

ORIGINAL ARTICLE

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Adsorption capacities and related characteristics of wood charcoals carbonized using a one-step or two-step process

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Abstract Sugi (*Cryptomeria japonica* D. Don) wood powder was carbonized at varying temperatures by a one-step process up to 1000°C and a two-step process using wood charcoal as the raw material up to 1600°C. This study was conducted to evaluate the adsorptive properties of wood charcoal and discuss the mechanism of its adsorptive function in relation to the physical and anatomical characteristics of wood after carbonization. Anatomical characteristics of carbonized wood materials were directly observed under heating using an environmental scanning electron microscope (ESEM); the cell wall structures were analyzed by high-resolution transmission electron microscope (HRTEM). The largest weight losses were observed at the highest temperatures, in both the one-step and two-step processes but leveled off above 800°C. Shrinkages in the tangential, radial, and longitudinal directions increased with carbonization temperature, peaking at 1000°C. Direct observations by ESEM showed distinct shrinkage at around 400°C. The first trial observations by HRTEM on the changes in the ultrastructure of cell walls of wood charcoals were done, and it was assumed to affect the formation of micropores. Adsorption was found to follow the Langmuir isotherm model. With the one-step carbonization process, the iodine adsorption capacities of the carbonized wood powders increased with increasing carbonization temperature, peaking at 800°C, but decreased at higher temperatures. The wood powder carbonized at 1000°C with the two-step process showed the highest capacity, but further heating up to 1400°C drastically decreased the adsorption. The shrinkage of cells was related to the

increases and decreases in its specific surface area. Specific surface area and total pore volume were evidently related to the adsorptive properties.

Key words Carbonized wood · One-step carbonization process · Two-step carbonization process · Shrinkage · Iodine adsorption · Specific surface area

Introduction

There are many possible uses of carbonized wood, some of which are as fire- and sound-resistant materials, electromagnetic shields, and so on. One of the most important and immediate applications of these materials is for environmental clean-up. The wood charcoal can be used to adsorb unwanted components in water systems, especially toxic substances such as metal and organic compounds. The properties of charcoal products can be designed by controlling the carbonization conditions. In our previous studies, sugi (*Cryptomeria japonica* D. Don) wood powders carbonized at different temperatures were found to remove heavy metals such as cadmium, lead, zinc, and mercury.^{1–3} Wood powders carbonized at 200°, 600°, and 1000°C removed mercury within a concentration range of 1–10 ppm but this capacity drastically decreased starting at a carbonization temperature of 1600°C. Mercury was preferably removed even when mixed with other heavy metals in solutions, and the specific surface area of the carbonized wood powders was found to play a secondary role in the removal of this metal.

Wood charcoals carbonized at different temperatures were also found to adsorb inorganic element such as iodine, one of the most extensively used adsorbate materials for the evaluation of adsorption capacity. Wood charcoals carbonized at 600°C under nitrogen gas were found to adsorb iodine at a faster rate than charcoals carbonized at other temperatures.^{4–5} High adsorption capacity was also observed at carbonization temperatures of 700°, 800°, and 900°C after longer adsorption times; and it decreased at

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1000°C. High specific surface area contributed to the high adsorption capacity of these materials. Specific surface area of wood carbonized at higher temperatures can be improved by high oxygen concentration in the carbonizing atmosphere.⁶ Adsorptive properties are considered to be markedly affected by the microporosities of wood charcoal structures, and the chemical characters of the surfaces of wood charcoal.

The main purpose of our study was to evaluate the adsorptive properties of wood charcoal from sugi (*Cryptomeria japonica* D. Don) and to discuss the mechanism of its adsorptive function in relation to the physical and anatomical characteristics of wood after carbonization. The adsorptive properties were evaluated and discussed mainly from the viewpoint of the microstructure properties of wood charcoal. The chemical surface properties of wood charcoal were discussed elsewhere.⁷⁻⁹

The formation of micropores and extent of specific surface areas were considered to be important factors for adsorption, and in this study the formation of micropores was considered to play a significant role in adsorption. The environmental scanning electron microscope (ESEM) and high-resolution transmission electron microscope (HRTEM) observations were introduced to discuss the formation of micropores in relation to the changes of cell shape and cell wall structures. The anatomical characteristics of sugi sapwood during and after carbonization at various temperatures were directly and dynamically observed under heating using ESEM, and cell wall structures were analyzed by HRTEM. ESEM is a new and useful microscopic tool equipped with a special chamber where heat can be applied while observing the specimen.

To improve the properties of carbonized sugi wood, a new method for carbonization – a two-step process – was tried. The adsorption properties of sugi wood powders carbonized at high temperatures are also described. These materials were characterized in terms of specific surface areas, pore volumes, and pore size distributions.

Materials and methods

Carbonization process

The wood powders from sugi (*Cryptomeria japonica* D. Don) passing a 20 mesh (840 μ m) sieve were oven-dried at 105°C for 24h before carbonization. Two carbonization processes, one-step and two-step, were used for the carbonization of wood powders.

With the one-step carbonization process, samples of wood powders were carbonized in a nitrogen flow at 400°, 600°, 700°, 800°, 900°, or 1000°C (hereafter called C400, C600, C700, C800, C900, C1000, respectively) using a rotary-type instrument. Nitrogen gas at 100ml/min was passed through the materials at a heating rate of 4°C/min. The temperature was kept at the target levels for 1h, then the heater was turned off.

For the two-step carbonization process, the wood powders carbonized at 600°C during the one-step carboni-

zation process were used as starting material. They were then further carbonized up to 700°, 800°, 900°, 1000°, 1200°, 1400°, or 1600°C (hereafter called CC700, CC800, CC900, CC1000, CC1200, CC1400, CC1600) at the same heating rate of 4°C/min in a nitrogen atmosphere and airflow rate of 2000ml/min using a furnace. The temperature was kept at the target levels for 1h before turning off the heater. The materials were cooled naturally to room temperature inside the furnace before they were taken out for analysis or adsorption experiments.

The rotary-type kiln and furnace used for the one-step and two-step processes can carbonize wood or related materials up to 1000°C and 1600°C, respectively. The sizes of the rotary kiln and furnace are different, but the gas atmosphere is almost the same. The volumes of the rotary kiln and furnace are 19.635m³ and 50.616m³, respectively.

