Characterization of Pyrolyzed Cedar (Cryptomeria japonica D. Don) Bark using N$_2$ Adsorption and Diffuse Reflectance Infrared Fourier Transform Spectroscopy

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Japanese cedar bark was pyrolyzed at 473-1273 K under atmospheric pressure in a flow of nitrogen. Morphology, adsorption properties, and surface properties of the products were examined to characterize the pyrolyzed cedar bark. Although elongated tubular cells and fibrous materials in the bark shrank during the heat treatment, features of fibrous cedar bark were macroscopically preserved in the samples pyrolyzed even at higher temperatures without significant decay of the morphology. The development of microporosity was observed for the samples pyrolyzed at 773 K and higher temperatures; $S_{\text{BET}}$ (specific surface area) 80-448 m$^2$g$^{-1}$, $V_p$ (pore volume) 0.07-0.21 mLg$^{-1}$, and $D_m$ (mean pore diameter) 0.46-0.77 nm. $\alpha$-plot indicated that surface properties of cedar bark pyrolyzed at 1073-1273 K were similar to those of carbon black, whereas those of samples pyrolyzed at 873 K and lower temperatures were different from them. Diffuse reflectance FT-IR spectra showed that functional groups such as substituted aromatic rings and ether groups were present on the surface of the samples pyrolyzed below 873 K, which would have effects on the surface properties of the resultant material.

Key Words: Japanese cedar bark, Adsorption characteristics, Pyrolysis, FT-IR, Surface property

1. Introduction

It has been known that large amounts of cedar bark residues are produced by the forest industry. A certain amount of this biomass are used as raw materials in particle board processing or paper production, and also consumed to generate energy as fuels, while the rest are mostly discharged in landfills. This sometimes causes environmental problems, especially in the runoff water from dumping sites of the bark residues. The development of potential applications for cedar bark residues from wood processing and forest maintenance is of great importance, since these residues are widely available and less economic value. One of the potential applications is the use of the residues as raw materials for activated carbon production. Recently, Edgehill et al. examined the adsorption properties of carbonized slash pine bark. The carbonized bark was used in adsorption capacity tests with phenol and pentachlorophenol, and could be utilized as an alternative adsorbent for eliminating the contaminants from aqueous solutions. More recently, Kurimoto et al. reported that carbonized cedar bark showed larger adsorption capacity for trichloroethene than that of commercial activated carbons, indicating the potential utility of the carbonized cedar bark to reduce chlorinated contaminants from aqueous systems. It is considered that fibrous materials of carbon can be manufactured from the cedar bark, if it can be converted into the carbon without significant decay during the carbonization, preserving the macroscopic morphology of the bark. In the previous communication, it was reported that microporous carbonaceous materials were obtained from the cedar bark while retaining its fibrous morphology through the two-step pyrolysis, i.e., all samples were treated at 673 K for 3 h and were then heated at a desired temperature between 773 and 1273 K in a stream of N$_2$. In this study, we investigate the morphology and adsorption characteristics of pyrolyzed cedar bark which were prepared by a single-step pyrolysis. The effects of pyrolysis temperature on the surface properties were examined using N$_2$ adsorption and FT-IR spectroscopy.

2. Experimental

Cedar bark from 65-75 year-old trees was cut into small pieces of sample ca. 10 mm $\times$ 10 mm $\times$ 5 mm. The samples of the bark placed on a sample boat of alumina were charged into a tubular reactor made of Pyrex or quartz glass. The samples were subjected to a single-step pyrolysis described below. The samples dried at 373 K for 1 h were usually heated in a flow of nitrogen (500 mL min$^{-1}$) with a rate of 7-17 K min$^{-1}$ to a desired temperature between 473 and 1273 K and held at the same temperature for 0-6 h. The temperature of the furnace was controlled within $\pm$1 K.

