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Preparation of fibrous activated carbons from wood fiber

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Short fibrous hollow activated carbons with a high aspect ratio were prepared by carbonization and carbon dioxide activation of softwood and hardwood fibers. The softwood activated carbon consisted mostly of micropores even though the degree of burn-off during the activation became higher. In the case of the hardwood fiber, on the other hand, meso- and macropores as well as micropores were formed and the ratio of these large pores increased with an increasing degree of burn-off. The adsorbed amount of water and toluene vapor on these fibrous activated carbons was compared with that of the commercial activated carbon fibers (ACFs). These fibrous activated carbons showed a high adsorption capacity comparable to that of the ACFs.

1. Introduction

Activated carbon fiber (ACF) is an excellent adsorbent which has characteristics of low-pressure drop to mass transfer and high contact efficiency different from powder or granular carbons. These features are due to their fibrous shape with a high aspect ratio. In general, the conventional carbon fiber is commercially produced using raw materials such as viscose rayon, polyacrylonitrile, coal tar pitch or phenol-formaldehyde resin etc. [1] and activated in oxidizing gas to convert them into the ACF. These ACFs are more costly than powder- or granular-type activated carbons because more than 70–80% of the expensive carbon fibers are burned off during the activation process. Thus, if a low cost fibrous material could be employed and transformed into the corresponding carbon fiber, cheaper ACFs could be manufactured and applied more widely to many fields.

It is well known that fibrous materials are easily produced from wood in the papermaking and fiberboard industry [2]. These materials possess features, such as tissue and cell structures originally existing in the wood component. Also, on the surface of a cell wall there are some pits, which can go through the cell wall. If these materials could be converted into carbonaceous ones without any drastic change by carbonization and activation, such unique structures could be more useful for the adsorption and separation process of various gases or liquids containing toxic substances.

The objective of this study is to prepare fibrous activated carbons from wood materials and to evaluate their pore characteristics. At the same time the adsorption capability of the activated carbons for toluene and water vapor are compared with that of the conventional ACFs.

2. Experimental

2.1. Sample preparation

Two kinds of fibrous materials derived from soft- and hardwood were employed as carbon precursors in this study. These fibrous materials were raw materials for fiberboard, which were a mixture of a few woods. The

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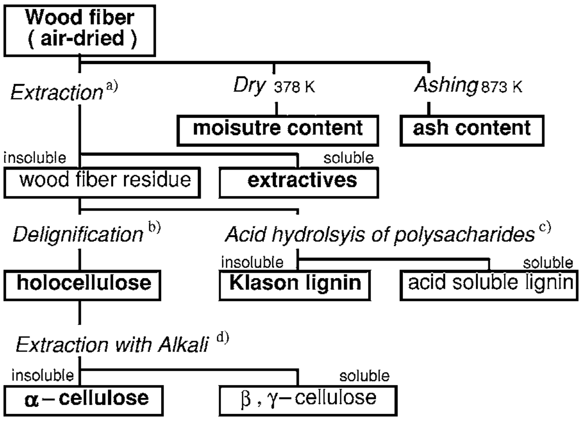

a) : Ethanol : Benzene = 1 : 2 (v / v), 6 h, Soxhlet extaract.
b) : $NaClO_2$, Acetic acid, 343 K, 3 – 4 h.
c) : 72 % - Sulfic acid, 3% -Sulfic acid (diluted), 4 h, superheating reflux.
d) : 17.5 % NaOH - aq, 293 K.

Figure 1 Fractionation procedure for wood fibers.

chemical component and ratio of wood constituent is different between soft- and hardwood. These may influence carbon microstructure, therefore, the chemical component of the wood fibers was analyzed. The fractionation procedure [3] for wood fibers is shown in Fig. 1.

The results of elemental and wood chemical component analysis for these fibrous materials are shown in Table I.

