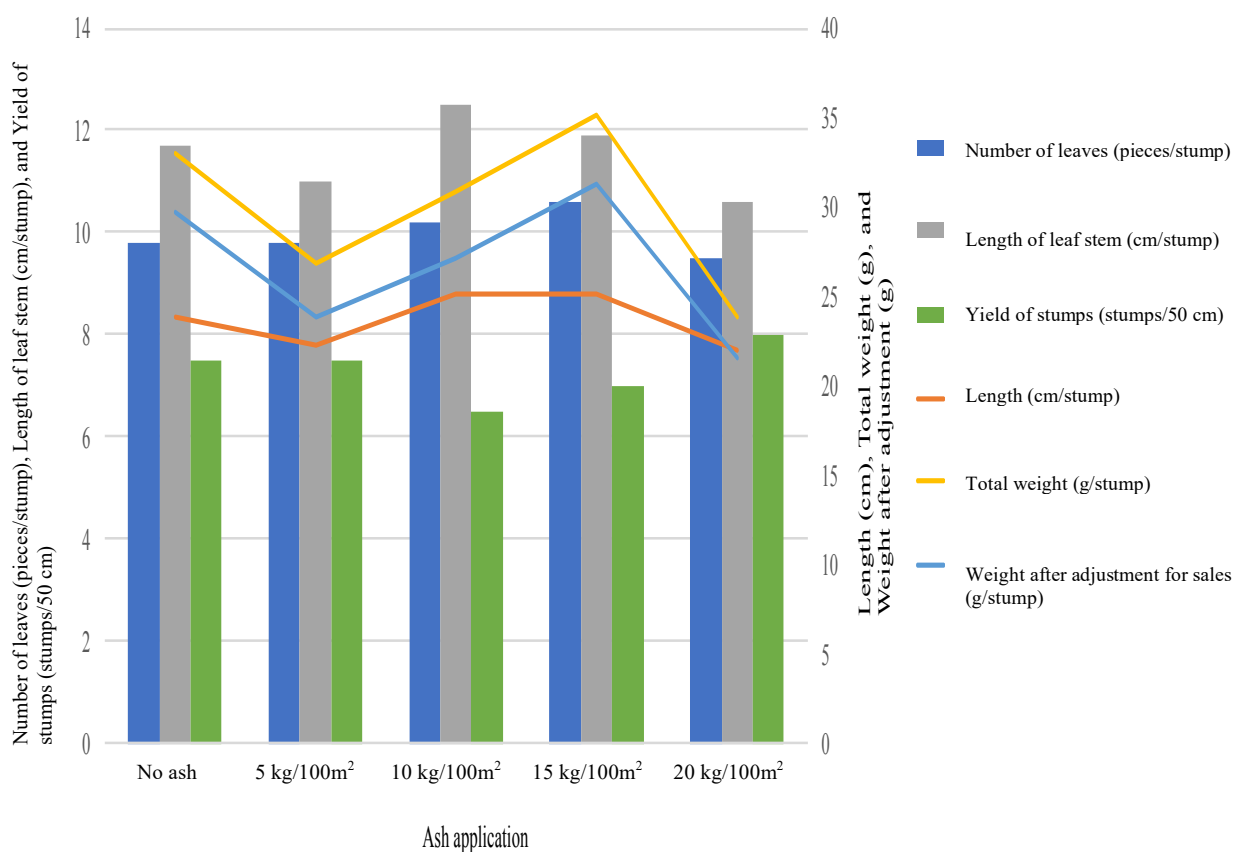
Fig. 4-2-11. Results of growth tests in the field

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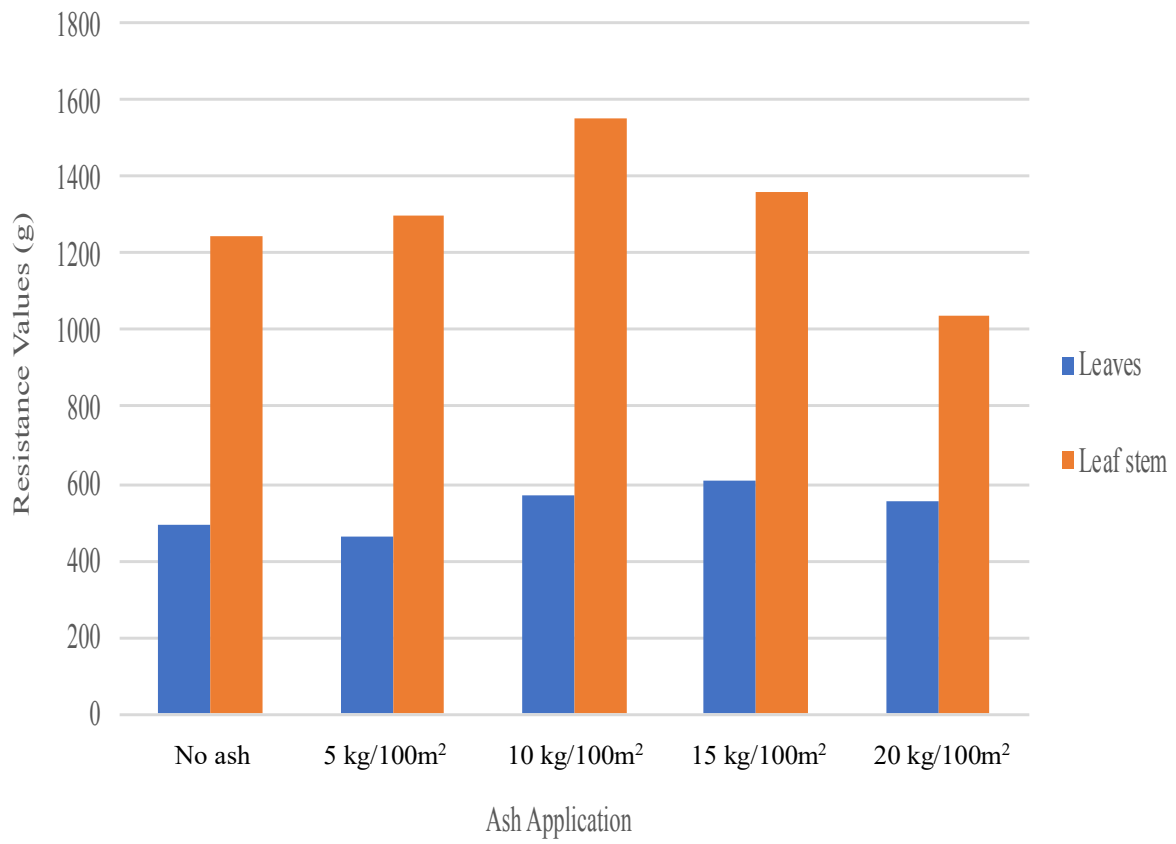
Fig. 4-2-12. Resistance values of leaves and leaf stems

CONCLUSIONS

In order to evaluate negative effects of rice husk ash application on komatsuna crops, three experiments were conducted. The following conclusions were obtained.

- Komatsuna grew significantly when the ash was used in combination with a fertilizer.
- Application of the ash without fertilizer did not result in significant improvement in the growth of komatsuna.
- Rice husk ash did not have a negative effect on the komatsuna, whether applied with or without fertilizer, in pot or field experiments.

Because of a previous experiment, which showed that rice husk ash did not impair the taste of rice (Sekifuji and Tateda 2017), it was concluded that it can be used safely for komatsuna. Thus, rice husk ash can be used for any kind of vegetables, without having negative effects on the plants. With fertilizers, ash had a significantly positive effects on komatsuna, and the plants became healthier.

