Environmentally Benign Reuse of Agricultural Wastes to Prepare High-Purity Silica from Rice Husks†

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Abstract

Rice husk, one of main agricultural wastes in South-east Asia countries, is well known as renewable resource to produce both energy and high-purity silica (SiO_2), because it consists of 70% organics and 20% amorphous SiO_2. The conventional process of recovering silica originating from rice husks requires a leaching treatment by strong acid solutions, such as sulfuric acid (H_2SO_4), hydrochloric acid (HCl) and nitric acid (HNO_3), to remove metallic impurities from the rice husks before combustion. The use of these acid solutions, however, is hazardous to the environment and human life, and difficult for process-cost-saving in mass-production due to expensive and complicated disposal systems. In this study, an environmentally benign, harmless to human as well as economical process to produce high-purity amorphous SiO_2 powder originating from rice husks has been established without using strong acids. From the viewpoint of a harmless influence on human body, carboxylic acids such as a citric acid or oxalic acid are employed in the acid leaching treatment of rice husks. In this alkali impurities are effectively removed from husks via a chelate reaction between carboxyl (-COOH) and alkali elements. In the experiment, first of all, it was shown that the carboxylic acid leaching was effective in promoting the hydrolysis of organics by DTA and GCMS. From experimental results on the optimization of concentration and temperature of the carboxylic acid solution by DTA, XRF and ICP analysis, it was found that a concentration of 5% or more was enough to both increase SiO_2 purity over 99% and remarkably reduce alkali metal impurities in the rice husk ashes. Amorphous SiO_2 powder originating from rice husks has a porous structure, so that it was also easy to control its particle size by dry milling or a grinding process.

KEY WORDS: (Rice Husk) (Silica) (Carboxylic Acid Leaching) (Hydrolysis) (Optimization Parameters)

1. Introduction

Rice husks are agro-wastes produced in large amounts of about 120 million tons per year in the world [1]. It is well known as one of the most promising agricultural by-products because of its possible use or application for the production of a variety of inorganic materials [2-4]. This is because the major constituents of rice husks are ash and organics such as cellulose, hemi-cellulose, and lignin [5]. Silicon atoms exist in the protuberances and hairs on the outer and inner epidermis of the rice husks [6], and are easily extracted as silica (SiO_2) ashes by burning in air. Their applications have been discussed for various industrial products and as raw materials. For example, refractory materials, ceramic or metal matrix composites, semiconductor materials, and additives of cement, concrete and metals are involved [7-11]. From the viewpoint of the improvement of silica purity, it is necessary to reduce alkali metal impurities of K and Na. This is because a eutectic reaction between alkali metals and SiO_2 occurs at elevated temperatures in burning, and carbon from the organics remains in the SiO_2 [12, 13]. In the previous studies, when removing metallic impurities from rice husks, a leaching treatment by strong acid solutions, such as sulfuric acid (H_2SO_4), hydrochloric acid (HCl) and nitric acid (HNO_3) has been employed [14-18]. These however, cause significant hazards to the environment and human life, and also cause economical problems; increase of the process cost due to a necessary use of expensive materials with corrosion resistance for leaching baths, repetition of water rinsing of acid-leached materials, etc. Special disposal treatments of used acid solutions and equipment are also required. From environmentally benign and economical points of view, the utilization of organic acid treatment was suggested[19]. This involved indicated the effective removal of metallic impurities and carbon of rice husks by oxalic acid leaching, and led to improved silica ash purity of 99% or more. The color and morphology changes were discussed in detail. However, the effect of carboxyl groups of organic acids on the effective removal of impurities was not mentioned at all.

In this study, a harmless to human and environment,

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and economical process to prepare high-purity amorphous silica from rice husks has been established by the carboxylic acid leaching treatment instead of the conventional strong acids. In the experiments, DTA and GCMS analyses were carried out to evaluate the hydrolysis and dehydration reaction of organics by carboxylic acid leaching, compared to the conventional strong acids. The effects of the concentration and temperature of carboxylic acid solutions on the content of SiO_2, carbon and other impurities of as-leached rice husks and their ashes are investigated by DTA, XRF and ICP analyses. Water-rinsing effects in acid-leached materials on the removal of metallic impurities are also investigated. Optimized conditions in the acid leaching treatment for high-purity amorphous silica ashes were suggested. Finally, characteristic of SiO_2 ashes such as crystal structure, particle size distribution and morphology, are investigated by XRD analysis, and SEM observation.