The moisture content given in Table I is reported on a dry basis, while the chemical component and ash are represented on the basis of constituents of dried fibers. The sum of determined wood chemical components exceeded 100% because this method was not based on a consecutive analysis and sometimes may cause lacking and/or overlapping sum of wood chemical components.

These wood fibers were so bulky that the dense samples were prepared by pressing them into plate-like shapes (size: length 25 mm, width 15 mm, thickness 5–10 mm, weight: 1.0–1.1 g) prior to carbonization. Each sample of 12–15 g was heat-treated up to 1173 K with a heating rate of 5 K/min under a nitrogen flow of 200×10^{-6} m^3/min. Thereafter it was held at this temperature for 1 h and then cooled down to room temperature. The carbon yield was 26.2 and 26.0% in dry-based raw materials for soft- and hardwood fiber, respectively. The carbonized sample was activated at 1153 K for 1–2 h by a carbon dioxide flow of 200×10^{-6} m^3/min. After the fibrous product had been activated, two kinds of the samples with different degrees of burn-off were prepared from each wood fiber. Finally, four kinds of samples, i.e., 43 and 68% burn-off for softwood, 40 and 70% burn-off for hardwood, were used for the next characterization. Also, three kinds of the commercially available ACFs were used for the comparison of pore structure and vapor adsorption. ACF 1, 2 produced from tar pitch and ACF 3 produced from phenol-formaldehyde resin were used.

TABLE I Elemental and wood chemical component analysis of wood fibers

	Softwood fiber (wt%)	Hardwood fiber (wt%)
C	48.5	49.3
H	6.4	5.9
O[a]	42.3	41.7
N	2.6	0.5
Ash	0.2	2.7
Holocellulose	59.8	70.8
α-cellulose	43.1	47.4
Klason lignin	24.3	29.2
Extractives	7.7	3.5
Ash	0.7	1.0
Moisture content[b]	6.9	7.2

[a] The oxygen is assessed by difference.
[b] Dry-based material.

2.2. Observation of the activated carbons

The morphological changes caused by the carbonization and the activation were observed by scanning electron microscopy (SEM).

2.3. Pore characteristics of the activated carbons

Information on the pore structure of the products was obtained by nitrogen adsorption isotherm at 77 K. A SORPTMATIC 1900 (FISONS Instrument Co. Ltd.) was used for the analysis of the activated carbons from wood fibers, while a BELSORP 18S (BEL JAPAN Co. Ltd.) was used for commercial ACFs. The specific surface area and the micropore volume of the samples was estimated from BET analysis [4], t-plot [5] and the subtracting pore effect (SPE) method [6] using α_s-plot. The total pore volume was calculated from the amount of nitrogen adsorbed at $P/P_0 = 0.94$–0.99. The average pore size was estimated from the BET surface area and the total pore volume.

2.4. Ash analysis

The minerals included in both wood fibers were analyzed by inductively coupled plasma (ICP) Emission Spectroscopies, SPS4000 of Seiko Instrument Co. Ltd and Optima 4300DV of Perkin Elmer Co. Ltd., using the ash from wood fibers which was air-burned at 873 K: the ash obtained was treated in a hot solution of hydrogen nitride and perchloric acid. The residue was then heat-treated in a furnace and immersed in sodium carbonate solution. Furthermore, the insoluble matter heat-treated at the same condition was added to a potassium hydrogen sulfate solution. All of the soluble fraction from these processes was collected for the ICP measurements.

2.5. Vapor adsorption of the activated carbons

One of the applications for these activated carbons is considered as vapor adsorbents in atmosphere. For example, adsorbents for volatile organic compound (VOC) and water vapor are suitable for their application. Therefore, toluene and water vapor as test