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**Chapter V   Key Elements for Establishing an Ideal Agriculture System
by Rice Husk Recycling**

5-1. Sustainability of a rice husk recycling scheme

INTRODUCTION

To evaluate the performance of a scheme, sustainability is key, and sustainable development is evaluated on the basis of economic, environmental, and social growth (Ameer et al 2012, Banerjee 2008). A scheme may persist if it is beneficial to the environment; thus, in academia, the scheme is considered sustainable. On the other hand, financial sustainability is often the simplest and most convincing economic parameter. Hence, a financially healthy scheme is also considered beneficial to the environment (Ameer et al 2012, Banerjee 2008). With respect to its contents, rice husk is considered a bio-ore of silica (Tateda 2016a). However, most stakeholders simply dispose of it as waste, a wasteful practice that is frequently encountered globally. Many researchers have studied rice husk recycling in terms of material (Rufai et al. 2012, Saceda et al. 2011, Uddine et al. 2018, Sekifuji et al. 2019a) and chemical (Minh et al. 2018) recycling as well as thermal recovery (Alhinai et al. 2018, Arnaldo et al. 2018, Azat et al. 2019, Eiamsa-ard et al. 2019, Fernandes et al. 2016, Martínez et al. 2011, Quispe et al. 2017). Since rice husks are combustible, they have been investigated in energy generation-related studies. Recycling rice husk into silica fertilizer has been proposed by some researchers (Ma et al 2002, Tateda 2016b). Ash from incinerated rice husks can be used as a fertilizer after heat collection, leading to the ideal agricultural loop shown in Fig. 5-1-1 (Sekifuji et al 2019).
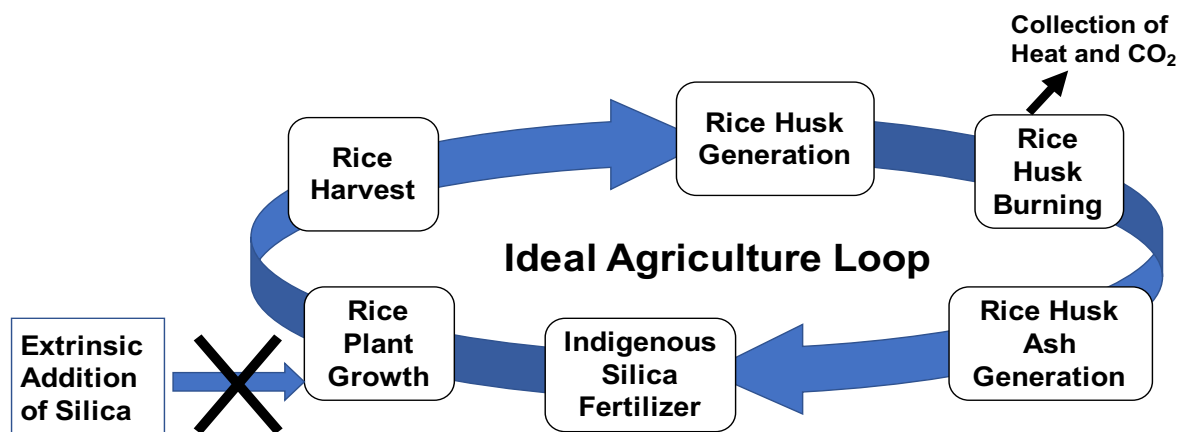

Fig. 5-1-1. Ideal agriculture loop based on rice husk recycling

The fundamental concept of the loop is to recover both heat and silicate resources from the combustible rice husk. In a previous study, the usefulness of rice husk in electricity generation and hot water production was compared, and it was found that hot water production makes the loop sustainable (Sekifuji et al 2019). It was also observed that there are three essential conditions for loop sustainability: free or low-cost rice husk collection and hauling, the silica in the incinerated rice husk ash should be in the amorphous state, and the complete recycling of the ash. Rice husk collection and hauling fees negatively affect the sustainability of the loop. The importance of collection and hauling has been investigated in several studies. In terms of solid waste management (i.e., collection, transportation, and disposal), 50–70 % of the total management cost can be attributed to the collection phase (Tchobanoglous et al. 1993). Demir et al. (2017) stated that minimizing the solid waste disposal cost minimizes the cost of collection and transportation. In a case study, a 37 kg CO_2/week emission reduction was expected, as per the results obtained from the optimization of sludge hauling routes (Passos et al. 2018). If the silica ash is in the crystalline state, it must be completely disposed of without recycling because of its potential carcinogenicity (WHO 1997). On the other hand, Prasara et al (2017) noted the importance of ash transportation when discussing the recycling of crystalline rice husk ash for products, including thermal insulators and refractory bricks. The incinerated ash obtained after heat recovery must be recycled given that large amounts are generated (20 % of the rice husk weight becomes ash). There is no specific order for the three conditions necessary for sustainability. However, the loop cannot be sustainable if any one of the three conditions is not fulfilled. In this study, the sustainability of the loop scheme was evaluated by financially balancing annual income and expenditure. If the loop scheme results in a negative balance, it implies that the scheme is unsustainable, and vice versa if the scheme results in a positive balance (Tateda et al 2019). The results of this study will be valuable and useful to stakeholders in rice-growing countries.

MATERIALS AND METHODS

Fundamental Information for the Ideal Agricultural Loop Recycling Scheme

The same boiler plant and associated conditions discussed in Sekifuji et al (2019b), as summarized in Table 5-1-1, were employed in this study.

Table 5-1-1.   Basic data for calculating annual balance

Category	Item	Value	Unit
Operation fundamentals	Boiler capacity	250	kg (rice husk as-obtained)/day
	Boiler operation	6	h/day
		220	d/year
Operation, maintenance, labor cost	Boiler cost	200000	USD/system
	Operation cost	1000	USD/month
	Maintenance cost	800	USD/month
	Pelletizer cost	200000	USD/system
	Operation cost	1000	USD/month
	Maintenance cost	1000	USD/month
	Labor cost	35000	USD/(year capita)
Miscellaneous	Kerosene price	0.9	USD/L
	Greenhouse area	3240	m^2
	Ash generation	20	% in weight of rice husks

Equation for Calculating the Financial Balance of Incomes and Expenditures

In this study, "Incomes" also included the "cost of saving necessities". For example, the cost of purchasing kerosene was compensated for by heat recovery, which was then considered as an income. Additionally, in this study, "Sustainability" was defined as a net zero balance in Eq. (1).

$$\underbrace{\boxed{\begin{array}{c}\text{Kerosene saving for rice drying}\end{array}} + \boxed{\begin{array}{c}\text{Kerosene saving for greenhouse heating}\end{array}} + \boxed{\begin{array}{c}\text{Fertilizer sale}\end{array}}}_{\text{incomes}} = \underbrace{\boxed{\dfrac{\text{Price of the boiler system}}{\text{Depreciation years: 8 yr}}} + \boxed{\begin{array}{c}\text{Yearly boiler cost}\end{array}} + \boxed{\begin{array}{c}\text{Yearly pelletizing cost}\end{array}} + \boxed{\begin{array}{c}\text{Rice husk hauling and collection fee}\end{array}} + \boxed{\begin{array}{c}\text{Ash disposal tipping fee}\end{array}}}_{\text{expenses}}$$

$$\cdots\cdots\cdots\cdots\cdots\text{Eq. (1)}$$

The data detailed in Table 5-1-1 correspond to a case without incurring "Rice husk collection and hauling" and "Ash disposal tipping" fees. The necessary information on income and expenses is shown in Table 5-1-2. In a previous study, the basic scheme was considered sustainable even though the final balance was -2949 USD/yr. This was because this negative balance was not significant and could easily be made up by implementing minor improvements/changes.