Measurement of weight losses

The weight losses of the carbonized wood powders were determined as follows:

$$\text{Weight loss (\%)} = \frac{(\text{initial weight} - \text{final weight})}{\text{initial weight}} \times 100$$

Elemental compositions (CHN analysis)

The carbon (C), hydrogen (H), and nitrogen (N) contents of materials were analyzed using a CHNS/O analyzer (Perkin Elmer Series II 2400). The amounts of samples analyzed ranged from 1.894 to 1.996mg, and analysis was done under a pressure of 758.9mmHg. The combustion and reduction temperatures were 925°C and 640°C, respectively.

The C, H, and N values were expressed in weight percentages. The percentage of oxygen was calculated as follows.

$$\text{O(\%)} = 100 - [C + H + N]$$

pH values

A 1-g aliquot of each of the carbonized wood samples was added separately to 20ml distilled water and stirred for 90min. The pH values of the mixtures were measured using a pH meter.

Dimensional shrinkage determination

Sugi blocks measuring 100mm (longitudinal, L) \times 10mm (radial, R) \times 10mm (tangential, T) were cut from the same annual rings of sugi sapwood. These blocks were oven-dried at 105°C for 24h.

For the one-step process, separate wood blocks were carbonized in a nitrogen flow at 200°, 300°, 400°, 500°, 600°, 700°, 800°, or 1000°C. For the two-step process, wood blocks were carbonized up to 1400° or 1600°C. Three replicates were prepared for each carbonization temperature.

The dimensional shrinkages in the tangential, radial, and longitudinal directions of the carbonized specimens were determined as follows:

$$\text{Dimensional shrinkage (\%)} = (I_o - I_f)/I_f \times 100$$

where I_o and I_f are the lengths in the radial, tangential, and longitudinal directions of the specimens after oven-drying and after carbonization, respectively.

ESEM observations

Small specimens ($2 \times 2 \times 2$ mm) were cut from the same annual rings of sugi sapwood. The specimens were soaked in distilled water under vacuum for total saturation of the specimens before cutting. The specimens were then dried at 60°C for 24 h before microscopic observations.

The wood specimens were placed inside the special chamber of the ESEM equipped with a heating apparatus. The samples were vacuum-treated at 200 Pa without any coating and then observed at an environment of increasing temperature using a mixture of 99% N_2 and 1% H_2 gases. The temperature inside the chamber was increased from 20°C to 1000°C at three heating rates (4°, 20°, 50°C/min) for separate samples. Video coverage was provided, and ESEM pictures of the dynamic changes in the specimens were obtained to compare the microstructures of the specimens. After the maximum temperature of 1000°C was reached, the temperature change was reversed; that is, the materials were cooled in the chamber at the same rate of temperature change (4°, 20°, 50°C/min).

For observation of the two-step heating process, wood charcoal carbonized at 600°C was cut into small specimens (same size as described above), which were placed in the ESEM chamber with the same conditions described above for direct observations at a heating rate of 20°C/min. The wood and charcoal specimens were observed at 15 kV, and the images of specimens were magnified at 400–500 \times .

HRTEM observations

Cylinder-like specimens with diameters of 30 mm and lengths of 60 mm were cut from sugi logs and then carbonized at 700°C using a laboratory-scale electric furnace. The temperature was increased at a heating rate of 4°C/min in an argon atmosphere. The temperature was kept constant at the target level for 30 min and then allowed to cool naturally.

Specimens for HRTEM were prepared using a Precision Ion Polishing System (Gatan, model 691). The microstructures of the wood charcoal were analyzed by HRTEM (Philips-CM200) operated at 200 kV. An objective aperture eliminated reflections that resulted from d -spacings less than 0.144 nm. The thickness of the sections observed by HRTEM was estimated to be less than 60 nm. The resolution of this imaging mode was estimated by gold crystal as 0.20 nm for point resolution and 1.4 nm for line resolution. The high-resolution image of the microstructure of wood charcoal was obtained with a transmission electron micro-

scope (TEM) (Philips-CM200) equipped with an objective lens having a spherical aberration constant $C_s = 1.2$ mm.

Measurement of porous structure

Specific surface areas (S_N), total pore volumes (V_N), and average pore diameters (D_N) of the carbonized sugi wood powders were determined using N_2 gas by gas sorption analyzer (NOVA 1200, Quantachrome Corp.) at the temperature of liquid nitrogen (77°K). The samples were out-gassed in a vacuum atmosphere at 200°C for 4 h before analysis.

The Brunauer-Emmett-Teller (BET) method¹⁰ in a relative pressure range of 0.01–0.15 was used to determine the S_N . The V_N was derived from the amount of N_2 gas adsorbed at a P/P_o close to unity with the assumption that the pores were filled with the liquid adsorbate. The D_N was computed based on the assumption that the structure of the pore is cylindrical.

Adsorption tests

Adsorption experiments were done based on JIS K 1474–1991 (Test methods for activated carbon using iodine as adsorbate). The carbonized wood powders were dried in an oven at 105°C for 24 h and used as the adsorbent. Weights of adsorbents ranging from 0.1 to 4.0 g were added to 50 ml iodine solution in 100-ml sample bins and continuously shaken at 20°C.

The effects of the contact time were determined using C600 for the one-step process and CC700 and CC1200 for the two-step method. Adsorbents weighing 0.5 g were separately added to 50 ml iodine solution and continuously shaken for 1, 3, 6, 17, 24, 48, 96, 120, 144, or 168 h at 20°C. The initial and residual concentrations of iodine in the solutions were determined using sodium thiosulfate solution 0.1 mol/l as titrating agent.

The equilibrium data can be fitted using the Freundlich equation, as suggested in JIS K 1474–1991 or the Langmuir equation. Langmuir equation is as follows.¹¹

$$c/q = 1/Q^\circ b + c/Q^\circ$$

where c is the equilibrium concentration (mg/cm³), and q is the amount adsorbed (mg/g), and Q° and b are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. Q° and b values can be determined from the slopes and intercepts of the linear plots of c/q versus c . The Langmuir equation was used to interpret the adsorption data instead of the Freundlich equation because the saturation adsorption amount of adsorbents can be obtained based on the Langmuir isotherm.