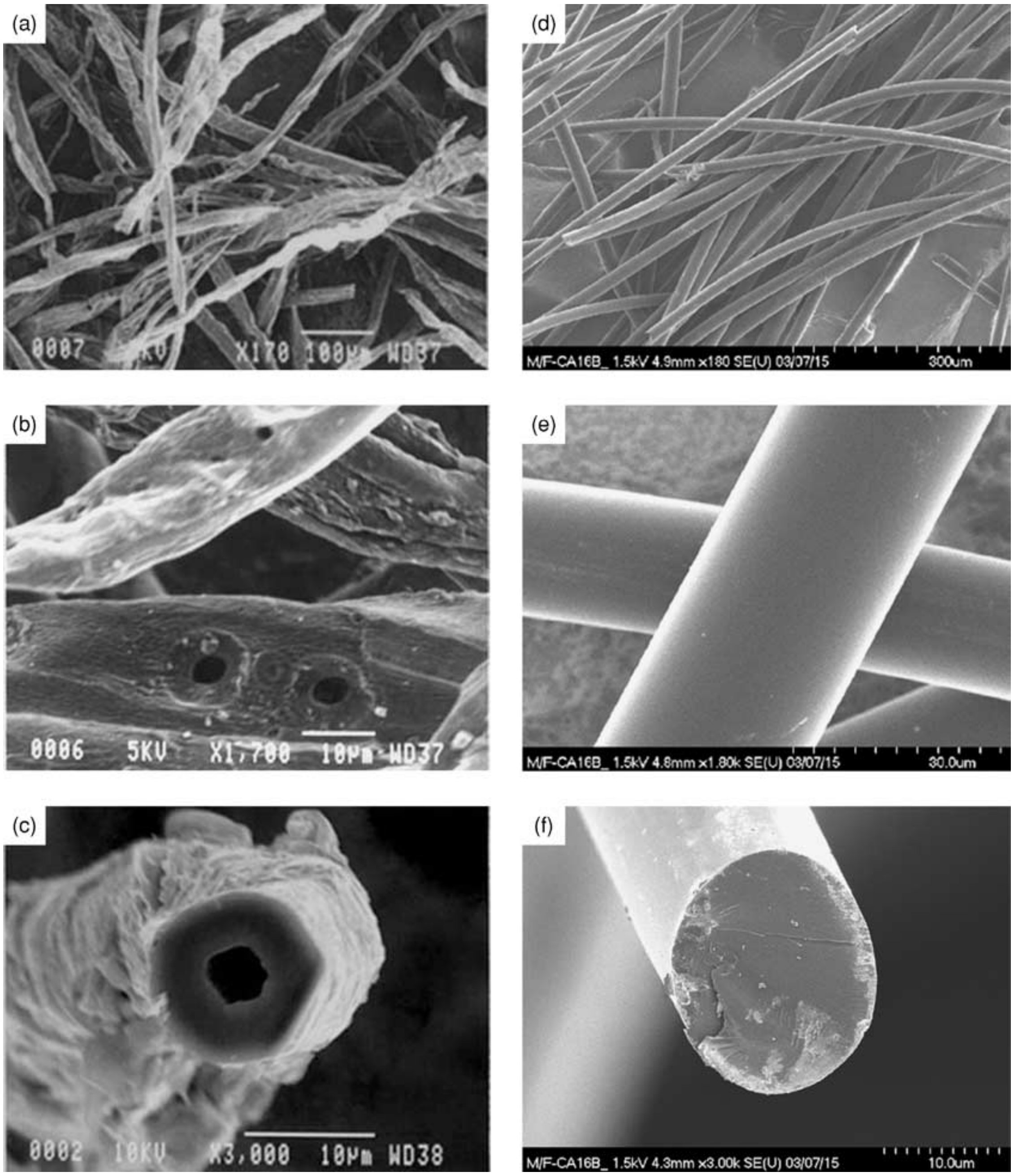

Figure 2 SEM images of softwood fibrous activated carbons: (a) and (b) 68% burn-off sample, (c) 43% burn-off sample and a commercial activated carbon fiber, (d), (e), (f): ACF 1. The magnification in (a) and (d), (b) and (e), (c) and (f) is respectively same for the comparison between the fibrous carbon and the ACF.

adsorbents were selected. The adsorption of toluene vapor was carried out by holding the dry sample in a desiccator with a beaker of toluene at 298 K and the adsorption of water vapor was carried out by holding the dry sample in a thermo-hygrostat at 298 K, 95 RH% i.e., the amount of saturated adsorption was weighed after the adsorption equilibrium had been reached.