Table 5-1-2.　Previously reported annual balance for a 6 h/day operated system (USD/year)

	Incomes			Expenditures		
Item	**Value**	**Remarks**	**Item**	**Value**	**Remarks**	
Rice drying	61875	25 L/h kerosene consumption	Boiler yearly cost	25000	8 year depreciations	
Greenhouse heating	32076	11 L/(m²·year) kerosene consumption	Yearly operation	12000		
Fertilizer sale	46200	0.7 USD/kg	Yearly maintenance	9600		
			Yearly labor	35000	1 person	
			Pelletizer yearly cost	20000	8 year depreciations	
			Yearly operation	12000		
			Yearly maintenance	12000		
			Yearly labor	17500	0.5 person	
Total	140151		Total	143100		

1 USD = 100 yen

Various Scenarios to Consider for Evaluating Sustainability

To evaluate sustainability, scenarios with different conditions based on a 6-h/d operation were considered (Table 5-1-3). Regarding rice husk collection and hauling, cases with rice husk collection and hauling free of charge or below 35 USD/m³ were considered. Regarding ash usage, 100 % usage, 50 % usage, and no usage (0 %) as fertilizer were considered. With respect to application as fertilizer, prices in the range 0–1 USD/kg were considered, while 0.7 USD/kg was considered as the basic price based on a previous study (Sekifuji et al 2019). A price of 0 USD/kg indicated that the ash could not be sold as a fertilizer and was disposed of as waste. For ash disposal tipping fees, a fee in the range of 0–35 USD/kg was considered. A tipping fee of 0 USD/kg (free) under 50 % and 0 % use of ash was also considered, even though this is an unlikely occurrence.

Table 5-1-3.   Various scenarios for system operation

Scenario	Rice husk collection and hauling fee (USD/m³)	Percentage of ash sold as fertilizer (%)	Fertilizer price (USD/kg)	Ash disposal tipping fee (USD/m³)	State of ash (pellet or as-obtained)
0	0	100	0–1	0	pellet
1	0	100	0–1	0	as-obtained
2	0	50	0.7	0–35	pellet
3	0	50	0.7	0–35	as-obtained
4	0	0	0	0–35	as-obtained
5	0–35	100	0.7	0	pellet
6	0–35	100	0.7	0	as-obtained
7	0–35	100	1	0	pellet
8	0–35	0	0	15	as-obtained

According to a previous study, the pellet state (Fig. 5-1-2(b)) is preferred for ash fertilizer over the initial state (Fig. 5-1-2(a)) (Sekifuji et al 2019). However, scenarios in which the as-obtained ash was used were also considered, given that the pelletizing process is costly. For Scenarios 4 and 8, only the as-obtained ash was considered because the stakeholders did not need to produce pellets for ash disposal. Therefore, "pellet ash" and "pellet fertilizer" as well as "as-obtained ash" and "as-obtained fertilizer" were considered synonymous. As shown in Table 5-1-3, the 24-h/d operation was also considered for some scenarios, and the basic data for this 24-h/d operation are shown in Table 5-1-4. The same greenhouse areas for the 6-h/d operation were used for the 24-h/d operation, given that there was no extension plan for the greenhouses. Rather, to limit kerosene consumption, the excess heat generated in the 24-h/d operated process was used for rice drying. Boiler operation and maintenance costs were multiplied by 3, since 24 hours is 8 hours multiplied by 3. The labor costs associated with the operation of the boiler system were also multiplied by three persons, and 1.5 persons were applied to the labor cost of the 24-h/d operated pellet production system.
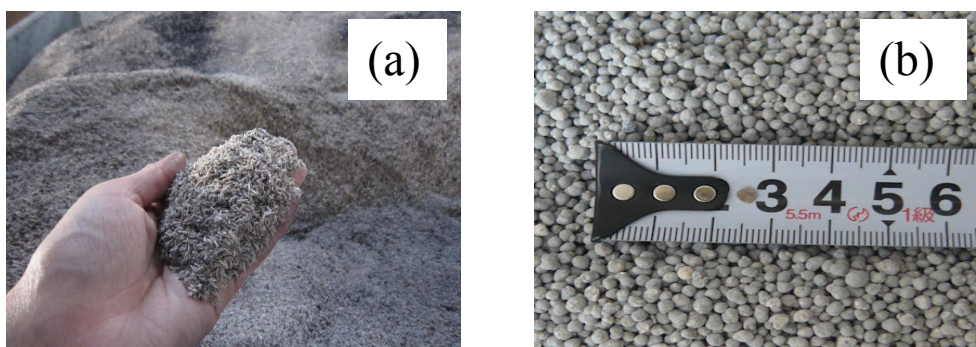
Fig. 5-1-2. Fertilizers (a) As-obtained and (b) In a pellet state

Table 5-1-4.   Previously reported basic data for a 24-h/day operated system (USD/year)

Incomes			Expenditures		
Item	Value	Remarks	Item	Value	Remarks
Rice drying	247500	25 L/h kerosene consumption	Boiler yearly cost	25000	8 year depreciations
Greenhouse heating	32076	11 L/(m²·year) kerosene consumption	Yearly operation	36000	
Fertilizer sale	184800	0.7 USD/kg	Yearly maintenance	28800	
			Yearly labor	105000	3 persons
			Pelletizer yearly cost	20000	8 year depreciations
			Yearly operation	36000	
			Yearly maintenance	36000	
			Yearly labor	52500	1.5 person
Total	464376		Total	339300	

1 USD = 100 yen

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RESULTS AND DISCUSSION

Comparison of Annual Financial Balance with Respect to Differences in Daily Operation Hours

Fig. 5-1-3 shows the difference in the annual balances of the 6 and 24-h/day operations. A fertilizer price of 0.7 USD/kg corresponded to the basic operation cost, as shown in the data presented in Tables 5-1-2 and 5-1-4. The 24-h/day operated system was sustainable at a fertilizer price of ~0.22 USD/kg compared with a fertilizer price of 0.7 USD/kg for the 6-h/day operated system. Therefore, an increase in daily operation hours enhanced sustainability, even though operation, maintenance, and labor costs increase when operation time increases. The fertilizer could be sold at a price 70 % cheaper if the boiler was operated for 24 h each day.
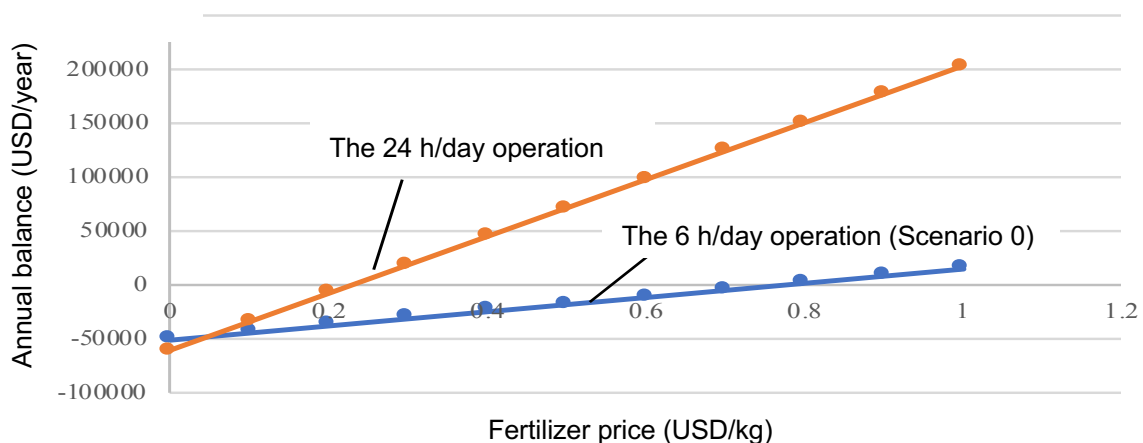
Fig. 5-1-3. Comparison of the 6- and 24-h/day operated systems

