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Properties of differently shaped activated carbon fibers

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Abstract−Differently shaped carbon fibers (R-, I-, C-, Y-, and X-type) were prepared from melt-spinning of reformed naphtha cracking bottom oil precursors through various shaped spinnerets. These carbon fibers were activated by steam and activation properties were compared. The decrease of hydraulic radius resulted in the extending of the external surface area of carbon fibers. Activation energy and rate of differently shaped carbon fibers were affected by external surface area. Especially, the activation rate of tetralobal carbon fibers (X-type) appeared much larger than other shaped carbon fibers due to the smallest hydraulic radius. Adsorption capacity of tetralobal activated carbon fibers was also larger than other shaped activated carbon fibers.

Key words: Activated Carbon Fibers, Petroleum, Process Control

INTRODUCTION

Carbon fibers have greater merit than other engineering materials, so they have very wide applications in industry. Particularly, high-performance carbon fibers are widely demanded as special properties [1,2]. Carbon fiber can be used as an intermediate material of activated carbon fiber (ACF), which is known as an excellent adsorbent for removal of pollutants from water or atmosphere [1,3]. Compared with activated carbon, ACF has a remarkable adsorption capacity and rate owing to the well-developed micropores. The application of ACF has been widely extended, not only as an adsorbent but also as a catalyst support, an electronic material, and an energy-storage device.

Nevertheless, many researchers have tried only to modify the surface functional groups of ACF with chemicals such as nitric acid, sodium hydroxide, or ozone to enhance the adsorption capacity [4,5]. Some researchers have impregnated metals such as Ag, Cu, Co, Pd, and Pt on ACF to enhance the catalytic activities [6-10]. However, no one has tried to develop ACFs in different shapes to enhance the activation efficiency and adsorption capacity.

Therefore, in this work, differently shaped carbon fibers were prepared through differently shaped spinnerets from pitch precursor and then these carbon fibers were steam activated. Characterization of these differently shaped ACFs was carried out in relation to the activation energy, rate and adsorption capacity.

EXPERIMENTAL

1. Preparation of Differently Shaped ACFs

Spinnable isotropic precursor pitch was prepared by reforming

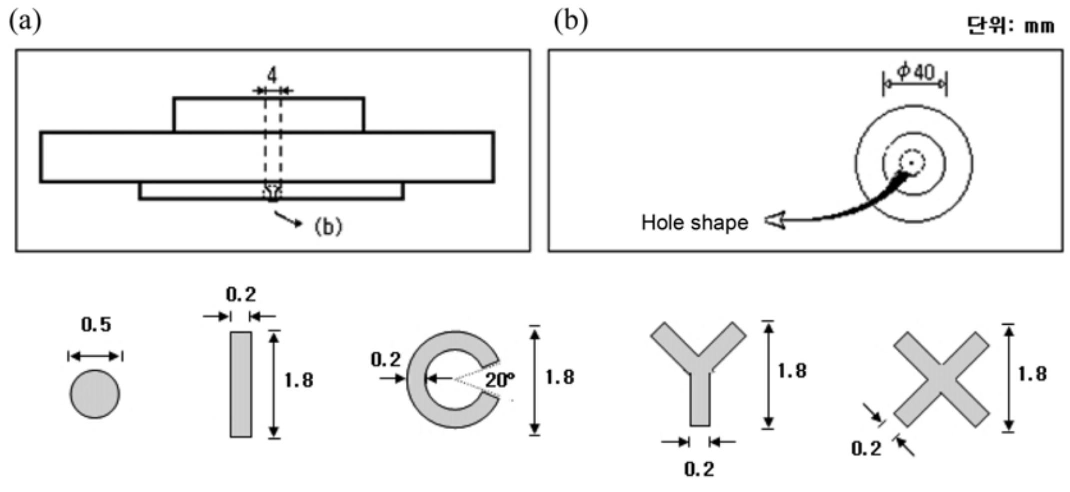

Fig. 1. Dimension of differently shaped spinnerets; (a) a front view, (b) a plane figure.

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naphtha cracking bottom oil following the previous work [11]. The spinnerets, which have different hole shapes (R=round, I, C, Y, and X shape), were prepared and attached to the bottom of melt-spinning cylinder. Fig. 1 shows the dimension of differently shaped spinnerets. The cylinder containing reformed precursor pitch was electrically heated to the spinning temperature. Nitrogen was blown through the melted pitch to improve the fluidity and retain inert surrounding. As-spun pitch fibers were collected on a winding machine, were placed in an air forced-convection oven and stabilized at 280 °C for 3 h. The stabilized fibers were cut into 5 cm length and carbonized at 1,000 °C for 0.5 h in nitrogen. The carbonized fibers were activated with steam diluted in nitrogen by changing the temperature and time. The carbon fibers and ACFs in different shapes were abbreviated to R-, I-, C-, Y-, X-CF and R-, I-, C-, Y-, X-ACF, respectively.

