Journal of
Engineering and
Applied Sciences

SINCE 2000
MEDWELL PUBLICATIONS

Designing of Synthesizing High Purity Silica by Decarbonization of Rice Husks by Air Flow Firing and Subsequently Hot Water Treatment of the Resulting Rice Husk Ash

Hidetoshi Miyazaki, Tetsuya Sugihara, Yuki Makinose, Michiko Egawa and Makoto Handa
Graduate School of Natural Science Technology, Shimane University, 1060 Nishikawatsu, Matsue, Shimane 690-8504, Japan

Key words: Rice husk, silica, purify, potassium

Corresponding Author:
Hidetoshi Miyazaki
Graduate School of Natural Science Technology, Shimane University, 1060 Nishikawatsu, Matsue, Shimane 690-8504, Japan

Page No.: 182-185
Volume: 16, Issue 5, 2021
ISSN: 1816-949x
Journal of Engineering and Applied Sciences
Copy Right: Medwell Publications

Abstract: Rice husk was fired at 400~1000°C under air flow and a white color rice husk ash was obtained. IR spectral data confirmed the absence of water (-OH group) and organics in the rice husk ash obtained after firing at low-temperatures (<700°C). XRD spectra revealed that the rice husk ash obtained at <700°C was amorphous and that the rice husk ash fired at 1000°C crystallized to the cristobalite phase. The rice husk ashes fired at 400 and 700°C were treated with ion-exchanged water at 80°C. Potassium and phosphorus were removed from these rice husk ashes by the hot water treatment, after which the potassium content in these rice husk ashes (fired at 400 and 700°C) decreased from 5% (before treatment) to 1.5% (after treatment). Summarizing, it was demonstrated that the silica in rice husk can be obtained in high purity by the above-described series of treatments.

INTRODUCTION

In Japan, approximately 1.8 million tons of Rice Husk (RH) is generated per year. Rice husk ash (RHA) obtained by firing RH, contains significant amounts of silica and is therefore used as a filler for eco-cement[1] and light weight bricks[2]. On the other hand, approximately 20% of the generated RH is wasted every year. Therefore, it is important to effectively use or recycle the large amount of wasted RH.

RHs are primarily composed of organic substances (~80 wt.%) such as cellulose and lignin[3]. Of the remaining 20 wt.%, silica constitutes approximately 90%; further, it also comprises inorganic substances such as potassium and phosphorus[4]. Potassium (K) content in the RHA obtained after firing RH is a few percent; therefore it is necessary remove the K_2O present in order to use RHA as a silica source. Furthermore, RHA generally retains the black color carbon derived from organic matter after firing RH[5]. In order to increase the purity of SiO_2 in RHA, it is also necessary to remove this carbon. Figure 1 shows the photograph of the RH used in this study and fired at 700°C for 1 h without airflow. As shown in the figure, the resulting RHA appeared black-gray in color. In order to use RHA as a silica source, it is also necessary to prevent the occurrence of residual carbon after firing.

Treatment of RHA with hydrochloric acid, alkali and other additives to remove potassium from RH or RHA have been previously reported[5-7]. On the other hand, we have previously reported the application of a hot water treatment or a hydrothermal treatment to remove Na from glass[8] and to exchange Ca ion to Na ion in bentonite clay[9]. Therefore, based on our previous reports, we expected that the potassium in RHA could be removed by the ion exchange of potassium and hydrogen using water as solvent.

Fig. 1: The Photograph of the overview of the fired RH at 700°C for 1 h

In the present study, we aimed to obtain high purity silica in the RHA obtained by firing RH as follows: Firing RH under an air flow in order to remove the carbon in RHA. Removing potassium and other elements from the obtained RHA by hot water treatment.