3. Results and discussion

3.1. Morphological characteristics of activated carbons

The morphology of the softwood carbons after the activation are shown in Fig. 2a–c. In addition, SEM images of ACF 1 are shown in Fig. 2d–f for comparison.

The morphology is very different between the softwood carbons and ACF 1. The hardwood carbons have a similar texture, thus their SEM images are omitted. It indicates parts of the wall structure due to the wood cell. That is, the original textures are still maintained during the carbonization and the activation process. Wood chips are treated under high pressure and temperature conditions in the manufacturing process of wood fiber, resulting in decomposed or modified hemicelluloses and lignin [7, 8]. As reported in the papers of Byrne and Nagle [9, 10], the shrinkage to axial, tangential and radial direction of wood is different in the thermal decomposition of wood monolith. But actually one can find that the wood cell wall structure is kept without any damage. Also, no morphological destruction was observed even with severe burn-off. After the activation, the samples have a fibrous shape of 1–2 mm with a diameter of 10–30 μm, whereas the hollow structure with a high aspect ratio is kept and there are some pits

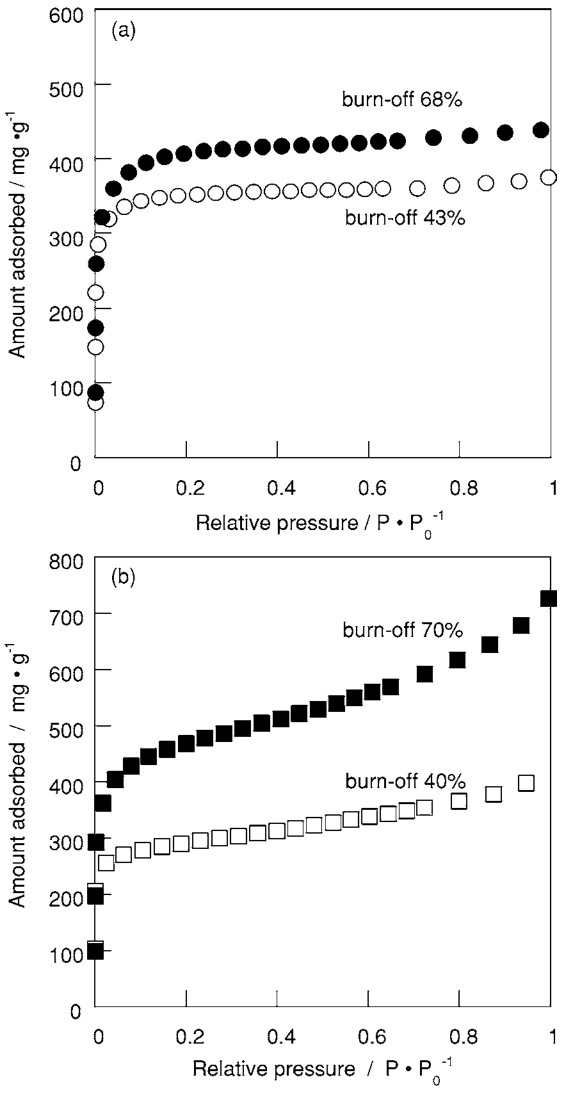

Figure 3 Adsorption isotherms of (a) softwood and (b) hardwood fibrous activated carbons with different burn-off.

left on the surface of the wall separating each cell. It is worth noting that the fibrous activated carbons can be easily obtained in such a manner as the conventional ACFs are generally manufactured.

3.2. Adsorption isotherms and pore characteristics

The nitrogen isotherms of softwood fibrous activated carbon with different burn-off are shown in Fig. 3a.

