

## Preparation of porous carbon/silica composites from rice husk powder

Takanori Watari\*, Hiroshi Tsubira, Toshio Torikai, Mitsunori Yada and Sachiko Furuta<sup>a</sup>

Saga University, 1 Honjo, Saga 840-8502 Japan

<sup>a</sup>Saga Ceramics Research Laboratory, Arita, Saga 844-0024 Japan

Porous carbon/SiO<sub>2</sub> composites were prepared by heating the compacts composed of the rice husk (RH) powders of small (<74 μm) (S) and medium (74-175 μm) (M) sizes. The packing density of the (S+M) mixture compact took a minimum value at S/(S+M) (in weight) (R)=0.5. The RH compacts were heated at 600 and 800°C in an alumina crucible covered with graphite granules to avoid the oxidation in air. The weight loss after the heat-treatment decreased with increasing R-value. The weight loss at 800°C was larger than that at 600°C. The carbon contents of the products at 800°C were 49-67 wt%. The porosity of the carbon/SiO<sub>2</sub> pellets decreased from 83% (R=0.3) to 51% (R=1) with increasing R-value. The macro-pore size in the products decreased from 33 μm to 7.5 μm with increasing R-value. The porosity and macro-pore size were not affected by the treatment temperature. The specific surface area (SSA) of the pellets heated at 800°C decreased from 262 to 207 m<sup>2</sup>g<sup>-1</sup> with increasing R-value. The pellets heated at 600°C had 221 m<sup>2</sup>g<sup>-1</sup> of SSA value at R=0.3, but those of R=0.5-1.0 showed very small SSA values, 16-45 m<sup>2</sup>g<sup>-1</sup>.

**Key words:** rice husk, porous material, carbon, silica.

### Introduction

Rice husk (RH), a waste agriculture by-product, consists of organic materials (e.g. cellulose, hemicellulose and lignin) (~75 wt%), amorphous SiO<sub>2</sub> (~15 wt%) and water (~10 wt%) [1]. By burning out the organics, a porous SiO<sub>2</sub> may be obtained [2]. The SiO<sub>2</sub> in the RH is very active and has been used as a raw material for the preparation of zeolite [3]. Also, SiC whiskers were fabricated by the reaction between the organic materials and SiO<sub>2</sub> in the RH at 1100-1400°C [1]. Furthermore, porous carbons with high specific surface area (SSA) were made by heating the RH under an inert gas [4, 5]. These methods included additional treatments in order to get the carbon with high SSA value. Recently, a new attempt to simplify the process has been investigated [6].

The present study also tried to obtain a porous carbon with a high surface area by a simple process using RH powders. The powder compacts made by the mixture of the RH powders with different sizes show a different pore structure depending on the mixing ratio. In this paper, the effects of the mixing ratio and treatment temperature on the properties of the resulting carbon/SiO<sub>2</sub> composites were investigated.

### Experimental procedure

Two commercial RH powders (S-RH (<74 μm) and

M-RH (74-175 μm), Daiso Trading Co., Ltd) were used in this work. Since the rice husk has a shell structure, the commercial RH powder, especially the larger M-RH powder, contains anisotropic plate-like particles. S- and M-RH powders were mixed homogeneously in the ratio, S/(S+M) (R), from 0.3 to 1.0 in weight. In order to avoid the change in size during mixing, a special mixer ("Hybrid Mixer", Keyence Co. Ltd) was used in this work. The mixed powder containing water was pressed at 1.3 MPa into a pellet (φ 10 mm × 5 mm) and put in an alumina crucible with an alumina cover. This crucible was put in a larger alumina crucible and covered with graphite powder. The outer crucible had an alumina cover in order to avoid the combustion of the graphite powder in air. This crucible set was heated at 600 or 800°C for 2h in air. The heating rate was 20 Kminute<sup>-1</sup>.

The thermal behaviors of the RH compact were evaluated using thermogravimetric analysis (TG) in a N<sub>2</sub> or air flow. The microstructures were observed with a scanning electron microscope (SEM). The specific surface area (SSA) was measured with a N<sub>2</sub> gas adsorption (BET) method. The pore size distribution of the product was measured with a mercury porosimeter (MP) and also calculated from the N<sub>2</sub> gas desorption behavior using one Berret-Joyner-Halenda (BJH) method.