MATERIALS AND METHODS

Experimental procedure: Rice Husk (RH, produced in Matsue, Shimane, Japan) was used as the starting material. All the firing and water treatments were performed without grinding the source RHs and RHAs. The RHs were fired at temperatures between 300 and 1000°C for 1~10 h under an air flow (0.8 L/min). The fired samples underwent immersion treatment twice in distilled water at 80°C. Subsequently, the liquid phase and the solid phase were separated by decantation. The resulting RHAs were dried at 150°C for 3h. The weights of all the RHAs before and after the treatment were measured. The pH of the treated water before and after the water treatment was measured with a pH meter (D-51, Horiba, Japan).

The RHA obtained after each treatment was powdered and its structure was evaluated by an infrared spectrometer (IR, Jasco FT-IR 4600, Japan) and an X-ray diffractometer (XRD, Rigaku Miniflex, Japan) with CuKα radiation (30 kV, 15 mA). An elemental analysis of the powders was performed using a wavelength-dispersive X-ray fluorescence analyzer (XRF, ZSX Primus, Rigaku, Japan).

RESULTS AND DISCUSSION

Figure 2 presents the overview photographs of the RHA after firing at various temperatures and time intervals. At 300°C, black tissues attributed to carbon on the RHA surface were observed even after prolonged firing (over 10 h firing). It is considered that the organic material was not completely fired and was only partially carbonized due to the low firing temperature. At 400°C firing, black tissues were observed after 1 h of firing, the color of the RHA became almost white after 10 h of firing. Black tissues were not observed in RHA after firing at 700 and 1000°C for 1 h. For these RHAs where black tissues were not observed, it was considered that the organics in the RH were sufficiently oxidized by the air flowing during firing. The relative weights of the RHA to the RH after firing were 20.46% at 300°C for 10 h, 19.75% at 400°C for 10 h and 19.41% for the sample fired at 700°C for 1 h and the relative weight was 18.85% for the sample fired at 1000°C for 1 h. The weight change after firing and the residual carbon of the obtained RHAs together with their IR measurements would be discussed later.

Fig. 2: The photograph of the overview of the RHA after firing at each temperature and time

Figure 3 illustrates the IR spectra of the source RH and the RHAs fired at various temperatures. Where, we employed the RHA fired at 400°C for 10 h which was assumed to have reacted well with the organics in the source RH. For the source RH, IR absorption peaks attributed to organics were observed at 1300-1700 cm^{-1} (OH, lignin, cellulose)[10], 2900 cm^{-1} (CH) and 3400 cm^{-1} (OH)[10] and the peaks attributed to SiO_2 were observed at 470, 800, 1100 and 1200 cm^{-1}[11]. In the RHA fired at 400 and 700°C, the IR peaks of OH were observed at around 1600 and 3400 cm^{-1} and the peaks corresponding to SiO_2 were observed at 470, 800, 1100 and 1200 cm^{-1}. The results suggested that water remained in the RHA fired

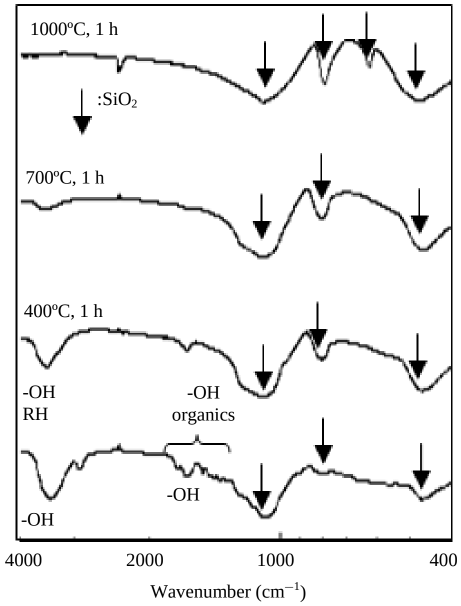

Fig. 3: The IR spectra for the source and the resulting RHA fired at various temperatures