Both isotherm curves are very similar to each other. The steep nitrogen uptake at very low relative pressure suggests that both samples contain a large quantity of micropores. But the amount adsorbed was almost saturated at higher pressure. According to the IUPAC classification [11], these isotherm curves are classified type I, showing a behavior typical to the materials with mainly micropores. As the curve for the 68% burn-off sample is higher than that for the 43% burn-off sample, it is clear that the longer the activation time, the more the microspores could develop. Fig. 3b shows the isotherms of the hardwood activated carbon. The amount adsorbed also indicates a steep rise at lower relative pressure. In this case, however, a gradual increase can be observed at higher relative pressures. This tendency appears more clearly on the 70% burn-off sample. It is evident that the activated carbon from the hardwood fiber contains a considerable amount of meso- and macropores as well as micropores. Since the desorption branch of the isotherms was not measured for these samples, the pore size distribution on mesopores could not be obtained. Pore characteristics of fibrous activated carbons and the commercial ACFs are shown in Table II.

Although the V_{micro} values are a little different between the two types of analysis methods, t-plot and α_s-plot, the ratio of micropore volume to the total volume in the hardwood activated carbons is much lower compared with that in softwood activated carbon and three commercial ACFs used as reference samples. This suggests that the hardwood carbons contain a considerable amount of meso- and macropores, while softwood carbons and ACFs consist predominantly of microspores.

3.3. Difference of pore structure between the softwood and the hardwood activated carbons

Table I shows that the content of holocellulose and Klason lignin components in hardwood are a little

TABLE II Pore characteristics of fibrous activated carbons and commercial ACFs

Sample	S_{BET}[c] (m^2/g)	V_{total}[d] (mm^3/g)	t-plot V_{micro}[e] (mm^3/g)	t-plot $V_{\mathrm{micro}}/V_{\mathrm{total}}$[f] (%)	α_s-plot V_{micro}[e] (mm^3/g)	α_s-plot $V_{\mathrm{micro}}/V_{\mathrm{total}}$[f] (%)	W_{avg}[g] (nm)
Softwood fiber							
Burn-off 43%	1087	464	419	90.3	417	89.9	0.85
Burn-off 68%	1269	542	491	90.6	484	89.2	0.85
Hardwood fiber							
Burn-off 40%	874	492	280	56.9	267	54.3	1.12
Burn-off 70%	1386	898	409	45.4	410	45.7	1.30
ACF 1[a]	1141	484	457	94.4	462	95.5	0.85
ACF 2[a]	1865	925	898	97.1	899	97.2	0.99
ACF 3[b]	1747	722	706	97.8	703	97.4	0.83

[a] Commercial activated carbon fiber made from coal tar pitch.

[b] Commercial activated carbon fiber made from phenol-formaldehyde resin.

[c] Specific surface area from BET analysis.

[d] Total pore volume estimated from adsorbed amount at P/P_0 (0.94–0.99).

[e] Micropore volume.

[f] $(V_{\mathrm{micro}}/V_{\mathrm{total}}) \times 100$.

[g] Average pore size $(2V_{\mathrm{total}}/S_{\mathrm{BET}})$.

TABLE III Elemental analysis of the wood fibers carbonized at 1173 K

	Elemental analysis (wt%)				
Sample	C	H	O[a]	N	Ash
Softwood fiber	90.2	0.5	4.9	2.5	1.9
Hardwood fiber	89.9	0.9	4.6	0.7	3.9

[a] The oxygen is assessed by difference.

TABLE IV Principal metals in the carbonized wood fibers. The ash collected by burning the carbonized samples in air at 873 K was treated in acid solution. The analysis was performed for a soluble fraction

Element	Softwood fiber (wt%)	Hardwood fiber (wt%)
Al	0.4	2
Ca	10	10
K	7	10
Mg	4	3
Na	20	1
Si	2	10

The error limits: $x/2 - 2x$.

higher than that of softwood. However, such a difference is not important because these components decompose completely during the carbonization. The ash content in the samples carbonized at 1173 K is shown in Table III.

