Effect of Carbonization Temperature
on the Physicochemical Structure of Wood Charcoal

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Characteristics and microstructure of wood charcoal change dependently upon the carbonization conditions. Hinoki (Cypress, *Chamaecy paris obtuse*) was carbonized at 400°C, 600°C, 800°C and 1000°C for 1h in nitrogen gas flow. Charcoals were analyzed with adsorption isotherms of nitrogen, Fourier-transform infrared (FT-IR) spectroscopy, elemental analysis, electrical resistivity and Raman spectroscopy in order to investigate about the effect of the carbonization temperature on the structure of the charcoal. Increase of the carbonization temperature developed formation of micropores of the charcoal. From result of Raman spectroscopy, it was found that the crystal structure of the charcoal remarkably changed in the temperature range between 600°C and 800°C.

Keywords: Wood charcoal, Carbonization temperature, Micropore, FT-IR, Raman spectroscopy

1. INTRODUCTION

Recently much attention has been paid to the recycling of biomass waste to charcoal which is applied for adsorption of volatile organic compounds (VOCs) [1-5]. There are many reports about the relation between carbonization conditions and characteristics of the charcoal [6-17]. However, little knowledge obtained about the changes in the physicochemical structure of the charcoal carbonized at above 800°C.

The purpose of this study was to investigate about the effect of carbonization temperature on the structure of the wood charcoal. The structure change in the charcoal dependent upon the carbonization temperature was analyzed with adsorption isotherms of nitrogen, Fourier-transform infrared (FT-IR) spectroscopy, Raman spectroscopy, elemental analysis and measurements of electrical resistivity.

2. EXPERIMENTAL

2.1 Carbonization

Sap wood of Hinoki (Cypress, *Chamaecy paris obutusa*) as a raw material was cut into 1 x 1 x 2 cm³. The wood sample in a crucible was placed in the center of a box typed furnace (FO 100: YAMATO) in nitrogen atmosphere with the flow rate of about 2 L/min. Carbonization temperatures at 400°C, 600°C, 800°C and 1000°C were selected. After the temperature reached to target temperature, it was maintained for 1h, and then the furnace was allowed to cool naturally.

2.2 Charcoal characterization

2.2.1 Adsorption isotherms of nitrogen

Adsorption isotherms of the charcoal were measured with automated volumetric gas adsorption apparatus (BELSORP 18) using nitrogen as an adsorbate at 77 K. Total micropore volume and specific surface area of the charcoal were calculated by t-plots and Brunauer-Emmett-Teller (BET) equation, respectively.

2.2.2 Fourier-transform infrared (FT-IR) spectroscopy

The infrared spectra of the charcoal were obtained with a FT-IR apparatus (Thermo Nicolet Avatar 360) using attenuated total reflection (ATR) technique in the 700-4000 cm⁻¹ range, and measured in nitrogen atmosphere with the rate of about 7 L/min.

2.2.3 Elemental analysis

The elemental analysis of the charcoal was measured with an elemental analyzer (EA1108, FISONS INSTRUMENTS). The sample of about 1 mg was put into combustion furnace at 1000°C with He gas. Then, combustion gases were passed through the reduction furnace of 650°C, and it reduced them to N_2, CO and H_2O. These compounds were carried to gas chromatogram (GC) system. The separated compounds were lead to thermal conductivity detector (TCD) at 65°C and were quantified. Sulfanilamide was used as a standard.

2.2.4 Raman spectroscopy

Raman spectra of the charcoal were obtained with Raman spectrometer (NRS-3000) using YAG laser (532 nm) in the 50-2000 cm⁻¹ range.