Comparison of the Annual Financial Balance of Pellet Ash vs. As-Obtained Ash for 6 h/day Operations

As previously reported, the fertilizer was pelletized because a significant number of farmers (80 %) preferred the fertilizer in pellet form. However, pelletizing is costly and requires high operation, maintenance, and labor costs. Fig. 5-1-4 shows a comparison of the two fertilizer states. As previously mentioned, the system was deemed "sustainable" when the fertilizer price was 0.7 USD/kg for the fertilizer in the pellet state (Scenario 0). On the other hand, the system could also be "sustainable" if the fertilizer was free of charge (Scenario 1). At the Y-intercept, Scenario 1 was sustainable although the fertilizer was "0 price." It can happen because the scenario has the incomes from the kerosine saving for rice drying and greenhouse heating

according to Eq. (1). Given that it is very difficult to use the as-obtained fertilizer owing to the fact that it disperses and can be inhaled by farmers (Fig. 5-1-5), its use by farmers was unlikely.
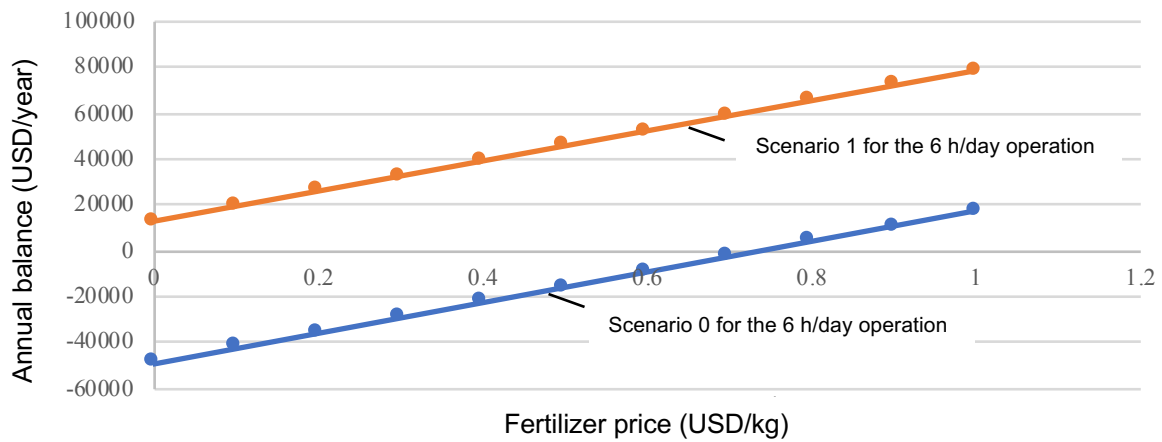
Fig. 5-1-4. Comparison of as-obtained ash and pelleted ash

Fig. 5-1-5. Scene showcasing application of as-obtained fertilizer

Comparison of Annual Financial Balance When Collection and Hauling are Charged for 6 h/day.

During the calculations, it was considered that the specific gravity of rice husk was 0.1 t/m^3. According to Fig. 5-1-6, when the pellet fertilizer was used, the annual financial balance became negative once a fee was charged for rice husk collection and hauling (Scenario 5). On the other hand, when the as-obtained fertilizer was used, the system was "sustainable" until the rice husk collection and hauling fee reached ~17 USD/m^3 (Scenario 6). However, it is still unlikely that the as-obtained fertilizer would be sold or used by farmers. If the pellet fertilizer

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could be sold and accepted by farmers at 1.0 USD/kg instead of 0.7 USD/kg, financial sustainability could be expected until rice husk collection and hauling fees reached 5 USD/m^3 (Scenario 7).
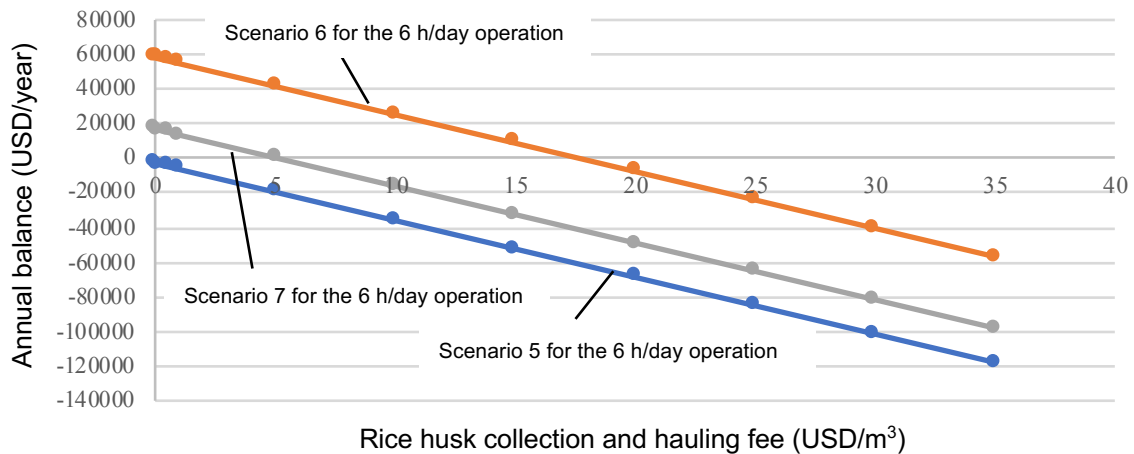
Fig. 5-1-6. Comparison of financial balance when rice husk collection and hauling are charged

When Fertilizer Cannot Be Sold and When 50 % Can Be Sold, While Disposing the Rest
In the calculations, a fertilizer price of 0.7 USD/kg was used, and the specific gravities of the pellet ash and the as-obtained ash were considered to be 1.1 and 0.07 t/m^3, respectively. As shown in Fig. 5-1-7, pellet fertilizer under a 6-h/day operation resulted in a significant negative financial balance, despite the fact that the ash disposal was free of charge (Scenario 2, 6 h/day operation). However, the scenarios became very profitable when the as-obtained ash was used during the 6 h/day operation (Scenario 3) and when the pellet fertilizer was used during the 24 h/day operation (Scenario 2).
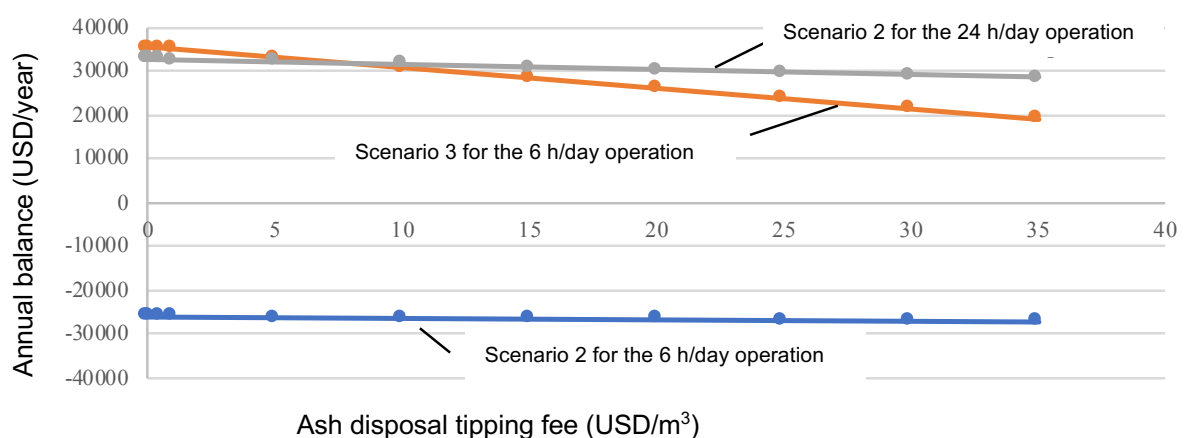
Fig. 5-1-7. Comparison of financial balance when ash disposal is charged