As a result it was found that the content from the softwood carbon is 1.9%, whereas that from the hardwood is 3.9%. The effect of mineral matter content on porous structure was reported by Linares-Solano *et al.* [12]; coal samples with a lower ash content yield higher micropore volumes when compared between the samples with the same extent of burn-off. Also, the elements contained in the ash of this sample were analyzed by ICP. Table IV indicates the amount of principal metals in a fraction dissolved by the acid treatment.

The existence of K or Na compounds in the form such as KOH or NaOH is known to generate exclusively the micropores during chemical activation [13, 14]. As is clear from Table IV, only the ratio of Na content in the ash from softwood fiber carbon is much higher than that from the hardwood one, except for Al and Si elements which are considered to have no catalytic effect to make micropores. Thus, the difference in the pore structure between activated carbons derived from soft- and hardwood may be explained in terms of the role of mineral species in the ash; The ratio of Na content occupied in the ash of softwood carbon is relatively higher, the Na compounds in the softwood fiber carbon may enhance the formation of the microspores. On the other hand, the ratio of Na occupied in the ash of hardwood fiber carbon is relatively lower, these may accompany the opening and widening of the microspores, bringing about the gradual development of larger pores. However, it is difficult to understand the generation of micropore by Na and K elements from only the ash analysis, therefore it is necessary to use some other techniques on the contribution of Na and another elements to clarify the micropore generation.

TABLE V Amount of toluene and water vapor adsorbed on fibrous activated carbons at 298 K

Sample	Toluene (mg/g)	Water (mg/g)
Softwood fiber		
Burn-off 43%	417	291
Burn-off 68%	481	372
Hardwood fiber		
Burn-off 40%	448	284
Burn-off 70%	779	619
ACF 1	383	274
ACF 2	835	798
ACF 3	641	522

3.4. Adsorption of toluene and water vapor

The adsorption of toluene and water vapor was carried out in order to evaluate the adsorption performance of the fibrous activated carbons obtained from woody materials. The results are shown in Table V together with those for the commercial ACFs.

It is observed that the adsorption amount of toluene and water vapor corresponds roughly to the specific surface area and pore volumes. When the amount adsorbed is compared between the adsorbents with a similar surface area, the adsorption capability is comparable to that for commercial carbons, ACF 1, ACF 2 and ACF 3. It is suggested that the adsorption ability of the fibrous activated carbons prepared in this study is by no means inferior to that of the conventional ACFs. In this case only the micropores in the activated carbons act as an adsorption sites for small molecules such as toluene or water. On the other hand, the activated carbon, prepared from the hardwood fiber with meso- and macropores as well as microspores, may be expected to be an adsorbent for macromolecules and also as an electrode for supercapacitors, and study of this is now in progress.

4. Conclusion

Short fibrous hollow activated carbons with a high aspect ratio were prepared by carbonization and carbon dioxide activation of softwood and hardwood fibers. The softwood activated carbon consisted mostly of micropores even if the degree of burn-off during activation became higher. The specific surface area of the softwood activated carbon was 1087 and 1269 m^2/g for burn-off 43%, 68% respectively. In the case of the hardwood activated carbon, on the other hand, meso- and macropores as well as micropores formed and the ratio of these large pores increased with increasing the degree of burn-off. The specific surface area of the hardwood activated carbon was 874 and 1386 m^2/g for burn-off 40%, 70% respectively. The difference in pore character between the soft- and hardwood activated carbon was considered to be due to the content of Na which has a catalytic effect on the activation process. The amount adsorbed of toluene and water vapor was compared with commercial ACFs and these fibrous activated carbons. In particular, the maximum amount adsorbed of 779 mg/g and 619 mg/g for toluene and water vapor, respectively, was obtained for the hardwood activated carbon with a burn-off 70%. The adsorption capacity of these fibrous activated carbons was found to be comparable to that of the commercially available ACFs.

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