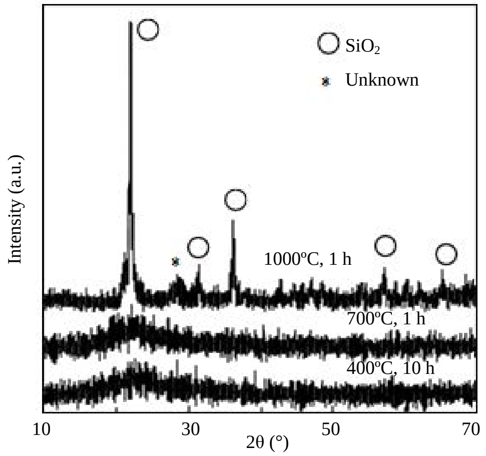

Fig. 4: The XRD patterns for the RHA fired at various temperatures

at 700°C or lower. IR peak attributed to dioxin was not observed for both the RHAs. For the RHA fired at 1000°C, only the peaks corresponding to SiO_2 were observed and the peaks of water (OH) were not observed. From the weight change (described above) and IR results, it was suggested that there were almost no residual organics at 400°C for 10 h and 700°C for 1 h and that water remained in the RHAs. For the RHA fired at 1000°C, no water remained in the RHA and its reduced relative weight in comparison with the RHA fired at a low temperature was attributed to water loss.

Figure 4 depicts the XRD pattern of the resulting RHAs. No XRD peak was observed for the RHAs fired at 700°C or lower indicating that amorphous SiO_2 was obtained in these firing conditions whereas cristobalite SiO_2 peaks were observed in the RHA fired at 1000°C.

Therefore, it was confirmed that the RHA obtained by firing at a low temperature was the amorphous silica containing-OH. These RHAs have an amorphous (metastable phase) structure and it is considered that elements such as potassium present in them can be easily removed by hot water (or hydrothermal treatment) when compared to the crystalline RHA (cristobalite, firing RH at 1000°C). The RHAs that were fired at 400°C for 10 h (hereinafter RHA 400) and 700°C for 1 h (hereinafter RHA 700) were immersed for 4 h twice in 80°C ion-exchanged water. The pH of the water before and after the immersion treatment was as follows: “Before treatment: pH<7, RHA400: first immersion-pH = 9.51, second immersion-pH = 8.46, RHA700: first immersion-pH = 9.17, second immersion-pH = 8.62”. The pH of the solution increased for all the treatment. We assumed that potassium was removed from the RHA and hydrogen ions in the water were intercalated into the RHA (K-H ion exchange occurred), the details pf which will be discussed later using elemental analysis data. The weight loss after hot-water treatment when compared to the initial weight was 6.36% for RHA400 and 4.98% for RHA700 indicating that RHA400 showed significant weight loss by hot water treatment. Since, the firing temperature of RHA400 was low, large amount of structural water (from IR results) remained in RHA400 suggesting that ion diffusion/exchange occurred easily.

Table 1 indicates the elemental analysis results of the main elements before and after the two immersion treatments. The RH before the treatment contained 5.18 wt.% of K_2O and after the treatment, the K_2O content significantly reduced to 1.28 wt.% for RHA400 and 1.51% for RHA700. The contents of other elements also decreased substantially, thereby increasing the SiO_2 content in RHA after immersion treatment. Here, some quantity of SiO_2 in the RHA was also assumed to elute in the water solvent. Phosphorus and sulfur were not observed in the water solvent after treatment of RHA400. It was found that RHA obtained by low-temperature RH firing could easily remove plant-derived elements such as phosphorus. On the other hand, a slight residue (P_2O_5, CaO, etc.) was observed in the water solvent of RHA 700. In short, by using RHA heat-treated at 700°C or less as the source, high-purity silica could be obtained by hot water treatment.

