General paper

Performance of Carbonized Sugi Wood and Bark for Humidity Control

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Abstract: Sugi (Japanese cedar, *Cryptomeria japonica* D. Don) wood or bark were heated at 500 - 900 °C for 3h to investigate the effect of treatment temperature on the surface properties and the humidity control capacity of carbonized materials. The specific surface area of micropore (pore radius = 0.64 - 1.0 nm) and mesopore (> 1.0 nm) were estimated by the adsorption isotherm of nitrogen gas at 77K. The humidity control tests were carried out in a sealed batch system at a temperature range of 15 - 25 °C for 3 - 24h cycles. The initial relative humidity (RH) at 20 °C was 65%. The micropore surface area of the carbonized woods varied depending on the treatment temperature. These increased significantly from 0 m²/g to 441 m²/g when the temperature increased from 500 °C to 900 °C. In contrast, the mesopore surface area was almost constant regardless of the treatment temperature, being 39 - 79 m²/g. The maximum performance of humidity control was obtained with the wood or bark carbonized at 600 °C in 3h and 6h cycles. The change in RH for 24h cycle at the sample of 3.0 mg/cm³ was kept within a range of 3%. In addition, the ability for 3 to 24 hour-cycle humidity control was equivalent to that of 1 to 3/5 of a commercial silica gel used in museums. Carbonized wood and bark prepared at any temperature did not differ from un-carbonized wood in the humidity control capacity at 24h cycle.

Key Words: Sugi, *Cryptomeria japonica*, Carbonization, Humidity control, Carbonized wood

1. INTRODUCTION

Charcoals from wood offer a wide range of applications. Among these, humidity control material with low cost suggests the high potential for commercial use of agricultural and forestry residues as charcoals.

Abe et al. [1] reported humidity control capacity of 18 kinds of charcoals. The humidity control capacity at 25 °C was defined as a difference in weight before and after adsorption, that is, a sample weight at relative pressure of 0.90 minus a sample weight at 0.55. Results showed that the capacity of the charcoals was 20 - 30 mg/g regardless of the wood species. The effects of heat-treatment temperature of hinoki (Hinoki cypress, *Chamaecyparis obtusa* Endl.) wood on the humidity control capacity were also measured by the same manner [2]. The samples carbonized at 600 °C under air or N₂ gas showed maximum performances among the samples carbonized at 400 - 1000 °C, being 35 - 40 mg/g.

In our daily life, there are two reasons for the change in relative humidity (RH) in an uniform space [3]. One is a change in temperature between the daytime and the night, and the other is moisture that comes in and out. When the space is closed, the former would control the change in RH. The studies mentioned above suggest the applicability

of charcoals as humidity control materials. However, it is difficult only from these data to estimate a suitable mass of charcoal that keeps the RH constant in the closed space. Further, no information related to other humidity control materials such as silica gel has been reported.

In order to quantitatively determine the humidity control capacity, we used the procedure (B value) reported by Maki et al. [4]. This method is useful to estimate a relationship between the mass of sample and the change in RH. In a closed space, an approximate linear relationship can be established between the logarithmic value of RH and the temperature. The B value means the slope of its equation. When RH is kept constant at any temperature because the sample adsorbs or desorbs moisture, no slope is found between the two, indicating that the B value is 0 °C⁻¹. In contrast when a sample has no humidity control capacity, the slope, i. e., the B value, shows a minimum value of -0.0255 °C⁻¹ [3].

In this study, we estimated the humidity control capacity of sugi (Japanese cedar, *Cryptomeria japonica* D. Don) wood and bark heat-treated at 500 - 900 °C by the B value. The humidity control tests were carried out using a sealed stainless vessel at a temperature range of 15 - 25 °C for 3h, 6h and 24h cycles. The maximum performance of the materials was compared with the performances of untreated

Table 1. Characteristics of sugi (*Cryptomeria japonica* D. Don) wood carbonized at 500 - 900 °C.

Heat-treatment temperature (°C)	Total surface area, S_t (m ² /g)	Total pore volume, V_p (cm ³ /g)	Mean pore radius, R_p (nm)	Micropore surface area, S_{micro} (m ² /g)	Mesopore surface area, S_{meso} (m ² /g)	S_{micro} / S_t
500	79	0.088	2.23	0	79	0
600	395	0.168	0.85	328	67	0.83
700	348	0.158	0.91	280	68	0.80
800	475	0.178	0.75	436	39	0.92
900	491	0.190	0.77	441	50	0.90

wood and a commercial silica gel used in museums.

2. MATERIALS AND METHODS

2.1. Materials

Sugi wood and bark were air-dried and ground to powders using a Wiley mill. Particle sizes of the wood and bark powders were 16 - 42 mesh and less than 30 mesh, respectively. A commercial silica gel (Art sorb 60, 5 - 10 mesh) obtained from Fuji Silysia Chemical Ltd. (Kasugai, Japan) was used as a reference for humidity control tests. Art sorb is a typical material used in museums to offset the changes in RH in an exhibition box.