Results and discussion

Weight loss after carbonization

Figure 1 shows the weight losses of sugi wood powders after carbonization. Weight loss of more than 60% of the original

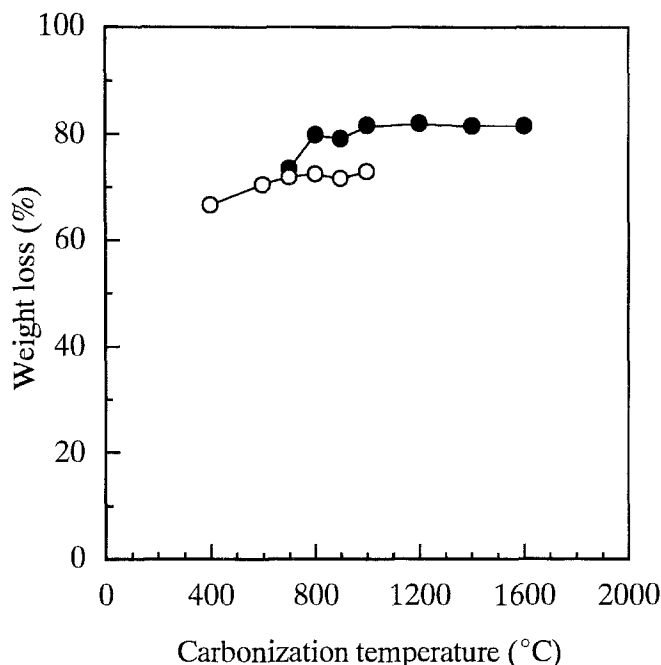


Fig. 1. Weight loss of sugi wood powders after carbonization. *Open circles*, one-step; *filled circles*, two-step. One-step: process of carbonization of raw wood under different temperatures; two-step: process of carbonization of wood charcoal carbonized at 600°C under various temperatures

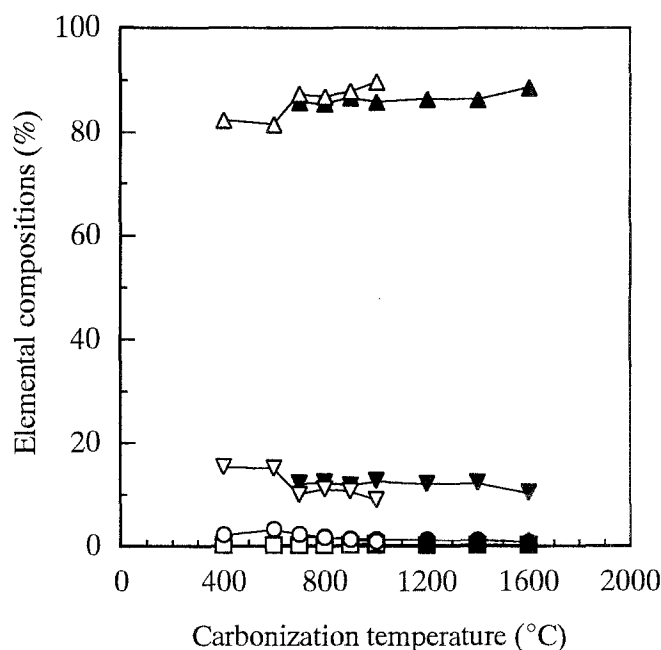


Fig. 2. Elemental compositions of sugi wood powders carbonized using one- or two-step process. One-step, *open symbols*; two-step, *filled symbols*. *Triangles*, carbon; *circles*, hydrogen; *squares*, nitrogen; *inverted triangles*, oxygen

weight of the materials was observed at 400°C. During the pyrolysis of wood, hemicellulose breaks down first at 200°–260°C, cellulose at 240°–350°C, and lignin at 280°–500°C.^{12,13} The rapid degradation of hemicellulose and cellulose is believed to be responsible for the high percentage weight loss at a carbonization temperature of 400°C. Above this temperature, weight loss gradually increased because of the degradation of the remaining carbonized material¹⁴; and at 1000°C about 70% weight loss was observed.

When C600 was further carbonized in the two-step carbonization process, weight loss at CC700 was 73% and continued to increase thereafter. The highest values were observed at the highest temperatures of C1000 and CC1600 during the one- and two-step carbonization processes, respectively.

Elemental composition

The elemental composition of carbonized wood depends on the final carbonization temperatures.¹⁵ C contents generally increase, whereas H and O contents decrease with increasing carbonization temperature.

Figure 2 shows the C, H, N, and O contents of carbonized sugi wood powders. As the carbonization temperature increased, the C contents in the materials increased during both the one- and two-step processes. The C contents increased to about 82% from 400° to 600°C and continued to increase thereafter. During the carbonization of wood, the process is almost complete within this temperature range, and the C content usually attains about 80%.¹⁶

Above 600°C, little difference in the C content is observed in almost all carbonized wood powders, and the same is true for those carbonized using the two-step process.

The O and H contents decreased with carbonization temperature, whereas the N content was almost the same at all temperatures with both the one- and two-step carbonization processes.

pH values of carbonized wood materials

Wood charcoals, as with other carbons, can have basic or acidic pH values in aqueous solutions.¹⁷

Figure 3 shows that with the one-step process C400 was observed to be acidic, indicating incomplete carbonization at this temperature. As carbonization increased from 600° to 1000°C, the pH value abruptly increased, reaching 10.59. With the two-step process, the pH values from carbonization temperatures of 800° to 1000°C increased or were almost the same as those carbonized using the one-step process. The pH values of the wood charcoal, however, dropped for CC1200 and then increased again starting from CC1400. The acidic and basic properties in the carbonized sugi wood powders can be attributed to the presence of acidic and basic surface groups, respectively.^{17–19}

Microscopic observations using ESEM

The condition of sugi wood during the carbonization process can be directly detected by in situ observations

through ESEM as shown in Figs. 4 and 5. Figure 4 shows the early- and latewood cells when sugi wood was heated under nitrogen atmosphere in the ESEM chamber at a heating rate of 4°C/min. No distinct differences in the structure of early- and latewood cells were recognized starting from a heating temperature of 20°C up to 400°C. However, shrinkage of cells was detected at about 430–500°C especially around the earlywood zone. No further shrinkage of the cells was observed with a further increase in temperature up