We completely dried the supernatant water solvent of the RHA400 and also performed an elemental analysis for this powder by an XRF analyzer as shown in Table 2. This dried powder was found to contain a large amount of SiO_2 and additionally, K_2O, P_2O_5, CaO were also observed. This result agreed well with the elemental

Table 1: The elemental analysis of RHAs before and after hot water treatment

Elemental analysis	SiO_2	K_2O	CaO	MnO	P_2O_5	SO_3	Other
RHA (400)	90.39	5.18	1.94	0.75	0.59	0.42	0.74
After treatment of RHA (400)	95.78	1.43	1.28	0.79	-	-	0.60
RHA (700)	89.73	5.48	2.05	0.77	0.67	0.52	0.78
After treatment of RHA (700)	94.68	1.51	2.00	0.79	0.20	0.18	0.63

Weight ratio (%)

Table 2: The elemental analysis of the dried powder of the supernatant water treated with hot water of the RHA400

Element	SiO_2	K_2O	P_2O_5	CaO	SO_3	Other
Weight ratio (%)	54.56	35.37	2.66	2.32	1.87	3.22

analysis results before and after the hot water treatment of the RHA400 (on Table 1). In short, it was confirmed that elements such as K_2O, CaO and P_2O_5 eluted in the water solvent during the immersion treatment of the RHA. Because the raw material (RH) is plant-derived and the resulting sample was composed of SiO_2, K_2O, CaO and P_2O_5, it is considered that the treated water or a dried powder of it can be reused as fertilizer.

CONCLUSION

White colored RHA without any carbon-derived black ash content could be obtained by firing the RH under air flow. RHAs obtained by firing RH at a low temperature of 700°C or less were composed of amorphous SiO_2 as the main phase and contained other compounds such as OH, K_2O and P_2O_5. The RHAs fired at 400 and 700°C were treated with ion exchange water at 80°C where K_2O, P_2O_5 and other elements were removed in the resulting RHAs. Through these simple procedures, we have suggested that silica can be purified from RH.

REFERENCES

01. Antiohos, S.K., V.G. Papadakis and S. Tsimas, 2014. Rice Husk Ash (RHA) effectiveness in cement and concrete as a function of reactive silica and fineness. Cement Concrete Res., 61: 20-27.
02. Raut, S.P., R.V. Ralegaonkar and S.A. Mandavgane, 2013. Utilization of recycle paper mill residue and rice husk ash in production of light weight bricks. Int. J. Arch. Civil Mech. Eng., Elsevier, 13: 269-275.
03. Barana, D., A. Salanti, M. Orlandi, D.S. Ali and L. Zoia, 2016. Biorefinery process for the simultaneous recovery of lignin, hemicelluloses, cellulose nanocrystals and silica from rice husk and *Arundo donax*. Ind. Crops Prod., 86: 31-39.
04. Kumagai, S., 2011. Utilization of rice husk through thermal processes. Wood Carbonization Res., 8: 10-17.
05. Shen, Y., 2017. Rice husk silica derived nanomaterials for sustainable applications. Renewable Sustainable Energy Rev., 80: 453-466.
06. Shinohara, Y. and N. Kohyama, 2004. Quantitative analysis of tridymite and cristobalite crystallized in rice husk ash by heating. Ind. Health, 42: 277-285.
07. Patel, M., A. Karera and P. Prasanna, 1987. Effect of thermal and chemical treatments on carbon and silica contents in rice husk. J. Mater. Sci., 22: 2457-2464.
08. Yoshida, S., H. Miyazaki, S. Sugawara, Y. Seike, H. Suzuki and T. Ota, 2015. [Synthesis of radiatively cooled Si_2N_2O particles using silicon dioxide main component powder obtained by hydrothermal treatment of waste glass powder (In Japanese)]. Waste J. Resour. Recycl. Soc., 26: 84-88.
09. Miyazaki, H., Y. Kitano, Y. Makinose, M. Handa and T. Nakashima, 2020. Synthesis of large-swelling Na-type bentonite by hydrothermal ion exchange. Clay Sci., 23: 47-53.
10. Zhang, H., X. Ding, X. Chen, Y. Ma, Z. Wang and X. Zhao, 2015. A new method of utilizing rice husk: Consecutively preparing D-xylose, organosolv lignin, ethanol and amorphous superfine silica. J. Hazard. Mater., 291: 65-73.
11. Miyazaki, H., K. Okada, K. Jinno and T. Ota, 2016. Fabrication of radiative cooling devices using Si_2N_2O nano-particles. J. Ceram. Soc. Japan, 124: 1185-1187.