2.2. Carbonization Process

About 12 - 15 g of the wood and bark powders placed in 120-cm³ crucibles were pyrolyzed in a closed vessel at 500 - 900 °C for 3h using an electric oven. Before the heating, air in the vessel was replaced with nitrogen gas. The oven temperature was programmed to reach the desired temperature in 40 min. After the processes, the carbonized wood powders were sieved to the range of 22 mesh to 30 mesh. The carbonized bark powders were sieved to the range of 30 mesh to 42 mesh.

2.3. Surface Area and Porosity of the Carbonized Materials

Characterizations of the carbonized materials were determined by N₂ gas adsorption at 77K using NOVA-1200 porosimetry system (Quantachrome, Boynton Beach, FL, USA). Outgas of the samples was carried out in *vacuo* at 200 °C for 4h. Total surface areas (S_t) and micropore (pore radius = 0.64 - 1.0 nm) surface areas (S_{micro}) were calculated from t -curves based on the N₂ adsorption isotherms [5]. Mesopore (> 1.0 nm) surface areas (S_{meso}) were defined as a difference between the S_t and the S_{micro} , since the macropore's surface area is assumed to be 0.1 - 0.2 m²/g [6]. The total pore volumes (V_p) were estimated from the amount of N₂ adsorbed at a relative pressure of 1.0. Mean pore radii (R_p) were calculated using the following equation [7]:

$$R_p = 2000 \times V_p / S_t. \quad (1)$$

Fig. 1. Cycles of temperature-change in the humidity control tests.

2.4. Humidity Control Tests

Humidity control tests were carried out in a 10.9-liter stainless vessel that can be sealed with silicon rubber. Three replicates of the samples ranging from 1.09 g to 32.7 g were placed in the vessel in a room at 20 °C and 65% RH. Before the test, each sample was conditioned for more than one week in the above mentioned room. Whole vessel with the samples was then put into an electric chamber with temperature programs (PL-4S, Tabai Espec Corp., Osaka, Japan), and the temperature around the vessel was continuously changed between 25 °C and 15 °C for 3h, 6h, and 24h cycles as shown in Fig. 1. The changes of temperature and RH inside the vessel were monitored using a detector (MR6661, Chino Co Ltd., Yamagata, Japan).

3. RESULTS AND DISCUSSION

3.1. Effect of Heat-Treatment Temperature on the B Value

Table 1 shows some of the characteristics of sugi wood carbonized at temperatures of 500 - 900 °C. The total surface areas (S_t) and the total pore volumes (V_p) were largely increased from 79 m²/g to 491 m²/g and 0.088 cm³/g to 0.190 cm³/g, respectively, when the temperature increased from 500 °C to 900 °C. The increases in S_t at more than 600 °C were attributed to increases in their micropore sur-

Fig. 2. Relationship between the B value and the weight per unit volume of sugi wood carbonized at 600 °C.

face areas (S_{micro}). The value of S_{micro} was 280 m²/g to 441 m²/g, the proportion of S_{micro} to S_t reaching 80 - 92%. There was no micropore for the sugi wood heat-treated at 500 °C. The S_t comprised only mesopore surface area (S_{meso}). Therefore, the mean pore radius (R_p) showed the value of more than 1.0 nm.

The weight-dependence of the B value of carbonized sugi wood at 600 °C is shown in Fig. 2. The B value for 24h cycle increased rapidly during the first few weighing, then gradually, and reached -0.0022 °C⁻¹ at 3.0 mg/cm³. The B value more than -0.002 °C⁻¹ means that the changes in RH inside the vessel are kept in a range of 3%. If the sample has no humidity control capacity, the change in RH is about 39%. It is thus clear that moisture adsorbed or desorbed by sugi wood char varied with the mass of sample.

The effects of the heat-treatment temperature of sugi wood on the B values for 24h cycle are shown in Fig. 3. There are no differences in the B values at the same weight of sample. When the weight of sample increased from 0.1 mg/cm³ to 2.0 mg/cm³, the B value of any carbonized sample increased from near -0.014 °C⁻¹ to -0.002 °C⁻¹. This indicates that the heat-treatment temperature from 500 °C to 900 °C resulted in the same efficiency for humidity control.

It is interesting that the humidity control capacity for 24h cycle did not depend on the treatment temperature. This is quite different from the trend in the adsorption of volatile chlorinated hydrocarbons. In general, adsorption abilities of carbonized materials were influenced by their surface area, that is, the larger the specific surface area, the higher the adsorption capacity. For the removal of trichloroethylene (TCE) from aqueous solutions [8], the adsorption capacity of sugi bark carbonized at 900 °C, 596 m²/g, was about five times larger than that carbonized at 500 °C, 62 m²/g. Further, Abe et al. [9] reported that charcoals with high adsorption capacities do not always have large surface areas. They showed that the adsorption capacities for TCE and chloroform were significantly increased, when the mean pore diameter was less than 1.5 nm.