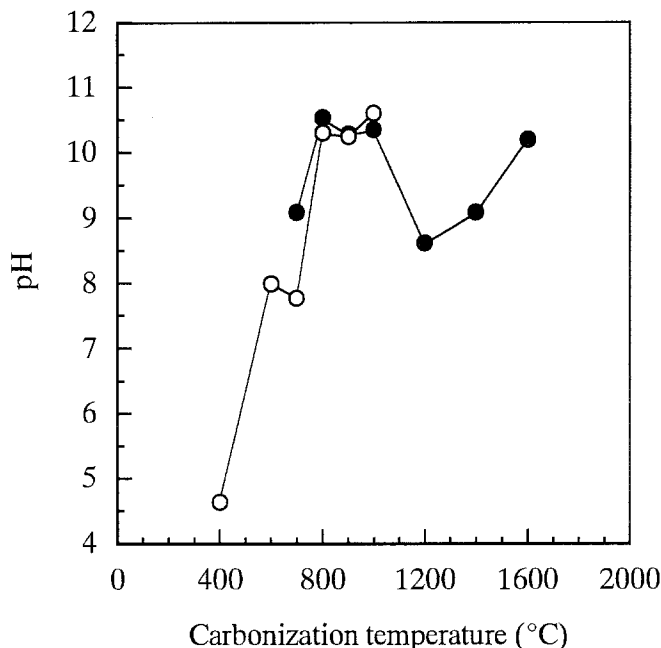


Fig. 3. pH values of carbonized sugi wood powders. *Open circles*, one-step; *filled circles*, two-step

to 1300°C. When the materials were cooled to the original temperature of 20°C, there were no changes in the structures of the cells, which shows that the shrinkage was irreversible. As the carbonization temperature is increased, the microfibrillar structure of the wood is destroyed, resulting from degradation of cellulose and hemicelluloses accompanied by rearrangement of carbon into a structure approaching that of graphite.²⁰ As a result, shrinkage may become extensive.

The same trend was observed when sugi wood was heated at 20°C/min, but there was little difference in the shrinkage of early- and latewood cells or in the anatomical characteristics of cell shape and cell wall structure. The same trend was observed when wood was heated at the most rapid heating (50°C/min). Shrinkage of earlywood cells was more prominent than that of wood heated under more gentle heating rates of 4°C/min or 20°C/min.

Prominent shrinkage, especially in the earlywood cells, was observed as a result of the high heating rate. The latewood cells were observed to be more stable than the earlywood cells. The earlywood cells were sometimes seen to be partially collapsed. The greater shrinkage of the earlywood cells is attributed to the more open and flexible cellular structure of these cells. Latewood cells are believed to have better thermostability than earlywood cells, giving the whole wood an inherent thermoresistance.^{21,22} As a result, the latewood cells tend to stabilize the whole wood because of their higher stability.

Figure 5 shows that when C600 was further heated to 1300°C at a heating rate of 20°C/min no apparent changes in the early- and latewood cells were observed; even when the temperature was cooled to the original carbonization temperature of 600°C there were no changes. During the carbonization process, when C600 was further carbonized

Fig. 4. Environmental scanning electron micrographs of sugi wood under elevating temperatures at a heating rate of 4°C/min. **A** 20°C. **B** 430°C. **C** 510°C. **D** 1000°C

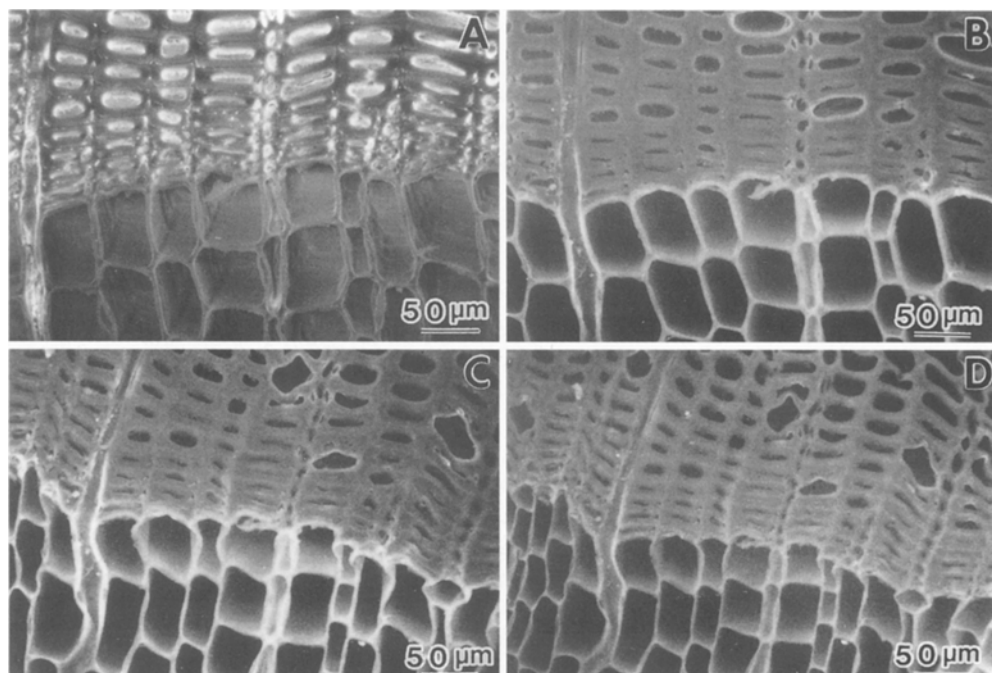
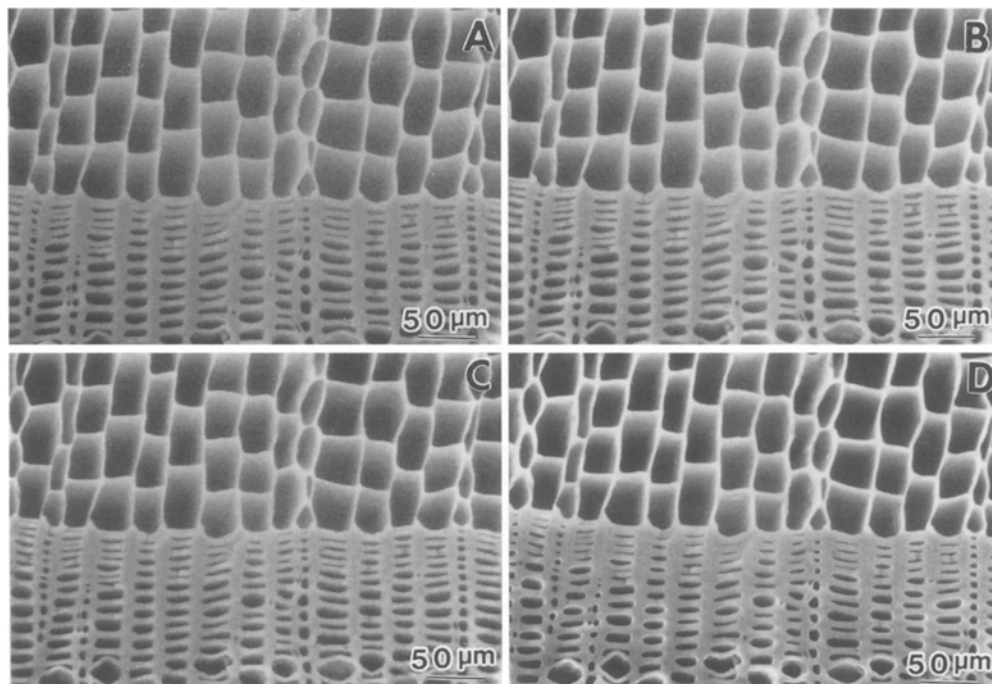