2. Experimental

The acid leaching parameters such as concentration and temperature of carboxylic acid solutions, and combustion temperature of rice husks were optimized to reduce both alkali metal impurities and carbon contents of the ashes as much as possible. Raw materials of rice husks harvested in Niigata, Japan were employed. Citric acid ($C_6H_8O_7$), oxalic acid ($C_2H_2O_4$) and malic acid ($C_4H_6O_5$) were selected in this study. 20g of rice husks were soaked in the carboxylic acid solution of 500ml for 900s; the concentration was 1%~30%, and its temperature was controlled at 293~353K. The repetition of water rinsing treatment on acid-leached rice husks was carried out to completely remove the acid from them. After drying husks at 383K for 7.2ks in air, they were combusted in air to completely remove organics of cellulose, hemi-cellulose and lignin. The crystal structure of silica ashes strongly depends on the burning temperature of rice husks, that is, high temperature combustion causes the silica transformation of amorphous to crystalline structure such as quarts, crystobalite and trydymite. The temperature range from 873 to 1423K was applied in burning rice husks.

The effect of the carboxylic acid leaching treatment on a hydrolysis of some organics in husks was evaluated by the exothermic or endothermic heat of each acid-leached husk in DTA (Differential Thermal Analysis) data by using Shimadzu DTG-60. It was measured at 293 ~1273K with a heating ratio of 10C/min. GCMS (Gas Chromatograph Mass Spectrometer, Agilent-5973N) analysis was also carried out to analyze the hydrolysis behavior of organics in heating at 673K and 873K. The quantitative analysis of SiO_2, carbon and other elements of the ash was conducted using XRF (X-ray fluorescence) and ICP (Inductively Coupled Plasma). Dependence of the crystallization of silica ashes on the combustion temperature was examined by XRD (X-ray Diffraction) analysis (Shimadzu XRD-6100).

3. Results and Discussion

The utilization of carboxylic acid leaching instead of strong acid is expected to both progress hydrolysis reaction of organics and reduce or remove alkali metal impurities such as K and Na from rice husks in order to prepare high-purity amorphous silica ashes. In particular, the removal of metallic impurities is possibly accelerated by a chelate reaction of carboxyl (-COOH) groups with metal ions in solutions. **Figure 1** shows DTA profiles of rice husks leached by citric acid (a), oxalic acid (b) and sulfuric acid solution (c), compared with as-received raw materials without any leaching treatment. When using carboxylic acids in Fig.1 (a) and (b), they indicate an endothermic heat at 343K~623K, not a large exothermic heat at 683K~773K shown in as-received raw husks of (d). There is no significant difference of DTA profiles in the case of leaching treatment by between carboxylic acid and sulfuric acid shown in (c). The previous study indicates this endothermic heat due to the hydrolysis of cellulose generating levoglucosan [20].

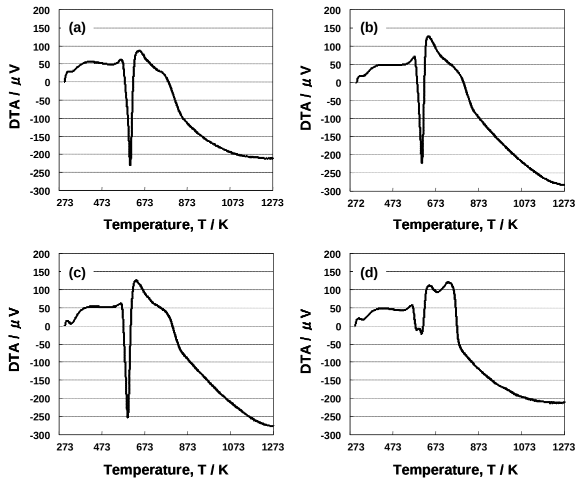

Fig.1 DAT profiles of rice husk leached by different acid solution (a) ~ (c) and raw material (d); citric acid (a), oxalic acid (b) and sulfuric acid solution (c).

Figure 2 reveals GCMS results on rice husk heated at 673K via citric acid leaching, compared to that via sulfuric acid washing. In both profiles, typical peaks are detected in retention time at 2.3 min. and 7.5min., which correspond to furfural ($C_5H_4O_2$) and levoglucosan peaks, respectively. The former is generated from hemi-cellulose via xylose ($C_5H_{10}O_5$) by hydrolysis and dehydration. Levoglucosan is also from cellulose by thermal resolution via hydrolysis reaction. That is, the endothermic heat of DTA profiles shown in Fig.1 (a) and (b) is caused by the hydrolysis of organics contained in rice husks, and the carboxylic acid leaching treatment has the same effect to accelerate hydrolysis as the conventional strong acid solutions. The comparison of the endothermic heats of DTA is available to quantitatively evaluate the effect of the carboxylic acid leaching conditions on the hydrolysis and thermal resolution of some organics. This result is the same as that in the previous study in using H_2SO_4

leaching process on rice husks [20].