When All the Ash Must be Disposed, It Cannot Be Sold As a Fertilizer

When all the ash must be disposed of, only the as-obtained ash state was considered. According to Fig. 5-1-8, the system showed sustainability until the ash disposal tipping fee reached 15 USD/m^3 (Scenario 4, 6 h/day operation). However, a tipping fee of 15 USD/m^3 is unrealistic and too low, considering the 30 USD/m^3 solid waste disposal fee in Japan. In Turkey, the cost of solid waste collection falls in the range of 30–40 USD/t (Demir et al. 2017). In Japan, it is higher, and is in the range of 42–56 USD/m^3 for solid waste with a specific gravity of 1.4 t/m^3 (Yesiller et al. 2014). The 24-h/day operated system remained sustainable until the tipping fee reached 22 USD/m^3 (Scenario 4, 24-h/day operation). This indicated a financial improvement relative to the 6-h/day operation; however, the fee was still lower than it would be accepted in practice. Therefore, the system is unrealistic. Self-consumption is usually the last and best resort to solve the challenges associated with recycling. However, the ash could not be used because the constituent silica was crystalized and became carcinogenic.
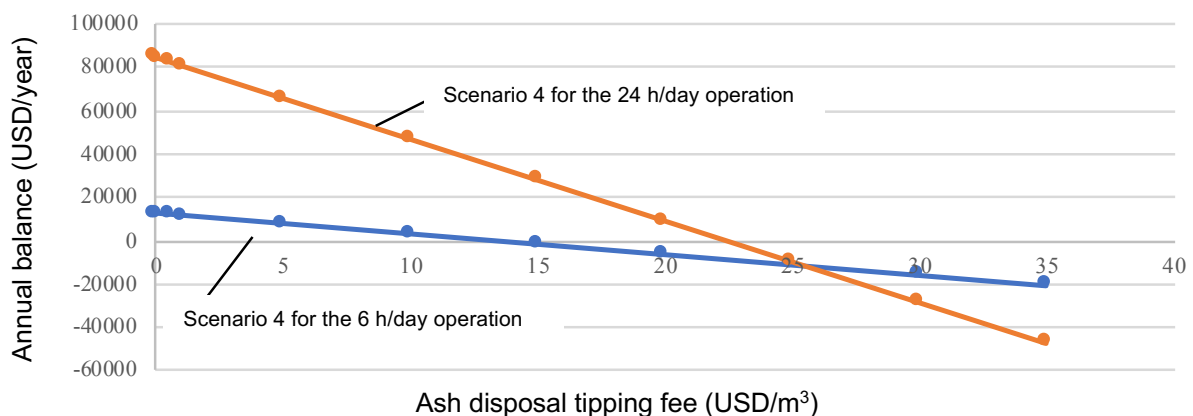
**Fig. 5-1-8. Comparison of the 6- and 24-h/day operations
when all ash must be disposed of**

When Rice Husk Collection and Hauling are Charged with Ash Disposal at 15 USD/m^3

The worst-case scenario is when stakeholders have to pay for both rice husk collection and hauling, and ash disposal (Fig. 5-1-9). Even though this is unrealistic, a 15 USD/m^3 ash disposal tipping fee was chosen because it allowed for financial sustainability (see previous section). The annual balance became more negative for the 6-h/day operation as rice husk collection and hauling cost increased (Scenario 8, 6 h/d operation). A slightly positive annual balance was observed for the 24-h/day operation; however, it became negative after rice husk collection and hauling fees reached 3 USD/m^3 (Scenario 8, 24 h/day operation). A 3 USD/m^3

fee for rice husk collection and hauling was unrealistically low; thus, the system was unsustainable under both 6- and 24-h/day operated systems when the ash disposal tipping fee was set at 15 USD/m^3. It was easy to ascertain the annual financial balance with an ash disposal tipping fee of 30 USD/m^3, which is the normal minimum.
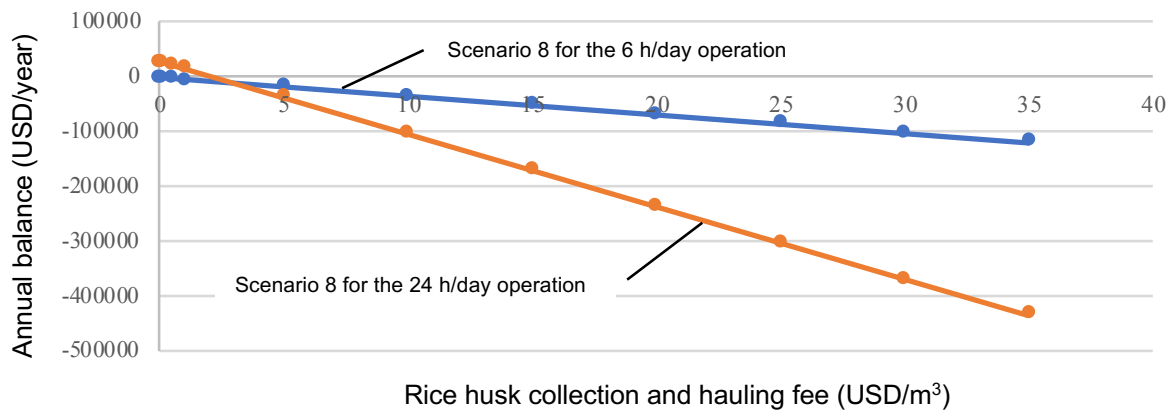
Fig. 5-1-9. Cases when both rice husk collection and hauling and ash disposal are charged

Sustainability of the System

Many financially "sustainable" scenarios were observed where income outweighed expenses. However, the conditions necessary to ensure sustainability were very limited, and most often, the scenarios were impractical. For example, the as-obtained fertilizers could not be sold, and a high ash disposal tipping fee hindered sustainability.

Considering all the results obtained (Table 5-1-5), it can be concluded that the following conditions are necessary to ensure sustainability: free or low-cost rice husk collection and hauling, the silica in the incinerated rice husk ash should be in the amorphous state, and the complete recycling of the ash. An example of a checklist for system sustainability is summarized in Fig. 5-1-10. Any of the three conditions can be the starting condition, i.e., "Collection and hauling" must not be the initial step as shown in the figure. The figure depicts only the cases that guarantee system sustainability; a system was considered unsustainable even if only one of the three conditions was not met.