Fig. 5. Environmental scanning electron micrographs of sugi wood charcoal carbonized at 600°C under elevating temperatures at a heating rate of 20°C/min. **A** 700°C. **B** 900°C. **C** 1300°C. **D** 600°C



with the two-step process under nitrogen and oxygen atmosphere, weight loss increased from CC700 to CC800 and continued to increase up to CC1000 (Fig. 1). Starting from CC1000, however, no further weight loss was observed. The difference in weight loss between C800 and CC800 can be attributed to the presence of oxygen in the carbonization process. In the absence of oxygen, no difference can possibly be observed between these two carbonized materials. Starting from C1000, there was no further increase in weight loss; The weight loss during the carbonization process can also be correlated with the shrinkage of cells observed by ESEM, although oxygen was not introduced into the system during ESEM observations. A change is possible when oxygen is present.

The observations using ESEM are not considered to coincident identically with the changes caused under the carbonization process using the one-step and two-step processes because of the specimen size, the method of holding the specimen, and the ambient conditions in the chamber. However, the anatomical characteristics observed by ESEM can provide useful information and meaningful suggestions on the structural changes of wood cells under thermal conversion. ESEM, a direct in situ observation method, can analyze structural changes of wood cells with changes in temperature. At present, the same conditions during ESEM observations and the carbonization process are not possible.

Shrinkage of wood after carbonization

Figure 6 shows dimensional shrinkage in the tangential, radial, and longitudinal directions after carbonization.

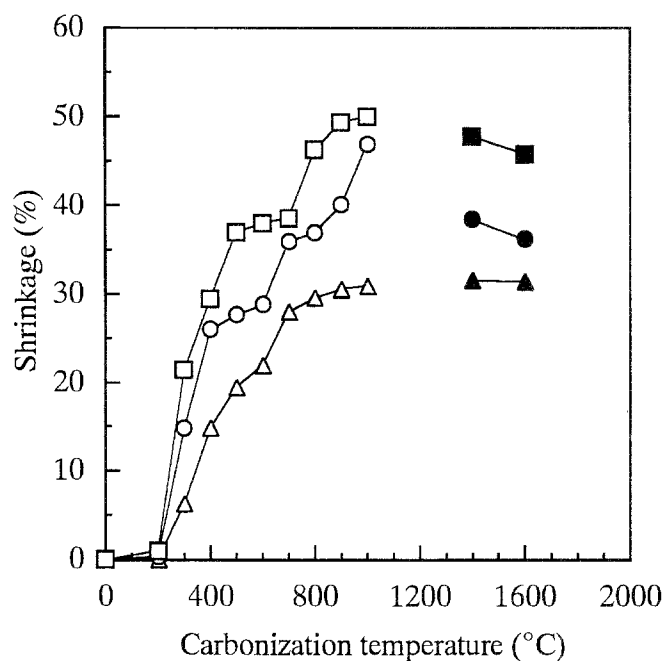


Fig. 6. Shrinkage in the tangential (T, squares), radial (R, circles) and longitudinal (L, triangles) directions of sugi wood after carbonization. One-step; open symbols; two-step, filled symbols

Shrinkages averaged 40%–50% for both radial and tangential directions and about 30% in the longitudinal direction. Little change was observed at 200°C. The shrinkage in the tangential and radial directions was observed to increase abruptly at a temperature of 400°C; the weight loss due to carbonization was more than 60% at 400°C. From 400°C, further tangential and radial shrinkage was observed with a corresponding decrease in the weight loss rate of

wood substances, followed by leveling off to approximately 70% weight loss for 1000°C. The cellular component and microfibrillar structure of lignocellulosic components in the original wood material may have delayed or altered shrinkage during the low temperature treatment, although degradation of those components could occur.^{20,21} The arrangement and orientation of the cell components may have contributed to the large shrinkage in the tangential and radial directions around this carbonization temperature. The increases in tangential and radial shrinkages were greatest and started to level off at 1000°C. Among the three directions, least shrinkage occurred in the longitudinal direction.

The shrinkage increased rapidly at carbonization temperatures around 400°–500°C and then leveled off. However, from a carbonization temperature of 600°–700°C, the shrinkage increased again. At a carbonization temperature of 500°C the degradation of wood components such as cellulose and lignin increased and around 600°–700°C rearrangement of carbon elements occurred owing to shrinkage. That is, within 600°–700°C, new micropores might be formed around onion-like carbon structures and the interstices of these microstructures. The spherical graphitic particles in wood exhibited concentric fringe or onion-like images, as first observed by Hata.²³ These observations may have some effect on their porous characteristics, such as specific surface area and pore volume, as shown in Table 1. The specific surface area of carbonized wood materials increased abruptly with increasing carbonization temperatures of C600 to C700 and decreased with increasing temperatures of C700 to C800 and thereafter.

When carbonized sugi wood at 600°C was further carbonized to 1400° or 1600°C in a furnace, the shrinkage was almost the same for those of C1000 treated by the one-step process. Further carbonization did not have any substantial effect on the dimensional shrinkage of these materials.

HRTEM observations

The microstructural properties of wood charcoal are important, particularly when used in industrial applications.