The morphological change during pyrolysis was observed using a biological microscope equipped with an automatic...
photomicrography system (OLYMPUS, BHS-323, PM-10AK). Pore structures of the pyrolyzed cedar bark were evaluated by N₂ adsorption at 77 K. An automated sorption apparatus (Japan Bell, Belsorp 18) was used to obtain the N₂ isotherms. Pretreatment of the samples was carried out in vacuo (less than 0.2 Pa) at 473 K for 2 h before adsorption measurement. Specific surface area ($S_{BET}$) was calculated from the standard BET plots in the relative pressure ($P/P_0$) range of 0.01-0.2. External surface area ($S_{EXT}$) and micropore volume ($V_{mic}$) were obtained from the t-method and the Dubinin-Radushkevich equation applied to the N₂ isotherm, respectively. Total pore volume ($V_p$) was evaluated from the amount of N₂ adsorbed at relative pressure extrapolated to $P/P_0 = 1$. Diffuse reflectance infrared Fourier transform spectra (DRIFTS) of the samples were recorded and functional groups of the surface were identified by an FT-IR spectrometer (Perkin-Elmer, SPECTRUM 2000). The pulverized sample was dried at 378 K for 24 h and mixed with KBr powder. Weight ratio of the sample to KBr was 3:100. The spectra were obtained by integration of 256 scans at a resolution of 4 cm⁻¹ in the range of 400-4000 cm⁻¹. Values of pH of aqueous suspensions containing pyrolyzed cedar bark were determined according to JIS K 1474.

3. Results and Discussion

3.1 Yield of pyrolyzed cedar bark

Figure 1 shows the effect of heating temperature on the yield of pyrolyzed cedar bark. It is apparent that the yield of pyrolyzed products depends on the temperature of pyrolysis. It has been reported that decomposition of hemicellulose begins at ca. 453 K and proceeds until approximately 573 K, and temperatures of decomposition for cellulose and lignin generally range 513-673 K and 553-773 K, respectively. At higher temperatures, further weight loss was observed, indicating that thermal degradation is still incomplete and secondary thermal decompositions such as demethanation and/or dehydrogenation take place at higher temperatures. Values of the yield in this study were 3.5-5.7% higher than those in the previous one, indicating that volatilization of thermal decomposition products were rather suppressed during the single step pyrolysis.

3.2 Morphology of pyrolyzed cedar bark

Photomicrograph of the cedar bark pyrolyzed at 1273 K is shown in Photo. 1 in comparison with that of the original bark. The original bark was comprised of elongated tubular cells aligned with the axis of the tree trunk. The diameters of these longitudinal cells, or distance between fibers ranged from 20 to 40 μm. It was observed that the cell size became small in the pyrolyzed bark. The shrinkage of the fibers during the pyrolysis was mainly due to decomposition of lignin contained in the middle lamella which connects the tubular cells of fibers. It should be noticed that cedar bark carbonized at high temperature (1273 K) can give fibrous materials which retain macroscopic features of the precursor. This means that the fibrous morphology of the cedar bark was kept macroscopically without significant decay during the pyrolysis at high temperatures.

3.3 Adsorption characteristics of pyrolyzed cedar bark

Adsorption isotherm: Adsorption isotherms of N₂ at 77 K on the pyrolyzed cedar bark were shown in Figure 2. Amount of adsorption on the samples pyrolyzed at 673 K and lower temperatures (not shown here) were small, suggesting that formation and development of pores were not significant in these samples. On the contrary, it is apparent that drastic increase in the amount of adsorption was observed for the samples treated at higher temperatures. Steep increase in the isotherms at low relative pressures indicates the development of microporosity, porosity consisted of pores with widths not exceeding 2 nm, for the samples pyrolyzed above 773 K. Mesoporosity, porosity composed of pores
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Table 1 Surface area and pore volume of pyrolyzed cedar bark

<table>
<thead>
<tr>
<th>Pyrolysis</th>
<th>Temperature / K</th>
<th>Time / h</th>
<th>( S_{BET}^+ ) / m²/g</th>
<th>( S_{BET}^- ) / m²/g</th>
<th>( \V_{total}^+ ) / m³/g</th>
<th>( \V_{total}^- ) / m³/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>573</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>0.012</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>673</td>
<td>3</td>
<td>7</td>
<td>7</td>
<td>0.028</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>773</td>
<td>3</td>
<td>159</td>
<td>13</td>
<td>0.101</td>
<td>0.070</td>
<td>-</td>
</tr>
<tr>
<td>873</td>
<td>3</td>
<td>445</td>
<td>11</td>
<td>0.210</td>
<td>0.190</td>
<td>-</td>
</tr>
<tr>
<td>973</td>
<td>3</td>
<td>448</td>
<td>9</td>
<td>0.198</td>
<td>0.385</td>
<td>-</td>
</tr>
<tr>
<td>1073</td>
<td>3</td>
<td>315</td>
<td>11</td>
<td>0.155</td>
<td>0.132</td>
<td>-</td>
</tr>
<tr>
<td>1173</td>
<td>3</td>
<td>79</td>
<td>18</td>
<td>0.072</td>
<td>0.031</td>
<td>-</td>
</tr>
</tbody>
</table>