### Results and Discussion

#### Powder compaction

Zok *et al.* [7] examined the compact density depending on the effect of the mixture ratio between two kinds of powders with different sizes. The compact density

\*Corresponding author:  
Tel : +81-952-28-8683  
Fax: +81-952-28-8591  
E-mail: watarit@cc.saga-u.ac.jp

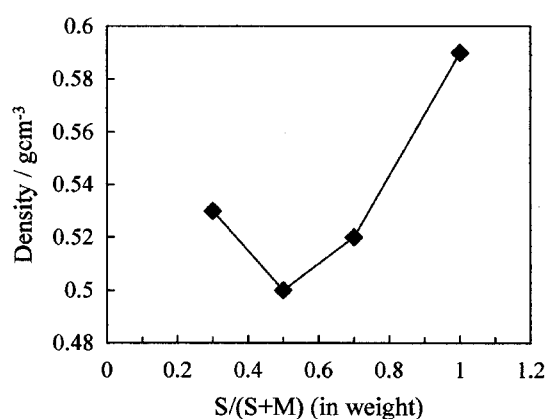


Fig. 1. Change in density of (S-MH+M-RH) powder compact with mixing ratio.

increased by the mixing and took a maximum value when the content of the larger particles was 73.5 wt%. In the present work, however, the change in the density of the RH powder compact with the R-value showed a different behavior (Fig. 1). The compact of R=0 was very weak and its density could not be measured. The density of the RH compact (R=1) was 0.59 g cm<sup>-3</sup>, but it decreased by the addition of the larger M-RH powder. This may be due to the disturbance in the S-RH powder packing by the anisotropic particles contained in M-RH powder. According to Fig. 1, it could be assumed that the pore structure of the compact also changes with the mixing ratio.

### Thermal behavior

The organic compounds decompose on heating in an inert gas and partly change to H<sub>2</sub>O, CO<sub>2</sub>, and volatile compounds [8, 9]. The change in the weight loss of an RH compact (R=0.5) with temperature under N<sub>2</sub> flow is depicted in Fig. 2. The specimen was heated up at 20 K minute<sup>-1</sup> and kept at 600°C for 2h. Three steps of the weight loss were observed up to 600°C. The first one (<150°C) is due to the water vaporization, and the second and third ones occurred from the decomposition

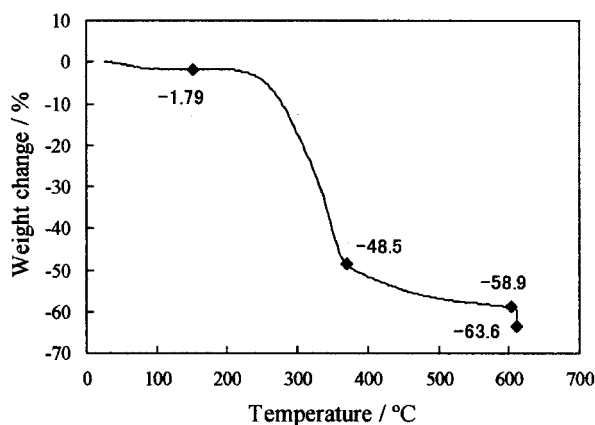


Fig. 2. Weight change of RH compact (R=0.5) with temperature under N<sub>2</sub> flow.

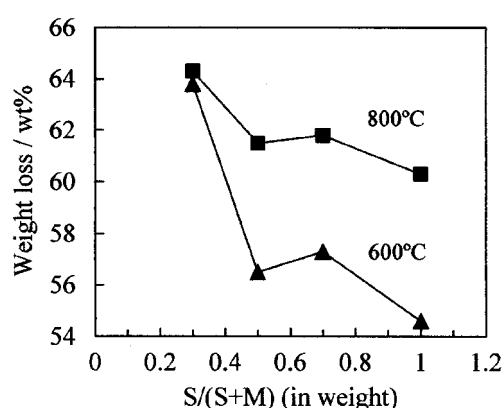


Fig. 3. Change in weight loss of RH compact after heat-treatment with mixing ratio.