The ESEM and HRTEM observations were introduced to discuss the formation of micropores. The changes in the ultrastructure of the cell walls of wood charcoals observed by HRTEM were assumed to affect the formation of micropores.

The shrinkage observed by ESEM during the heating process influences the physical properties to some degree. The porosity of carbonized sugi wood was indirectly imaged using HRTEM, as shown in Fig. 7. Note the 002 lattice fringes (LF) plane parallel to that of graphite crystallites showing the randomly arranged structures of sugi wood charcoal. The gap of the LF image is within 0.5 nm. The spherical carbon in the image is the micelle close to the graphite, and the porosity can be the contact portion of this carbon.

Cell wall structures in charcoal observed by HRTEM provide definite data and represent a characteristic that can be correlated with the adsorption functions of this material.

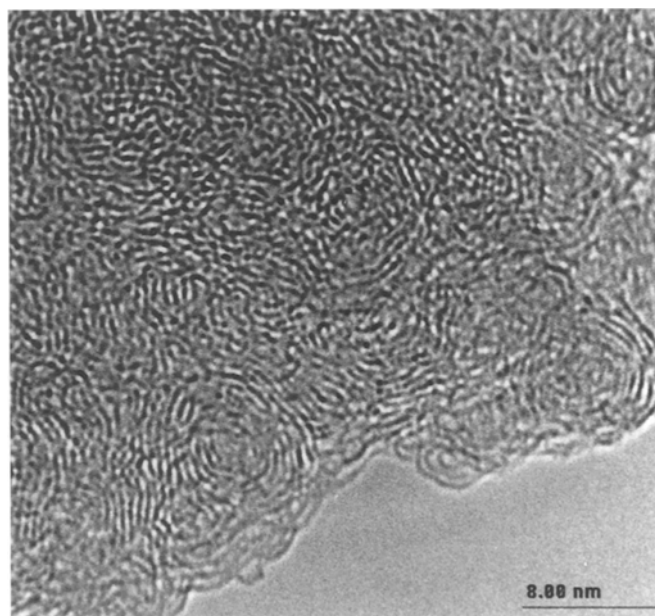


Fig. 7. High-resolution electron microscopic image of sugi wood carbonized at 700°C for 30 min

Table 1. Specific surface areas, pore volumes, and average pore diameters calculated from adsorption isotherms of nitrogen

Carbonization temperature (°C)	Specific surface area S_N (m ² /g)		Total pore volume V_N (ml/g)		Average pore diameter D_N (nm)	
	One-step	Two-step	One-step	Two-step	One-step	Two-step
400	0.56	—	—	—	—	—
600	49.70	—	0.036	—	2.86	—
700	230.70	441.35	0.113	0.193	1.95	1.76
800	146.65	471.43	0.085	0.200	2.31	1.69
900	26.50	562.85	0.017	0.242	2.56	1.72
1000	33.70	638.77	0.019	0.283	2.30	1.77
1200	—	424.02	—	0.196	—	1.85
1400	—	250.80	—	0.120	—	1.91
1600	—	105.10	—	0.074	—	2.80

Although the carbonization condition is different, this particular charcoal property can be a useful and meaningful observation.

Pore characteristics

Table 1 shows the S_N , V_N , and D_N of the carbonized wood materials calculated from the nitrogen adsorption measurement. The specific surface area of carbonized wood materials increased abruptly with the increasing carbonization temperature from C600 to C700 and decreased again with the increasing temperature from C700 to C800 and thereafter. Among the specimens, C700 had the highest S_N followed by C800. High S_N was due to formation of pores as evidenced by the high total pore volume V_N . Tars from the decomposition of hemicellulose, cellulose, and lignin were formed and prevented the formation of pores by blocking the already formed pores or impeded the continuity of pores at low temperatures (or both), resulting in low total pore volumes and specific surface areas.^{24,25} The heat energy was assumed to be not enough around this temperature zone to evolve the volatile matters necessary for pore development.²⁶ They were probably volatilized at higher temperatures such that C700 and C800 showed higher S_N and V_N . Most of these materials might have evaporated into gaseous substances at the carbonization temperature of 700°C or above. The specific surface area decreased at relatively high temperatures, around 900° and 1000°C. Studies showed that low S_N is considered to be due to insufficient carbonization at low temperatures and the shrinkage of pores at high temperatures.^{4,6,26} It is thought that pore apertures constrict at high temperatures owing to the gradual thermal transformation of the carbon structure.²²

Micropores have not been developed, as evidenced by the low pore volume of C400, which can be attributed to the high tar content and the pores filled with the tar. Release of a significant amount of volatile matter at low temperatures¹⁶ remained in C400, blocking the pores. Micropores started to develop at C600 and were fully developed at C700; pore volume decreased abruptly starting from C900 but were not as low as in C400.

When C600 was further heated to 700°C by the two-step process, the S_N increased to about twice that of C700, which was carbonized by one-step process. S_N increased with an increase in carbonization temperature, peaking at CC1000. Starting from CC1200, S_N decreased again; the lowest value was observed at CC1600. The micropores started to develop in the starting material, C600, and further developed during the two-step process. The formation of initial pore structures during the one-step process was followed by activation in a nitrogen and air environment. The oxygen in the carbonizing atmosphere is considered to activate the carbonized wood powders.⁶ The activation reaction might have occurred because of the slight amount of air purged into the charcoal during the second carbonization process. At a carbonization temperature of 1400°C, the S_N drastically decreased but was almost equal to that of C600, which was the starting material processed to the two-step process. The D_N of carbonized wood powders in the two-step method was generally lower than that of those carbonized using the one-step process.

Adsorption of iodine

Figure 8 shows the effect of adsorbent–adsorbate contact time on the adsorption of iodine using C600, CC700, and CC1200 as representative samples for the one-step and two-step carbonization processes. The percentage removal increased with an increase in contact time. Higher percentage removals were observed with CC700 or CC1200 as adsorbent compared to that of C600. The equilibrium saturation was attained at 24–48 h for CC700 and CC1200 and at 168 h for C600, with more than 44% and 36% removals, respectively. The adsorption rate of the latter is slower than that of the former. For the subsequent experiments a contact time of 168 h was employed.