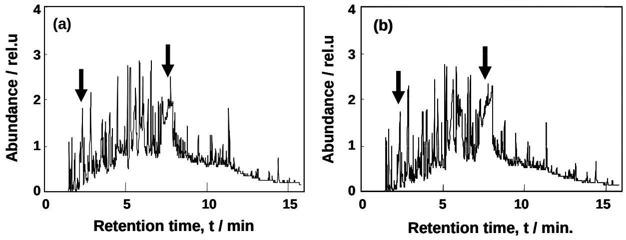

Fig.2 Gas Chromatograph Mass Spectrometer results on rice husk heated at 673K via citric acid leaching process, compared to that via sulfuric acid washing.

Figure 3 indicates the comparison of endothermic heats of rice husks leached by carboxylic acid solutions (citric acid and malic acid) with strong acid ones (sulfuric acid and hydrochloric acid). The concentration of all solutions is 10%, and temperature and soaking time is controlled at 333K and for 900s, respectively when leaching rice husks. The endothermic heat in the use of conventional strong acids is 4.2~4.8 J/mg. On the other hand, that of carboxylic acid leaching is 5.7~6 J/mg, and larger than the former. That is, from a quantitative evaluation point of view, the hydrolysis effect by carboxylic acid solution leaching on rice husks is superior to the strong acid washing treatment.

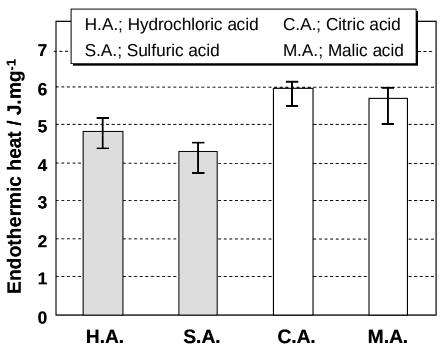

Fig.3 Endothermic heats in DTA on rice husk leached by carboxylic acid solutions (citric acid and malic acid) with strong acid ones (sulfuric acid and hydrochloric acid).

The hydrolysis behavior dependence on acid solution temperature is discussed. **Figure 4 (a)** shows DTA profiles of rice husks using 20% oxalic acid solution at 293K, 323K and 353K, compared to as-received ones with no leaching treatment. The utilization of oxalic acids also clearly reveals endothermic behavior of every material. This means the oxalic acid leaching is also available for hydrolysis of organics of rice husks. As shown in **Fig. 4 (b)**, its dependence on solution temperature is examined when using citric acid and oxalic acid with 20% concentration. It suggests that a higher temperature of acid solution is more effective in accelerating the hydrolysis and dehydration, that is, to remove the carbon remains in rice husk ashes. From an economical point of view, however, the suitable temperature of each acid solution is 323K~333K under mass-production using large scale leaching equipment systems.

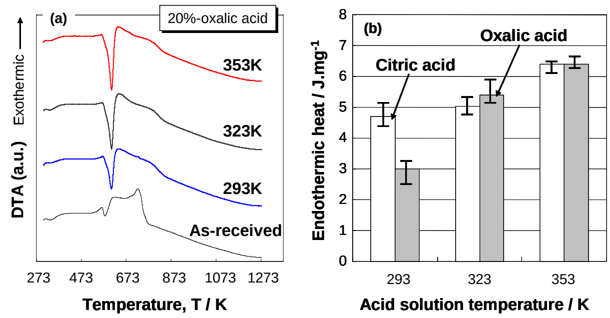

Fig.4 DTA profiles of rice husks using 20% oxalic acid solution at 293K, 323K and 353K, compared to as-received ones (a), and endothermic heat in DTA when using rice husks leached by each acid solution at elevated temperature.

The dependence of endothermic heat on the concentration of citric acid solution (353K) is investigated in **Fig. 5**. It gradually increases with increase in the concentration up to 5%, and is significantly larger than that of as-received rice husks with no leaching. When its concentration is over 5%, it stably saturates, that is, the remarkable acceleration of hydrolysis and dehydration of organics does not occur.

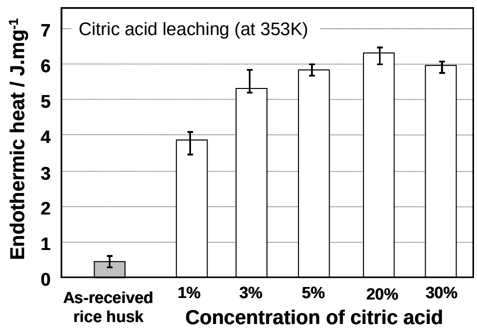

Fig.5 Dependence of endothermic heat in DTA of rice husks on concentration of citric acid solution at 353K.