Table 5-1-5.   Results of sustainability evaluation for Table 5-1-3

Sce-nario #	State of ash	Varying factor	Sustainability evaluation	Remarks
0	pellet	Fertilizer price	Sustainable @ $\geq$ 0.7 USD/kg for fertilizer price	Basic operation @ 0.7 USD/kg for fertilizer price
1	as-obtained	Fertilizer price	Sustainable	Difficulty of ash sale as fertilizer
2	pellet	Ash disposal tipping fee	Sustainable @ the 24-h/day operation	-Fertilizer price 0.7 USD/kg fixed -Half sold of fertilizer
3	as-obtained	Ash disposal tipping fee	Sustainable	-Fertilizer price 0.7 USD/kg fixed -Half sold of fertilizer -Difficulty of ash sale as fertilizer
4	as-obtained	Ash disposal tipping fee	-Sustainable @ $\leq$ 15 USD/m^3 for the 6 h/day operation for ash disposal tipping fee -Sustainable @ $\leq$ 22 USD/m^3 for the 24-h/day operation for ash disposal tipping fee	-Difficulty of ash sale as fertilizer -Ash disposal tipping fee is usually $\geq$ 30 USD/kg
5	Pellet	Rice husk collection and hauling fee	Unsustainable	-Fertilizer price 0.7 USD/kg fixed
6	as-obtained	Rice husk collection and hauling fee	Sustainable @ $\leq$ 17 USD/m^3 for rice husk collection and hauling fee	-Fertilizer price 0.7 USD/kg fixed -The less rice husk collection and hauling fee is, the more sustainable it is.
7	Pellet	Rice husk collection and hauling fee	Sustainable @ $\leq$ 5 USD/m^3 for rice husk collection and hauling fee	-Fertilizer price 1 USD/kg fixed -The less rice husk collection and hauling fee is, the more sustainable it is.
8	as-obtained	Rice husk collection and hauling fee	-Unsustainable for the 6-h/day operation -Sustainable @ $\leq$ 3 USD/m^3 for the 24-h/day operation and for rice husk collection and hauling fee	-The less rice husk collection and hauling fee is, the more sustainable it is. -Ash disposal tipping fee 15 USD/m^3 fixed. -Ash disposal tipping fee is usually $\geq$ 30 USD/kg

```
Collection and hauling
        │
        ▼
  Cheap or no cost ────────────────────────►  Expensive
        │                                          │
        ▼                                          │
Physical state of incineration ash                 │
        │        ╲                                  │
        ▼         ╲                                 │
   Amorphous       ►  Crystalline ──────────►       │
        │                                           │
        ▼                                           │
Recycling of incineration ash                       │
        │        ╲                                  │
        ▼         ╲                                 │
       Yes         ►  No ──────────────────►        │
        │                                           │
        ▼                                           ▼
  Rice Husks can                          Rice Husks can
  be recycled.                            NOT be recycled.
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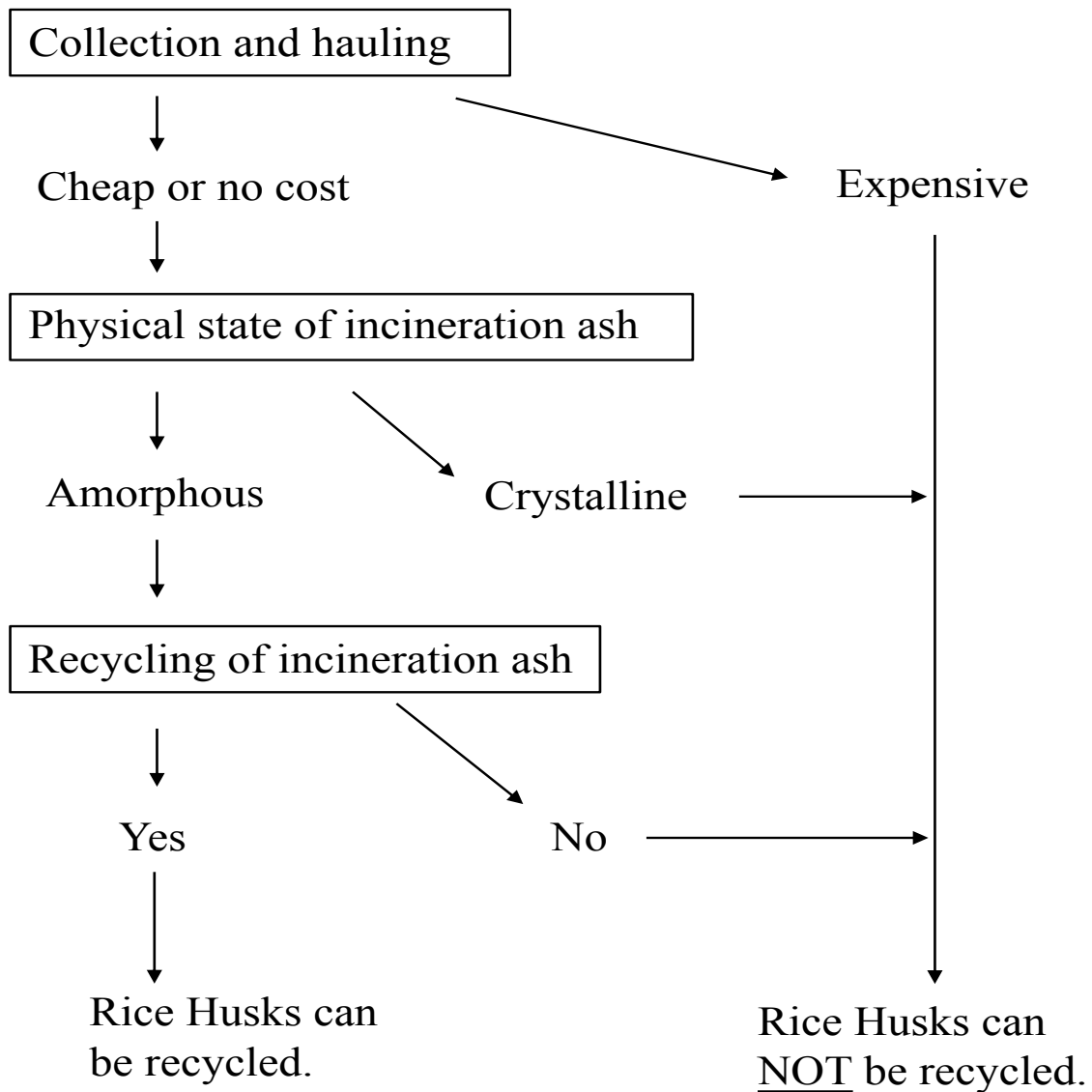
Fig. 5-1-10. Sustainability flow chart

Free collection and hauling, which is part of a typical Japanese agricultural business system, was discussed in our previous study (Sekifuji et al 2019). Additionally, in Japan, most farmers belong to a local agricultural association (Fig. 5-1-11), and they take their agricultural products to the shops operated by these local associations. At times, members of these associations receive agricultural advice regarding the purchase of materials, such as fertilizers and machinery. Additionally, they can borrow money and even request funeral services. A local agricultural association is part of the famers' lives. Farmers bring their harvested paddies to the rice centers operated by these local associations, where the rice is milled and sold. Under the association scheme, rice husk is gathered at the community rice center free of charge and is used by the association for energy recovery; further, the fertilizer developed from the

incinerated rice husk ash after recovery is sold. The association can sell the silica fertilizer to members, given that these members also buy agricultural materials from the association.

Collection and hauling process (at no cost)
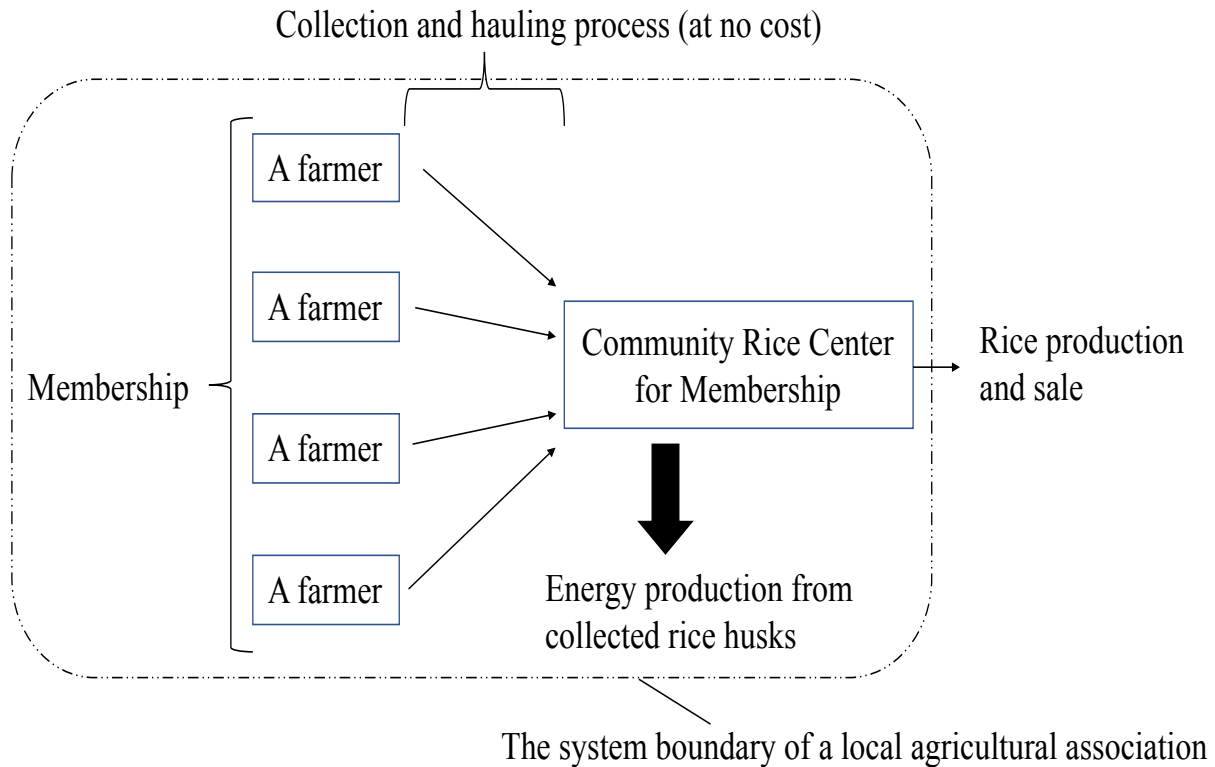
Fig. 5-1-11. System boundary of a local agricultural association

Obtaining silica in the amorphous state after incineration of the rice husk is essential. As previously reported (Sekifuji et al 2019), controlled rice husk incineration is essential to keep the silica in the amorphous state, which has a wide variety of applications, including fertilizers, solar panels, insulators, refractories, high-performance concrete, waterproofing chemicals, food, healthcare, and cosmetics (Pode 2016). For a local agricultural association, selling the ash as fertilizer is tremendously advantageous over selling it as a raw material for other products because it can be sold to farmers, who are members of the association. If the fertilizer cannot be sold and the silica is still amorphous, it is essential that the ash be disposed outside the local association's jurisdiction or to be freely given to users. In this study, to better reflect the costs considered by Armington et al (2018), administrative costs were not considered. Therefore, the results obtained are not an adequate reflection of the system given that administrative costs, which often represent an additional expenditure, were not considered.

Given that a considerable amount of ash is generated, it is necessary for the ash to be completely used— 20 % of the weight of rice husk is converted to ash compared with only 0.1 % for wooden biomass. Moreover, with respect to returning the silica to its original source, a paddy field is ideal for recycling. Silica is applied between the soil and the rice plants continually, resulting in an ideal agricultural loop. Notably, the essential conditions described herein are extremely important with respect to pursuing a sustainably ideal agricultural system.

CONCLUSIONS

The following conclusions were drawn from this study:
- A 24-h/day operated system is more profitable than one that is operated at 6-h/day.
- The pelletizing process is costly; however, the fertilizer in the pellet form can be sold at a relatively higher price.
- The as-obtained fertilizer is considerably cheaper in terms of production cost; however, selling puts sustainability at risk because it cannot be sold at a high price.
- The system becomes unsustainable when rice husk collection and hauling are charged.
- The system becomes unsustainable when ash disposal is charged.
- To ensure recycling, the silica content of the ash must be in the amorphous state.
- All the ash must be recycled in order to make the system sustainable.