Representative adsorption isotherms from adsorption data fitted in the Langmuir equation showing the adsorption of iodine between sugi wood powders carbonized using the one- and two-step processes are illustrated in Fig. 9. Higher adsorption capacities were observed in wood powders carbonized by the two-step process. Table 2 shows

Table 2. Langmuir isotherm constants

Carbonization temperature (°C)	Langmuir isotherm constant					
	One-step			Two-step		
	Q° (mg/g)	b (mg/l)	r^2	Q° (mg/g)	b (mg/l)	r^2
400	333.3	0.50	0.99	–	–	–
600	333.3	3.00	1.00	–	–	–
700	500.0	1.11	1.00	500.0	6.67	0.99
800	500.0	1.00	1.00	500.0	6.35	1.00
900	333.3	0.70	1.00	500.0	4.83	0.99
1000	142.9	0.75	0.99	1000.0	3.33	0.98
1200	–	–	–	500.0	5.88	1.00
1400	–	–	–	333.3	1.74	1.00
1600	–	–	–	90.9	0.55	0.98

r^2 , correlation coefficient

Contact time = 168 h

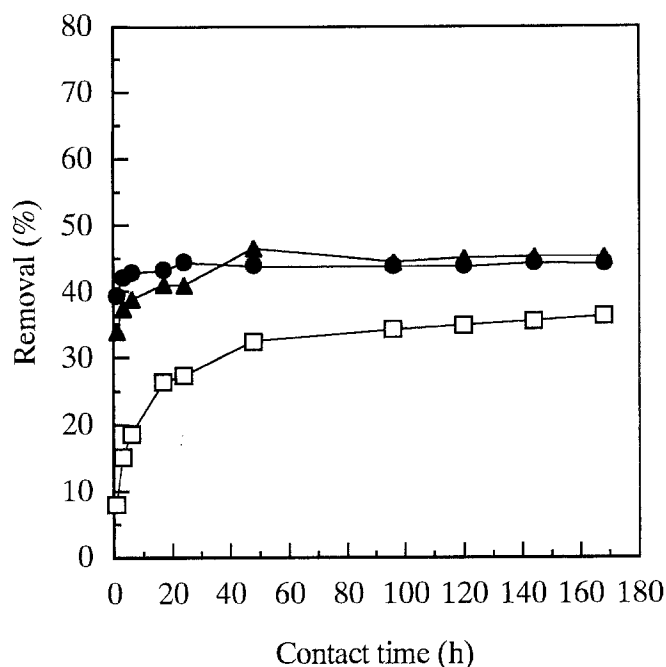


Fig. 8. Effects of contact time on iodine removal using carbonized sugi wood powders. One-step (open squares), 600°C. Two-step; filled circles, 700°C; filled triangles, 1200°C

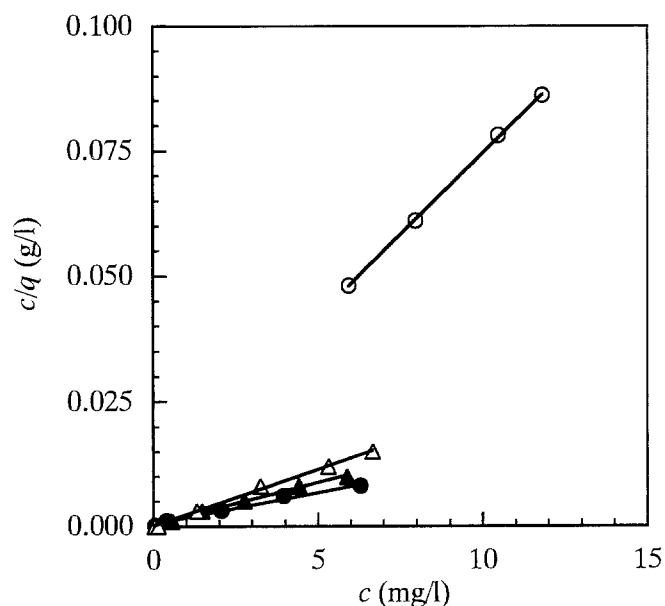


Fig. 9. Langmuir isotherm for iodine adsorption on carbonized sugi wood powders using the one- or two-step process. One-step: open symbols. Two-step, filled symbols. Circles, 700°C; triangles, 1000°C

the Q° and b values. The Q° values indicate the adsorption capacity for iodine on carbonized wood powders. Q° values were maximum at C700 and C800 for the one-step process. The same Q° values were observed at the same temperatures, CC700 and CC800, using the two-step process. Comparing all adsorbents, the highest adsorption was observed in CC1000 followed by CC900, CC800, CC700, and CC1200. Further heating of C600 to 1400°C drastically

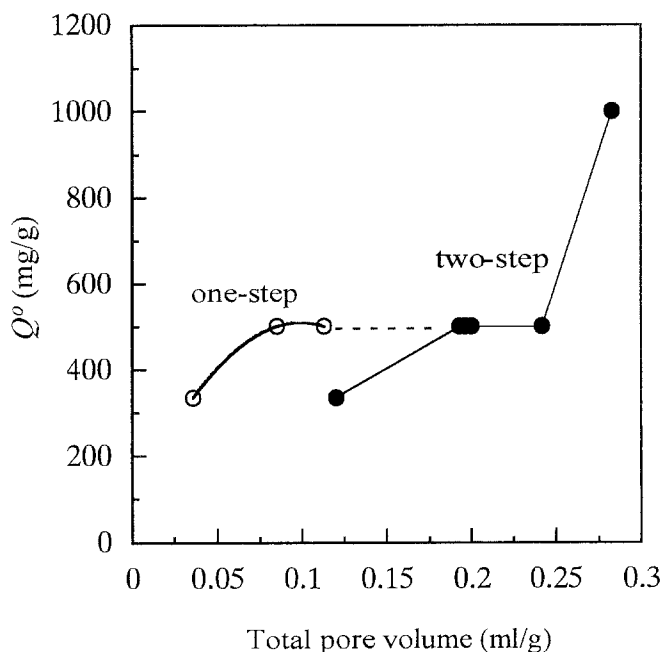
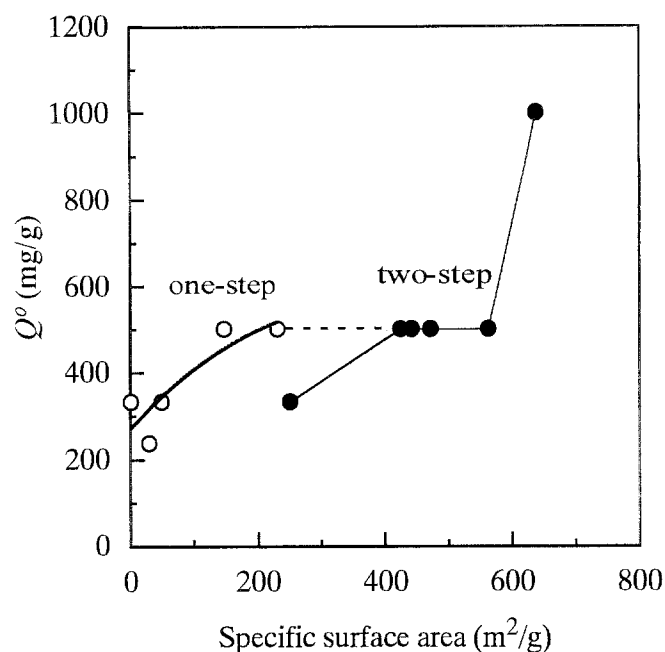