Table 1 shows the chemical compositions of rice husk ashes by XRF and ICP analysis when employing husks leached in the citric or oxalic acid solution at 5% concentration and different temperatures, compared to as-received ones with no leaching. They were combusted at 1073K for 900s in air. From a viewpoint of carcinogenic risks to humans, the burning temperature was decided to completely hinder SiO_2 crystallization transformation to crystobalite [21], according to the previous results [20]. The content of alkali elements of K and Na is drastically decreased by using both carboxylic acid solutions. In particular, the content of K_2O is 1/20~1/100 or less than that of ashes without any leaching treatment. The other metallic oxide impurities are also remarkably reduced by using acid leaching. The carbon content of ashes decreases to less than 0.1% due to the decrease of alkali element impurities as mentioned above. Compared to citric and oxalic acid, the effect of carbon reduction by the former is much larger than that by oxalic acid leaching. The reason is, however, not clear at this moment. As the results of the above impurities reduction show, the carboxylic acid leaching of rice husks is able to prepare ashes consisting of high-purity SiO_2 of about 99% or more. In particular, a hot acid solution makes it possible to significantly increase SiO_2 purity of ashes. On the other hand, SiO_2 content of ashes via no leaching treatment is less than 95%, and metallic impurities, in particular a large amount of K_2O remains even after burning at 1073K. Particle size distribution analysis and SEM observation on rice husk ashes were carried out. The specimens were prepared via 5% citric acid leaching at 323K and combustion at 1073K, and granulated by milling for 10.8 ks. **Figure 6 (a)** indicates the mean particle size is about 6μm, and the maximum is less than 30μm in diameter. As shown in **(b)**, the silica powder consists of fine and spherical primary particles with less than 1μm. Therefore, such a segregated silica powder is useful to improve the flow ability required to concrete, medicine and food additives.

Table 1 Chemical compositions of rice husk ashes burned at 1073K after each acid leaching compared that with no leaching.

(mass%)	Without leaching	Citric acid leached			Oxalic acid leached		
Temp.		293K	323K	353K	293K	323K	353K
Conc.	——	5%	5%	5%	5%	5%	5%
Rinse	——	○	○	○	○	○	○
SiO_2	94.58	99.01	99.14	99.30	98.79	98.88	99.25
Al_2O_3	0.00	0.00	0.03	0.00	0.01	0.01	0.01
MgO	0.31	0.16	0.08	0.06	0.09	0.06	0.05
Na_2O	0.41	0.12	0.06	0.09	0.05	0.07	0.00
P_2O_5	0.41	0.33	0.29	0.27	0.29	0.30	0.19
S	0.11	0.05	0.03	0.01	0.04	0.05	0.07
K_2O	3.69	0.16	0.12	0.04	0.11	0.11	0.05
CaO	0.56	0.28	0.16	0.13	0.52	0.42	0.31
MnO	0.08	0.02	0.01	0.01	0.02	0.01	0.01
Fe_2O_3	0.04	0.03	0.03	0.02	0.02	0.02	0.01
BaO	0.04	0.02	0.03	0.03	0.02	0.03	0.00
C	0.60	0.10	0.10	0.09	0.17	0.18	0.19

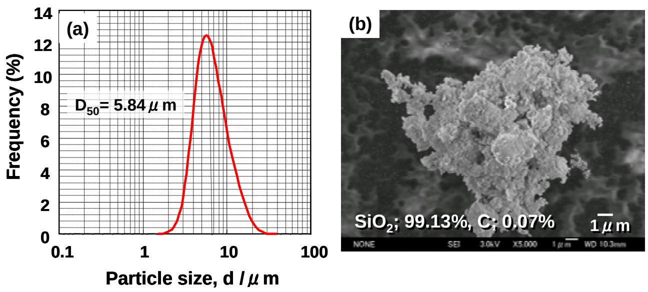

Fig.6 Particle size distribution of granulated rice husk ashes (a) and their morphology observed by SEM.

4. Conclusion

An environmentally benign recycling process of agricultural wastes such as rice husks was developed to produce high purity silica. It consists of carboxylic acid leaching of rice husks, instead of the conventional strong acid solutions, and air combustion process. DTA analysis and GCMS results indicate the carboxylic acid washing treatment is much more effective to accelerate hydrolysis and dehydration of organics, compared to the use of strong acid. It also reduces alkali metals and other metallic impurities by the chelate action of the carboxylic. Concerning the optimization of acid leaching process parameters, higher solution temperature is better, and 5% concentration is enough to produce silica ashes with a purity of 99% or more.

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