- \( S_{BET}^+ \): Specific surface area by BET plot.
- \( S_{BET}^- \): Total surface area by t-plot.
- \( \V_{total}^+ \): Total pore volume obtained from amount adsorbed extrapolated to \( P/P_0 = 1 \).
- \( \V_{total}^- \): Micropore volume by DR plot.

Table 1 provides the surface area and pore volume of pyrolyzed cedar bark at various temperatures and times. The results suggest that the surface area and pore volume are significantly affected by the pyrolysis temperature and time. Higher temperatures generally lead to an increase in surface area and pore volume, which indicates the formation of micropores and mesopores. The specific surface area (\( S_{BET}^+ \)) and total pore volume (\( \V_{total}^+ \)) are particularly high at 1073 K, whereas the micropore volume (\( \V_{micp}^+ \)) is more prominent at lower temperatures. The results are consistent with the observed changes in the isotherms (0.2 < \( P/P_0 < 0.75 \)) for the samples, indicating the presence of micropores.

Figure 2 Adsorption isotherm of N₂ at 77 K for pyrolyzed cedar bark

Figure 3 Pore size distributions of pyrolyzed cedar bark

Figure 2 shows the adsorption isotherm of N₂ at 77 K for pyrolyzed cedar bark, which demonstrates the variation in adsorption capacity at different relative pressures (0.2 < \( P/P_0 < 0.75 \)). The isotherms indicate the presence of micropores and mesopores in the pyrolyzed samples. The isotherms are shown for temperatures ranging from 673 K to 1273 K, with distinct changes observed at higher temperatures.

Figure 3 illustrates the pore size distributions of pyrolyzed cedar bark, showing the variation in pore radii. The distributions are presented for temperatures ranging from 673 K to 1273 K, with peaks corresponding to the size distributions of micropores and mesopores. The pore size distributions provide insights into the吼e characteristics and structural properties of the pyrolyzed samples.

the resultant materials. In the latter case, on the other hand, the characteristics of the resultant solids may not be influenced greatly by the volatile matters, since most of the volatile products are easily separated and removed from the solid by the flow of nitrogen.

Specific surface area and the pore volume of the sample pyrolyzed at 973 K were 448 m²g⁻¹ and 0.198 mLg⁻¹, respectively. These values were smaller than those of conventional commercial activated carbons and activated carbon fibers, i.e., 700-2500 m²g⁻¹ and 0.3-0.8 mLg⁻¹, respectively. Low surface area and small pore volume may be responsible for the preparation procedure applied. In the present study, the samples were not subjected to "activation", but to thermal decomposition. It is well known that "activation" generally produces porous solids with a high surface area through partial gasification with steam, CO₂, or combustion gases at high temperatures, whereas thermal decomposition leads to the formation of carbonaceous precursor for activated carbons with low surface area and small pore volume.

3.4 Surface property of pyrolyzed cedar bark

αs-analysis: αs-plot is the comparison plot proposed by Gregg and Sing hypothesis and originally applied to determine micropore volume, specific surface area, and external surface area of porous materials. Kaneko et al. and Sing et al. improved the resolution of the method at a low αs-region and gave detailed information on the microporosity for some activated carbons with different micropore structures.

The αs-plots for pyrolyzed cedar bark are shown in Figure 4. It is apparent that the upward deviations were observed at lower αs-region for every sample except for ones obtained at 673 and 1273 K. These deviations suggest the presence of the enhanced microporosity for some activated carbons with different micropore structures.