and volatilization of the organic substances. The second weight loss at 200–350°C was very large, ~45 wt%. Liou *et al.* [8] reported that the dehydration and depolymerization of organics, and the following volatilization and formation of intermediates occurred in this temperature range. During the third broad weight loss above 350°C, the intermediates changed to gaseous materials and tars. They reported the decomposition was complete at 580°C, but, in the present work, a weight loss from 60.0 to 63.6 wt% was observed even at 600°C. The decomposition behavior of the natural organics was very complicated [10]. Therefore, the difference in the decomposition conditions between this work and these in reference [8] may influence the weight loss behavior.

Porous carbon/SiO<sub>2</sub> pellets were made by heating the compact mixtures. The content of water (2 wt%), organics (87 wt%) and silica (11 wt%) were almost the same in dried S- and M-RH samples. Therefore, the weight loss of the compact mixture after the carbonization should not be affected by the mixing ratio. In this work, however, the total weight loss changed with the R-value as shown in Fig. 3. The weight loss at 600 and 800°C decreased from 63.8 to 54.6 wt% and from 64.3 to 60.3 wt% with increasing R-value, respectively. These behaviors can be explained by considering the difference in the density, that is, the pore structure, of the raw RH compact. The powder compact of R=0.3 must have larger pores because of the co-existing anisotropic RH particles. The larger pores in this compact make it easy for the volatile materials to leave through them. This also accelerates the decomposition of organics. On the other hand, in the compact of R=1.0, the pore size is small and this depresses the elimination of the gaseous organics. This microstructural change in the powder compact is supported by the SEM observation of the resulting carbon/SiO<sub>2</sub> pellets as shown later (Fig. 5). The higher temperature accelerates the decomposition and volatilization of the organics in the RH, therefore, a larger weight loss was observed at 800°C. The calculated carbon contents of the resulting pellets from the weight loss values were 69.2–72.3 wt%. The measured one at

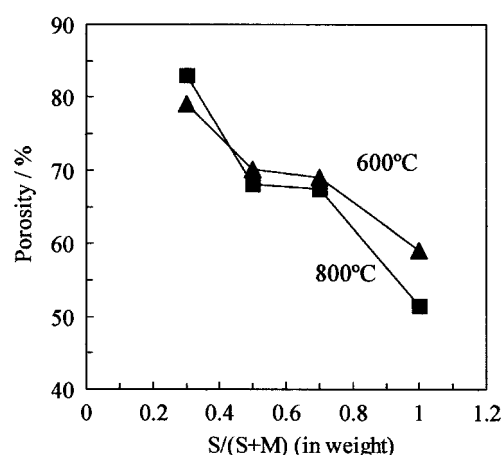


Fig. 4. Change in porosity of carbon/SiO<sub>2</sub> pellet with mixing ratio.

R=0.3 was 67.2 wt% and this is close to the calculated one, but the others at R=0.5-1.0 showed very low carbon contents, 49-56 wt%. This difference is under consideration.

#### Characterization of Carbon/SiO<sub>2</sub> composites

The density of the carbon/SiO<sub>2</sub> pellet varied from 0.40 to 0.56 gcm<sup>-3</sup>, which did not show a systematic change with the production conditions. The porosity of the pellet, however, decreased linearly from 83 to 51% with increasing R-value from 0.3 to 1.0 as shown in Fig. 4. This behavior is almost consistent with that in Fig. 3. The lower weight loss leads to the lower porosity. These results seem to be inconsistent with the compact