Based on the results, the following are essential considerations to ensure sustainability: free or low-cost rice husk collection and hauling, the silica in the incinerated rice husk ash must be in the amorphous state, and the complete recycling of the ash.

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Chapter VI   Conclusions

Chapter I

1-1.   At present, rice husk is being used in many applications as a biomass resource. The method of rice husk quality evaluation, especially solubility, is not codified and therefore values cannot be compared across regions and institutions. In this study, the solubility of silica in rice husk ash was analyzed, and a systematic measurement process was proposed so as to make global sharing of data easier. From the analysis results, we determined that the Japanese standard method 4.4.1.c could be simplified to reduce the complexity of the measurement procedure. For a consistent and high accuracy measurement of the solubility of silica in rice husk ash, an acid treatment procedure is necessary. Since solubility increases as the surface area of ash decreases, powdering of samples is not necessary and ash can be used as-is for solubility measurements. Ash became bulky as the burning temperature increased, indicating that the silica did not fully transit to crystalline state in the conditions tested. Fixed carbon, volatile matter, and moisture content may also affect solubility up to 800 °C.

Chapter II

2-1.   Amorphous silica in rice husk ash is a reliable and sustainable resource, although rice husks are currently an issue for farmers. Amorphous silica is a resource in various industrial applications and can easily be obtained from rice husks if they are treated correctly. If the treatment is not conducted properly, amorphous silica becomes crystalline, which is carcinogenic. In this study, physio-chemical observations of the transformation of amorphous to crystalline silica were conducted under "no-fixed carbon" conditions. It was found that amorphous silica in rice husks transformed into crystalline silica at burning temperatures of over 1,000 °C. Total silica (T-silica) in the ash burned at 500 °C—800 °C, almost equal to the burning temperature of soluble silica (S-silica), and beyond 900 °C, the non-S-silica portion of T-silica increased. From the morphological observations, at low temperatures the rice husk ash was fragile and did not hold its original shape; in contrast, the rice husk ash held its original shape at high temperatures. At extremely high temperatures, such as 1,000 and 1,500 °C, the original shapes seemed to shrink by melting on the ash's surface of the ash.

2-2.   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. 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. 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.

Chapter III

3-1. Optimal conditions were investigated for the operation of a boiler using rice husks as fuel. Superior operation resulted in the production of high quality ash as well as heat recovery. Good quality ash is a useful resource that can bring profits to a local community. Rice husks were burned in a boiler and the boiler operation was evaluated by measuring the ash solubility in an alkali solution. The operational factors influencing the performance were determined. The study was located at the local Imizuno Agricultural Association (IAA) in Imizu, Japan, the location of Toyama Prefectural University. Data were collected from June 2011 to March 2016. The quality of ash was evaluated by examining its solubility. The NaOH method and Testing Method 4.4.1.c were employed to measure solubility. The operational factors of temperature control, maximum temperature setting, air flow capacity, and fire grate movement pattern were chosen to determine the optimal boiler performance. The following was determined for temperature control: do not use the AUTO setting at the beginning of the process but engage the AUTO setting once the boiler has finished idling. The optimal maximum temperature was found to be 500 ˚C; the air flow capacity was 30 Hz; and the fire grate moving pattern was 5-5-6. For boiler burning or an exothermal reaction, two phases were needed to produce a better quality of ash: an exothermal reaction for the first phase and an endothermic reaction for the second phase.

3-2. The "amorphous" state of silica is the critical characteristic necessary for its use in various applications. Extensive experimentation has determined that the highest quality rice husk ash is obtained after treating the ash in two steps: a burning step followed by a curing step. The purpose of this study was to determine how to conduct these two steps such that the highest quality silica possible could be obtained from the ash. Using the solubility of silica as an indicator of the amorphous state, the quality of silica in rice husk ash produced by three treatment processes was evaluated; after all, rice husks were incinerated as a basic treatment.

Three treatment methods for the curing step were evaluated: a heating drum, insulating drums, and a sink within the incinerator system. As a result, the highest solubility silica was obtained from the sink, which produced silica with more than 70 % solubility, compared to about 40 % in other treatments. It can be concluded that the ash should be treated within the incinerator system without being exposed to cold temperatures outside.

3-3.   Rice husks are resources that should be recycled in a sustainable way, thus creating a win-win relationship between stakeholders, consumers, and society. Silica is a very valuable material and used for many industrial purposes. Rice husks contains 20 % of silica by weight, and can therefore be considered a biological silica ore. To recycle rice husks in a sustainable way, the ash produced from burning rice husks must also be used as a resource. In this study, based on the concept that rice husk ash should be recycled as silica fertilizer, we compared the economic feasibility of two recycling systems: Heat recovery from hot water and generation of electricity from hot water. Questionnaires were also conducted regarding farmers' expectations of silica fertilizer made from rice husk ash. We found that the system involving heat recovery from hot water was sustainable; however, generating electricity from hot water was cost-prohibitive. It must be noted that the validity of this result might be limited to Japan, where electricity generation is highly regulated. On the other hand, areas that already struggle to dispose of their rice husks should consider using rice husks to produce energy.

Chapter IV