The deviations were observed in the region below αs=0.5 in the present study, they were termed as the "filling swing" (FS) which should be associated with the "primary micropore filling" (PMF) proposed by Gregg and Sing hypothesis. It was reported that the FS or the PMF suggests empirically the presence of micropores whose diameters are less than 0.1 nm. This agrees well with the pore size distribution evaluated by MP method. The upward deviations were ceased and αs-plots lay on the straight lines through the origin for the samples treated at 1073 and 1273 K, as the values of αs approached to ca. 0.6. This means that surface properties of cedar bark pyrolyzed at these temperatures are similar to those of standard specimen, i.e., carbon black used in the present study. On the contrary, αs-plots for the samples pyrolyzed at 973 and 873 K lay on the straight lines which did not go through the origin, indicating dissimilarity in surface property between these samples and carbon black. These results suggest that functional groups of the cedar bark still partially remain, influencing the surface properties of the samples pyrolyzed below 973 K.

DRIFTS: FT-IR technique was used to provide the detailed information on the functional groups of pyrolyzed cedar bark. Diffuse reflectance infrared Fourier transform spectra (DRIFTS) of cedar bark and pyrolyzed ones at various temperatures are shown in Figure 5. These spectra were obtained as difference spectra with reference to that of carbon black. The assignment of a specific wavenumber to a given functional group may not be possible because of the overlapping and the shift of the characteristic bands of various functional groups, depending upon molecular structures and environment. However, a consensus in the assignment of frequencies to various functional groups is possible to a certain extent. The band assignment adopted in this work are summarized in Table 2, which are mainly based upon the literatures.

When the spectra for the products pyrolyzed at 673 and 873 K were compared to that for the original cedar bark, it was deduced that the heat treatment of the cedar bark at these temperatures...
induced some changes in the chemical structure of the samples. Decrease in the amount of OH, CH₂, CH₃, and C=O groups, and increase in \((C-H)\) vibrations of hydrogen atoms connected to aromatic rings were observed in these samples.

Since the broad band contains the overlapping of various individual absorption bands such as \((C-O)\) vibration bands in ether structure \((1240, 1110 \, \text{cm}^{-1})\) and \((\nu \phi-O-\phi)\) vibrations in ether linkages between aromatic ring sheets \((1250, 1016 \, \text{cm}^{-1})\), it may be concluded that small amounts of oxygen containing groups of ether structures still remain on the surface of the samples pyrolyzed at 923 and 973 K. These functional groups may be related to the surface properties which are different from those of carbon black.

In the spectrum for the sample pyrolyzed at 1073 K, any characteristic bands were hardly visible, meaning that surface functional groups of this sample was quite similar to that of the reference specimen, i.e. carbon black. This is consistent with the results derived from \(\alpha_s\)-analysis.

**pH of pyrolyzed cedar bark suspended water:** pH of water suspended with pyrolyzed cedar bark is listed in Table 3. Values of pH increased with increasing the temperature and time of pyrolysis of the cedar bark. It means that amount of acidic groups on the surface of the sample decreased in the course of the thermal treatment of the bark. DRIFTS spectra of pyrolyzed cedar bark showed decrease in the surface concentration of carboxylic acids and phenols which act as acid sites. The loss of carboxyl and phenolic hydroxy groups by the pyrolysis of woods was also reported using IR and NMR methods. Basic character was observed for the suspension containing samples pyrolyzed at higher temperatures. Higher values of pH may be ascribable to the loss of acidic groups during pyrolysis and/or inorganic components such as alkali and alkali earth elements in the bark.

### 4. Conclusions

Japanese cedar bark was pyrolyzed at 473-1273 K under atmospheric pressure in a flow of nitrogen. Morphology, adsorption properties, and functional groups of the samples were examined to characterize the pyrolyzed cedar bark. Although elongated tubular cells and fibrous materials in the bark shrank during the heat treatment, the features of fibrous cedar bark were preserved essentially without significant decay of the macroscopic morphology of the samples pyrolyzed at higher temperatures. The development of microporosity was observed for the samples pyrolyzed at 773 K and higher temperatures; \(S_{\text{BET}}\) (specific surface area) \(80-448 \, \text{m}^2g^{-1}\), \(V_p\) (pore volume) \(0.07-0.21 \, \text{mLg}^{-1}\), and \(D_i\) (mean pore diameter) \(0.46-0.77 \, \text{nm}\). Surface properties of cedar bark pyrolyzed at 1073-1273 K were similar to those of carbon black, whereas those of samples pyrolyzed at 873 K and lower temperatures were different from those of carbon black. Functional groups such as substituted aromatic rings and ether linkages were present on the surface of the samples pyrolyzed below 973 K, which might be responsible for the surface properties of the pyrolyzed cedar bark.

### References