2.2.5 Electrical resistivity

The electrical resistivity of the charcoal was measured using a four-probe method with a pulse thermal calorimeter at room temperature. The charcoal was shaped into a rectangle. The current electrodes were
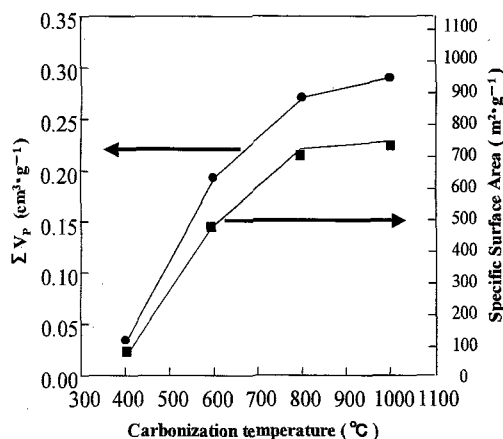
Fig. 1 Total micropore volume (●) and specific surface area (■) for charcoal of Cypress estimated by t-plots and BET equation, respectively. Carbonization temperature is 400°C, 600°C, 800°C and 1000°C.

Fig. 2 FT-IR spectra for the charcoal of Cypress carbonized at (a) 400°C, (b) 600°C, (c) 800°C and (d) 1000°C.

connected to two edge planes and the voltage electrodes were connected on one rectangular plane with a silver paste. The electrical resistivity was calculated by the voltage between the voltage electrodes and the current passed through sample, where the current used for measurements was 15 mA, and the measuring time was 5 minutes.

3. RESULTS AND DISCUSSION

3.1 Micropore volume and specific surface area

Total volume of micropores under 2 nm in diameter and specific surface areas of the charcoal were estimated from the adsorption isotherms of the charcoal in order to investigate about the effect of carbonization temperature on the micropore structure of the charcoal. Fig. 1 shows the changes in the total micropore volume and the specific surface area of the charcoal vs. the carbonization temperature. As carbonization temperature increases, both the total micropore volume and the specific surface area increase. These results suggest that development of the micropores increases the specific surface area of the charcoal [18, 19].

3.2 FT-IR, elemental analysis and electrical resistivity

FT-IR spectroscopy provides information on the chemical structure of materials. Fig.2 shows FT-IR
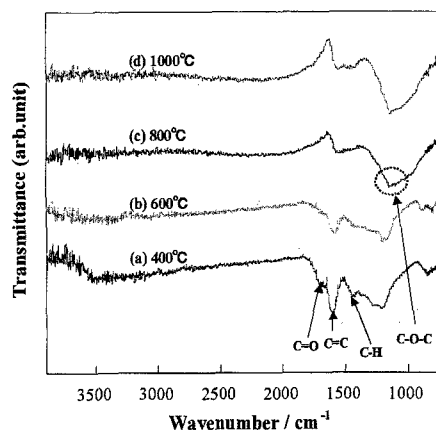
spectra of the charcoal carbonized at 400°C, 600°C, 800°C and 1000°C. The spectra present changes in the functional groups of the charcoal caused by developments of micropores. When carbonized at 400°C, the C=O mode (about 1700 cm^{-1}) and the C-H deformation vibration mode (about 1400 cm^{-1}) are weakly detected, and the C=C aromatic mode (about 1600 cm^{-1}) is clearly detected. These modes decrease with increasing carbonization temperature. Based on these results, it is suggested that the volatilization of H$_2$O and CO$_2$ during developing micropores proceeds with increasing carbonization temperature. It was assumed that the formation of the C=O and C=C modes temporarily were caused by formation of H$_2$O in a pyranose ring at the primary carbonization step because these modes dose not exist in the original cellulose [20]. On the other hand, when carbonized at 800°C and 1000°C, the large and broad band is observed at around 1100 cm^{-1}. This band was assigned to the C-O stretching and C-C stretching vibration mode. It is suggested, therefore, that these modes are originated in the bond formation among carbon atoms, C-OH, C-O-C in the pyranose ring and C-O-C between the pyranose rings [18, 21-24].

These modes in IR spectra were investigated on the other point of view with the measurements of elemental analysis and electrical resistivity, and the results are

Table 1 Elemental analysis and electric resistivity for charcoal of Cypress.