Fig. 10. Correlation of specific surface area and total pore volume with iodine adsorption Q° . Open circles, one-step; filled circles, Two-step

decreased the adsorption to even less than that of C700 or C800. The adsorption capacities of C1000 and CC1600 were the least among all types of adsorbents.

This result agrees with the trend in specific surface area and total pore volume, as shown in Fig. 10. The increase in the specific surface area and/or total pore volume enhances the adsorption of iodine using these carbonized materials. The reactivity of the carbonized wood materials was due to the presence of more active points on their surfaces caused by a large specific surface area. Surface adsorption occurred primarily during both one- and two-

step carbonization processes. The formation of pores enhanced the ability of the carbonized wood powders to adsorb iodine. By the two-step process, when the microporosity is more developed, as in samples CC900, CC1000, and CC1200, the amount of iodine adsorbed is much larger.

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References

- Pulido-Novicio L, Hata T, Kajimoto T, Imamura Y, Ishihara S (1999) Removal of mercury by carbonized wood materials from aqueous solutions of different types of mercury compounds. *Resources Proc J* 46(1):3–8
- Pulido-Novicio L, Hata T, Kajimoto T, Imamura Y, Ishihara S (1998) Removal of mercury from aqueous solutions of mercuric chloride using wood powder carbonized at high temperature. *Wood Res* 85:48–55
- Pulido LL, Hata T, Imamura Y, Ishihara S, Kajimoto T (1998) Removal of mercury and other metals by carbonized wood powder from aqueous solutions of their salts. *J Wood Sci* 44:237–243
- Abe I, Iwasaki S, Iwata Y, Kominami H, Kera Y (1998) Relationship between production method and adsorption property of charcoal (in Japanese). *Tanso* 185:277–284
- Hitomi M, Kera Y, Tatsumoto H, Ikuta N, Kawafune I, Abe I (1993) Evaluation of adsorption property of porous carbon materials (II) (in Japanese). *Tanso* 156:22–28
- Kitamura T, Matsumoto S, Katayama H (1999) The effect of carbonizing conditions on the properties of charcoal absorbent from *Cryptomeria* (in Japanese). *Mokuzai Gakkaishi* 45:171–177
- Kishimoto S, Kitsuta K (1969) Functional group and free radical on inner surface of charcoal (in Japanese). *Mokuzai Gakkaishi* 15:208–213
- Abe F, Kishimoto S, Unrinin G (1960) Studies on charcoal XI (in Japanese) *Mokuzai Gakkaishi* 6:188–193
- Nishimiya K, Hata T, Imamura Y, Ishihara S (1988) Analysis of chemical structure of wood charcoal by X-ray photoelectron spectroscopy. *J Wood Sci* 44:56–61
- Gregg SJ, Sing KC (1982) Adsorption, surface area and porosity, 2nd edn. Academic, London, pp 41–110
- Montgomery JM (1985) Water treatment principles and design. Wiley, New York, pp 174–190
- Byrne CE, Nagle DC (1997) Carbonization of wood for advanced materials applications. *Carbon* 35:259–266
- Slocum DH, McGinnes EA Jr, Beall FC (1978) Charcoal yield, shrinkage, and density changes during carbonization of oak and hickory woods. *Wood Sci* 11:42–47
- Levan S (1989) Thermal degradation. In: Schniewind AP (ed) Concise encyclopedia of wood and wood based materials. Pergamon, Oxford, pp 271–273
- Soltes EJ, Elder TJ (1981) Pyrolysis. In: Goldstein IS (ed) Organic chemicals from biomass. CRC Press, Boca Raton, FL, pp 64–99
- Pastor-Villegas J, Duran-Valle CJ, Valenzuela-Calahorra C, Gomez-Serrano V (1998) Organic chemical structure and structural shrinkage of chars prepared from rockrose. *Carbon* 36:1251–1256
- Boehm HP (1994) Some aspects of the surface chemistry of carbon blacks and other carbons. *Carbon* 32:759–769
- Tanso Zairyo Gakkai (1996) Tanso no hyomen tokusei (in Japanese). In: Introduction for carbonmaterials. Realize, pp 69–78
- Boehm HP (1966) Chemical identification of surface groups. *Adv Catalysis* 16:179–274
- McGinnes EA Jr, Kandeel SA, Szopa PS (1971) Some structural changes observed in the transformation of wood into charcoal. *Wood Fiber* 3(2):77–83
- Cutter BE, Cumbie BG, McGinnes EA Jr (1980) SEM and shrinkage analyses of southern pine wood following pyrolysis. *Wood Sci Technol* 14:115–130
- Szabo T, Fung DPC (1975) Thermal behavior of growth zones of Douglas-fir and loblolly pine. *Wood Sci* 8(1):411–414
- Hata T (1999) Micro structural analysis of bio carbon from wood (in Japanese). *Cellulose Commun* 6(3):127–133
- Mackay DM, Roberts PV (1982) The influence of pyrolysis conditions on yield and microporosity of lignocellulosic chars. *Carbon* 20:95–104
- Pastor-Villegas J, Valenzuela-Calahorra C, Bernalte-Garcia A, Gomez-Serrano V (1993) Characterization study of char and activated carbon prepared from raw and extracted rockrose. *Carbon* 31:1061–1069
- Lua, AC, Guo J (1998) Preparation and characterization of chars from oil palm waste. *Carbon* 36:1663–1670