density (Fig. 1). The RH compact with a relatively higher density (R=0.3) resulted in the highest porosity. This can be explained by the microstructures shown in Fig. 5. The pellet of R=0.3 had 10-100 μm pores. The larger pores are constructed by the larger skeletons of M-RH particles. The pellet with R=0.5 showed a denser packing structure than that of R=0.3, although the former has a lower compact density than the latter. This must be due to the rearrangement of the particles in the RH compact (R=0.5 and 0.7) during heating. This denser structure depressed the elimination of the decomposed gases as discussed above. Increasing the R-value lead to an increase in the amount of small particles and the pore size decreased. The sizes of the consisting particles are much smaller than the original S-RH particles. The decomposition, depolymerization and char formation must decrease the particle size. The pore volume decreased from 2.33 cm<sup>3</sup>g<sup>-1</sup> (R=0.3) to 1.09 cm<sup>3</sup>g<sup>-1</sup> (R=1.0) with increasing R-value. The medium pore (macro-pore) sizes of the compact, measured by the MP method, are shown in Fig. 6. The pore size changed abruptly from 32-33 μm (R=0.3) to 10-14 μm (R=0.5), and then decreased slowly to 7.5-7.6 μm (R=1.0) with increasing R-value.

The specific surface area of the specimens are shown in Fig. 7. The SSA value of the pellet at 800°C decreased from 262 to 207 m<sup>2</sup>g<sup>-1</sup> with increasing R-value. This behavior seems to be consistent with that of the porosity vs. R-value relation (Fig. 4), but inconsistent with the microstructural observation (Fig. 5). The larger particles (skeletons) in the pellet with R=0.3 has small

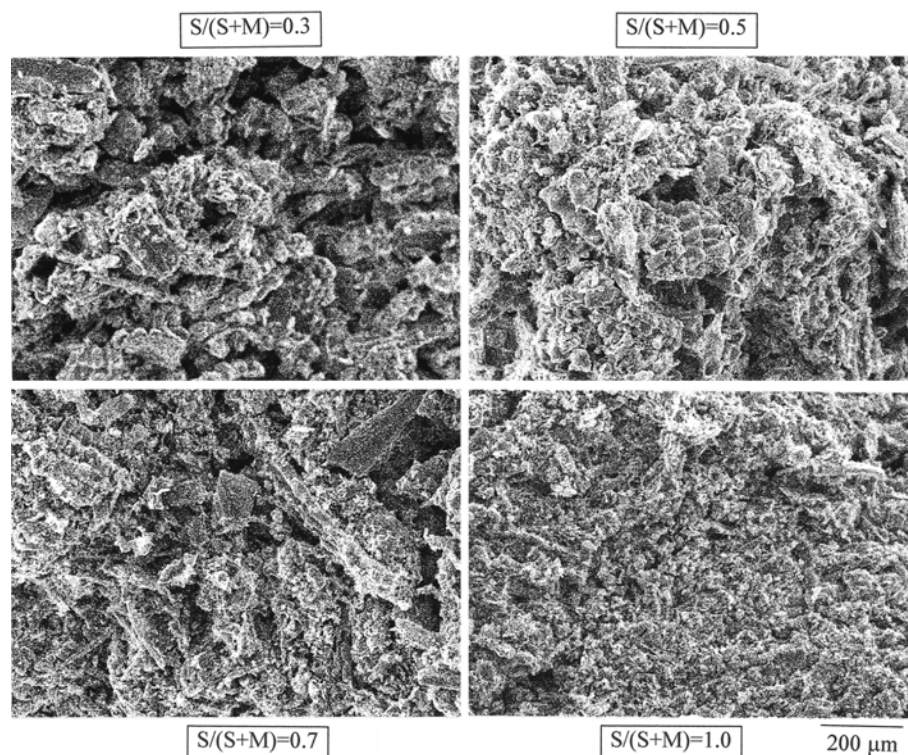


Fig. 5. Microstructures of carbon/SiO<sub>2</sub> pellets.

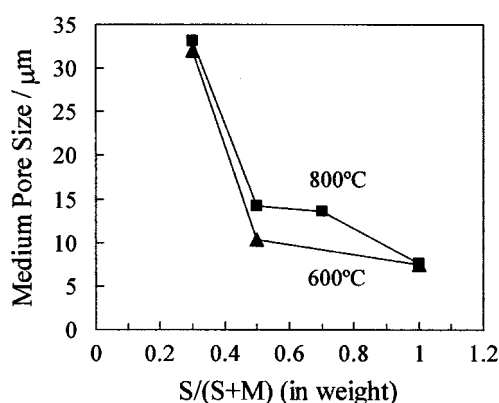


Fig. 6. Change in macro-pore size of carbon/SiO<sub>2</sub> pellets with mixing ratio.