Carbonization condition	Elemental analysis					Electric resistivity
	C wt%	H wt%	O wt%	H/C	O/C	Ω·cm
400°C(1h)	72.46	3.58	23.96	0.049	0.33	—
600°C(1h)	83.23	2.12	14.64	0.026	0.18	—
800°C(1h)	89.43	0.66	9.91	0.0074	0.11	0.76
1000°C(1h)	89.75	0.24	10.01	0.0027	0.11	0.50

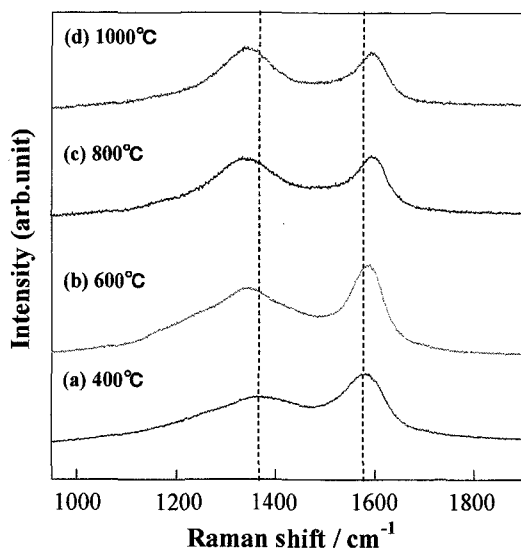shown in Table 1. The values of C wt%, H wt% and O

Fig. 3 Raman spectra for charcoal of Cypress carbonized at (a) 400°C, (b) 600°C, (c) 800°C and (d) 1000°C.

wt% show the weight percentages of carbon atoms, hydrogen atoms and oxygen atoms in the charcoal, respectively. The values of H/C and O/C decrease with increasing carbonization temperature, suggesting formation and volatilization of H_2O, CO and CO_2 gases [14]. When carbonized at 800°C and 1000°C, the oxygen atoms of 10 wt% is included in the structure of the charcoal. This suggests that the broad band at around 1100 cm^{-1} in Fig. 2 can be assigned to C-O-C. On the other hand, it was also found that when carbonized at below 600°C, the electrical conductivity of the charcoal was not detected. When carbonized at above 800°C, small electric resistivity was measured. It is suggested, therefore, that the electrical conductivity of the charcoal is caused by formation of intermolecular bonding and/or bridged structure between pyranose rings into bringing about macromolecule during the carbonization [14].

3.3 Raman spectroscopy

For the carbon materials, the Raman spectroscopy provides information on molecular and crystal lattice vibration in the charcoal. Fig. 3 shows changes in the Raman spectra for the charcoals carbonized at 400°C, 600°C, 800°C and 1000°C. The band at about 1580 cm^{-1} is assigned to graphite-band (G-band) originated in the crystalline carbon in the graphite, and the band at about 1350 cm^{-1} is assigned to disorder-band (D-band) originated from the defects in the lattice and the carbon with dangling bonds [25, 26]. It is found that the intensity ratio of D-band to G-band (I(D)/I(G)) increases with increasing carbonization temperature. It is assumed, therefore, that the generation of gases such as CO_2 proceeds to the formation of many dangling bonds in C-C structure by the carbonization which improves the electrical conductivity [15, 24]. It is also found shift of

the position of G-band into a higher wavenumber side and gradual shift of the position of D-band into a lower wavenumber side with increasing the carbonization temperature. Since the peak shift relates change of the molecular vibration mode, these results suggest the changes in the chemical bond state in the charcoal. It is suggested that the C=C bond formed in the pyranose ring in the charcoal changed into the C-C bond between 600°C and 800°C, which is starting point to formation of the macromolecule [15, 18, 22, 27].

4. CONCLUSIONS

It was found that carbonization temperature had affected the developments of micropores in the charcoal by the results of measurements of the total micro pore volume and the specific surface areas. FT-IR spectra, electrical resistivity and Raman spectra of the charcoal showed that the physicochemical structure of the charcoal had changed remarkably in the temperature range between 600°C and 800°C.

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