4-1.   The aim of this study was to evaluate the taste of rice grown in soil treated with rice husk silica in order to elucidate the potential use of rice husk silica as a fertilizer in terms of taste of rice. Rice plants were grown in soil treated with rice husk silica and officially approved, commercial silica fertilizer. The taste of the rice plants was compared based on their quality evaluation value (QEV). Paddy fields were divided based on the type and amount of silica applied. The rice plants were grown under different conditions. The growth of rice plants and silica sorption by rice plants were analyzed to obtain data on the physical state of the rice plants. Taste of rice was evaluated by the QEV based on four parameters, contents of protein, water, amylose, and fatty acid. It was observed that the taste of rice grown in soil treated with rice husk silica was not different from that of the rice grown in soil treated with commercial silica fertilizer. Rice husk silica can be used as a silica fertilizer in terms of taste of rice.

4-2.   This study aims to evaluate the potential negative effects of rice husk as a source of fertilizer on plant growth. Growth tests were conducted on komatsuna (*Brassica rapa* var. *perviridis*) using three types of experiment. A pot experiment was conducted to compare different fertilizers on an individual basis. A second pot experiment was conducted to compare different mixtures of fertilizers. Finally, a field experiment was performed to determine the effects of the application of different quantities of silica. The results showed that komatsuna grew better with the application of silica mixed with fertilizer, and that there was an optimal quantity of silica to be used, when used on its own. It was found that, in all cases, the silica in the rice husk ash did not have any measurable negative effects on the growth of the komatsuna. We therefore conclude that rice husk silica can undoubtedly be used for plant cultivation.

Chapter V

5-1.   To ensure the sustainability of rice husk recycling schemes, there are essential conditions that should be considered. In this study, a system in which a fertilizer was obtained after rice husk heat treatment, which also produces hot water as a heat recovery strategy, was considered, and its financial sustainability, based on different conditions in place, was then evaluated. Based on a previous study, three essential conditions that are necessary for the sustainability of the system were identified (i.e., free or low-cost rice husk collection and hauling, production of silica in the amorphous state, and complete recycling of rice husk ash). The necessity of these conditions was confirmed based on the sustainability of the financial balance of the system. A 24-h/d operated system is more profitable than one that is operated at 6-h/d. The pelletizing process is costly; however, the fertilizer in the pellet form can be sold at a relatively higher price. The system was unsustainable when rice husk collection and hauling as well as ash disposal fees, were charged. Therefore, the cost of rice husk collection, hauling, and ash disposal as well as the amorphous state of the ash, were confirmed as conditions that are necessary to ensure the sustainability of a rice husk recycling scheme.

Chapter VII   Recommendations and Considerations

The main goal of this study is to establish an ideal agriculture loop in Japan.

Knowledge obtained from this study is applicable to developing countries in Southeast Asia, where more rice is grown and more rice husks are generated compared with Japan. Furthermore, rice is harvested three or four times a year in Southeast Asia, whereas it is harvested only once yearly in Japan. Rice husks are discharged into water bodies (Fig. 7-1). In this context, the treatment of rice husks in Japan is the same as that in Southeast Asia. Furthermore, in Japan, rice husks are discharged from the boundary of residential areas as industrial waste.

Fig. 7-1. Discharged rice husks in water body in Myanmar

As mentioned earlier, rice husk is a useful resource as it contains a significant amount of silica, which is typically used in industrial products such as cosmetics, concrete, refractory materials, ceramics, fertilizers, and solar panels. In fact, Si is the second most abundant element in the crust of the Earth, following oxygen. Therefore, it can be concluded that a significant amount of silica exists in the crust; however, silica cannot be used because it is scattered across many locations. A resource must be stocked in one location for it to be utilized effectively. Rice

plants absorb silica from soil and accumulates it in the rice husk; hence, risk husks are known as the "bio-ore of silica."

Rice husk is a resource of silica and can produce energy when burned. Many communities in Southeast Asia do not have electricity in their villages. Rice husks have not been focused on by the society of developing countries. However, some smart villages in Myanmar produce electricity using rice husk (Fig. 7-2), thereby enabling the use of light, refrigerators, television, and other electric appliances that improve their quality of life.

Fig. 7-2. Village in Myanmar supplied with electricity by rice husk boiler

The results of this study show that rice husk burning ash is concentrated and contains a high amount of silica; therefore, the ash can be used as a silica fertilizer. It appears that the smart villages mentioned earlier are not aware of the possibility of using ash for silica applications. Moreover, the burning of rice husks may not be mature for producing amorphous silica. The white dots indicated in Fig. 7-2 are in fact flying ash in the air. Silica in the ash may appear in the "grey zone," and its safety to humans must be investigated.

Knowledge obtained from this study can be applied to improve the conditions of developing countries in terms of utilizing rice husks as an energy source and producing silica resources. It is strongly believed that rice husk, which is currently regarded as a waste product, will become

a useful resource when applied with the appropriate technologies. Rice husk is a sustainable resource since rice is planted annually as the main food crop in Japan and Southeast Asia; additionally, it is an ideal biomass for the carbon neutral concept.

The consumption of rice by "chopsticks countries" may increase in the future. Rice, as not only a food source, but also an energy source, may be key for establishing a sustainable society in the future. Cryptocurrency, robots, space, and metaverse are words of the future. It is envisioned that "rice husk" will be added to the list.

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