Fig. 3. Effects of heat-treatment temperature of sugi wood on the B values for 24h cycle. The numbers in figure indicate the weight per unit volume (mg/cm³).

In the case of humidity control capacity, no relationships between the B value and the S_t or R_p were found. It is expected that the surfaces of carbonized materials are highly hydrophobic. Whereas, remaining functional groups and/or ashes would act as hydrophilic sites for the adsorption of water. Under these circumstances, effective surface area for the adsorption of water molecule is assumed to be considerably smaller than that of N₂ molecule. This probably interfered with the dependences of humidity control on the surface area and pore size estimated from N₂ adsorption isotherm.

3.2. Effect of Test Cycle on the B Value

Cycle of temperature-change plays an important role in the humidity control capacity [10]. The effects of the cycle on the B values of carbonized sugi woods are shown in Fig. 4. When the cycle was shortened from 24h to 3h, the B values of all samples decreased. This means that

Fig. 4. Effects of test cycle on the B values of sugi wood carbonized at 500 - 900 °C. Weight per unit volume of any sample was 2.0 mg/cm³.

Fig. 5. Relationships between the B value and weight per unit volume of sugi wood carbonized at 600 °C, sugi bark carbonized at 600 °C and untreated sugi wood for 3h and 24h cycles.

the speed of adsorbing or desorbing moisture on the surfaces of samples was not so fast. On comparison of the B values at shorter cycles (3h and 6h), it is concluded that the sugi wood carbonized at 600 °C had the highest performance for humidity control. This treatment temperature corresponds to that reported by Abe et al. [2].

3.3. Humidity Control Capacities of Other Materials

The humidity control capacities of untreated sugi wood and sugi bark carbonized at 600 °C were compared with that of carbonized sugi wood at 600 °C (Fig. 5). The mechanism of humidity control of untreated wood quite differs from that of carbonized materials [11]. The surface area of untreated wood will change with the increase or decrease of RH because of the swelling or shrinkage. However, there are no differences in the B values of the samples with and without carbonization for both cycles. In addition, no large differences were found in the B values between the carbonized wood and the carbonized bark. It can be judged that these have almost the same ability for humidity control.

The comparisons of humidity control capacity between the silica gel and the sugi wood carbonized at 600 °C were shown in Fig. 6. There are no differences in the B values of the both samples for 3h cycle. However, in the cycle extended from 3h to 24h, the B values of silica gel became larger than those of the carbonized wood at any sample-weight. When the sample-weight of silica gel was 3.0 mg/cm³, the RH inside the vessel was kept constant (65% ± 0.4%). The humidity control capacity of the carbonized wood is 3/5 as much as that of the silica gel.

The humidity control capacity for untreated wood and carbonized woods was almost the same. However, it seems that the carbonized materials have advantages in actual applications.

It is well known that wood have distinctive odors,

Fig. 6. Comparison of the B values between the silica gel and the sugi wood carbonized at 600 °C.

which may be caused by the physiological function of cells or by the action of fungi, bacteria, or molds [12]. Terpenoids such as α -, β -pinene, sesquiterpenoids, etc, are the examples of the former. In the latter case, foul-smelling constituents such as low molecular weight fatty acids are produced. Further, acetic acid would be released from the monosaccharide units of hemicelluloses, when the acetyl groups are hydrolyzed under conditions of high temperature and high humidity. Whether the above mentioned odors may be pleasant or disagreeable, most sensitive selection of wood species or drying processes is necessary to apply wood for humidity control materials. When cultural properties such as painting, calligraphy, archaeology, sculpture, decorative art, etc, are exhibited or stored in a closed space, it is feared that some volatile materials may change the color or corrode the surfaces.

Whereas, wood is typically decomposed in a stepwise manner: the hemicelluloses are degraded in the temperature range of 200 - 260 °C, cellulose at 240 - 350 °C, and lignin at 280 - 500 °C [13]. During the pyrolysis processes, acidic compounds, aldehydes, ketones, etc, are produced as by-products. Most of these are possibly decomposed with increasing treatment temperatures, since the molecular weights are low. However, at the temperatures of more than 600 °C, the carbonized materials still include volatile matters of 6 - 15 wt% [14]. The effects of volatile matters on the cultural properties are being studied.

4. CONCLUSIONS

The relationship between the mass of carbonized materials and the humidity control capacity in a closed space could be quantitatively estimated. The maximum performance of the humidity control was obtained with the sugi wood or bark carbonized at 600 °C. The ability was the almost same as that of the untreated wood. On comparison of the humidity control capacity with a silica gel, the ability of the carbonized materials corresponded to that of 1 - 3/5 of the silica gel.

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