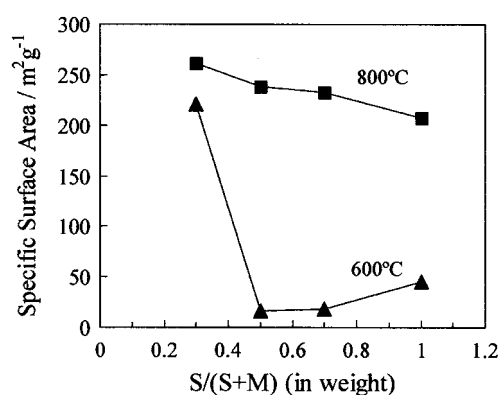


Fig. 7. Change in specific surface area of carbon/SiO<sub>2</sub> pellets with mixing ratio.

pores in itself. This increases the SSA value of the R=0.3 pellet. The pellet at 600°C had 221 m<sup>2</sup>g<sup>-1</sup> SSA value at R=0.3, but those of R=0.5-1.0 showed very small values, 16-45 m<sup>2</sup>g<sup>-1</sup>. The SSA value mainly depends on the amounts of micro-pores (<2 nm) and meso-pores (2-50 nm), and the porosity depends on the macro-pores (>50 nm). From this point-of-view, the pellets (R=0.5-1.0) at 600°C had macro-pores, but did not have meso-pores and micro-pores. The lower treatment temperature may result from the incomplete decomposition and volatilization of the organics in the RH.

The carbon/SiO<sub>2</sub> materials obtained showed the following disadvantages. Although the carbon/SiO<sub>2</sub> compact was expected to have high oxidation resistance due to

the existence of SiO<sub>2</sub> in the carbon, the oxidation of the carbon/SiO<sub>2</sub> pellet started at ~350°C, which is lower than that of the commercial activated carbon (~500°C). This is due to the lower heat treatment temperature in this work than the commercial process (1100-1250°C). Also, the resulting pellets were relatively weak. Further modifications of the productive process are needed.

## Conclusions

The pore characteristics of carbon/SiO<sub>2</sub> composites could be controlled by changing the mixing ratio of small and large rice husk powders. This is due to the change in the microstructure of the powder compact. The best properties, 262 m<sup>2</sup>g<sup>-1</sup> (SSA) and 83% (porosity) were obtained in the pellet of R=0.3 heated at 800°C. The SSA value, the strength of the pellet, and the heat-resistance, however, are not sufficient for an adsorbent application.

## Acknowledgments

The authors are grateful to Daiso Trading Co., Ltd for supplying the raw rice husk powders. This research was financially supported by the Regional Science Promotion Program of Japan Science and Technology Corporation.

## References

1. N.K. Sharma, W.S. Williams, and A. Zangvil, *J. Am. Ceram. Soc.* 67[1] (1984) 715-720.
2. C. Real, M.D. Alcala, and J.M. Criado, *J. Am. Ceram. Soc.* 79[8] (1996) 2012-2016.
3. A.K. Dalal, M.S. Rao, and K.V.G.K. Gokhale, *Ind. Eng. Chem. Prod. Res. Dev.* 24[3] (1985) 465-468.
4. T.H. Usmani, T.W. Ahmad, and A.H.K. Yousufzai, *Bioresource Technology* 48 (1994) 31-35.
5. N. Yalcin and V. Sevinc, *Carbon* 38 (2000) 1943-1945.
6. M.N. Alaya, B.S. Girgis, and W.E. Mourad, *J. Porous Mater.* 7 (2000) 509-517.
7. F. Zok, F.F. Lange, and J.R. Porter, *J. Am. Ceram. Soc.* 74[8] (1991) 1880-1885.
8. T.Z. Liou, F.W. Chang, and J.J. Lo, *Ind. Eng. Chem. Res.* 36 (1997) 568-573.
9. M.M. Tang and R. Bacon, *Carbon* 2 (1964) 211-220.
10. M. Ahmedna, W.E. Marshall, and R.M. Rao, *Bioresource Technology* 71 (2000) 113-123.