2. Characterization

Average perimeter, cross-sectional area and their ratio of differently shaped fibers were calculated from at least 100 observations of scanning electron microscopy (TOPCON, SM-500) images. To measure the burn-off level and the activation energies, the carbon fibers were weighed before and after activation, and activation energies were calculated by the Arrhenius equation. The adsorption isotherms of N_2 were measured at 77 K by using an ASAP 2010 (Micromeritics, USA) to study the porosity. BET surface area (S_{BET}) of ACFs was calculated by using the BET equation. Total pore volume (V_T) was estimated by using the liquid volume of nitrogen at a relative pressure of 0.99. Micropore volume (V_{micro}) was calculated by using the Dubinin–Radushkevich equation, and mesopore volume (V_{meso}) was obtained by subtracting the micropore volume from the total pore volume. Average pore diameter (D_P) was calculated by dividing the total pore volume by the specific surface area ($4V_T/S_{BET}$).

RESULTS AND DISCUSSION

1. External Surface Area

The total external surface area (S) of any type of fiber can be calculated by the perimeter of an individual fiber (P_s), number of individual fibers (n_f), and length (L).

$$S = P_s \cdot n_f \cdot L = \frac{P_s}{A_s} \cdot A \cdot L \quad (1)$$

Hydraulic radius (r_H) was defined as the ratio of cross-sectional area of channel (A_s) to perimeter of channel in contact with fluid (P_s) [12]. Thus, the external surface area was expressed by the hydraulic radius.

$$S = \frac{P_s}{A_s} \cdot A \cdot L = \frac{A \cdot L}{r_H} \quad (2)$$

According to the above equation, if differently shaped fibers have similar total cross-sectional areas and length, the fiber which has a smaller hydraulic radius, has the larger external surface area. Therefore, the hydraulic radius of carbon fiber is very meaningful for increasing the external surface area of carbon fiber.

The perimeter, cross-sectional area and hydraulic radius are summarized in Table 1. The hydraulic radius of the X-CF was the smallest, approximately 1.3 times smaller than that of the R-CF. Therefore, the external surface area of X-CF prepared under the same conditions, might have been approximately 1.3 times larger than R-CF.

Table 1. Perimeter, cross-sectional area, and the hydraulic radius of differently shaped carbon fibers

Shape	Perimeter (μm)	Cross-sectional area (μm^2)	Hydraulic radius (μm)
R	91.1	660.2	7.250
I	148.0	928.0	6.270
C	218.5	1333.5	6.103
Y	229.0	1477.6	6.452
X	232.0	1339.0	5.772

* Spun at 400 m/min

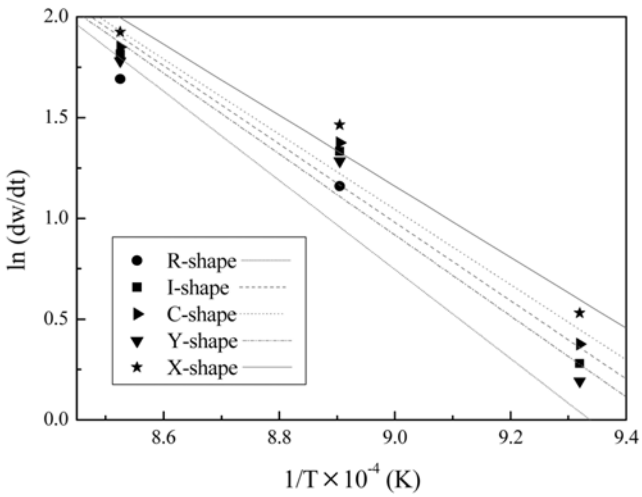

Fig. 2. Arrhenius plots of activation of differently shaped carbon fibers.

2. Activation Energy and Rate

To study the effect of fiber shape against the activation energy, differently shaped carbon fibers were activated at several different temperatures and times. Then, the activation energies were estimated by using slopes of the Arrhenius equation from Fig. 2. The activation energies of R-, I-, C-, Y-, and X-CF were 183, 161, 154, 166, and 146 kJ/mol, respectively. These results have shown that the activation energy was affected by the external surface area or hydraulic radius. If the hydraulic radius decreased, the activation energy of carbon fiber also decreased.

If carbon fibers of different shapes but with the same mass are activated, the activation rate (=burn-off/activation time) of the carbon fiber which has larger external surface area will be larger. In other words, the corresponding burn-off will be obtained in a shorter time with larger external surface area carbon fiber. Fig. 3 shows the burn-offs of differently shaped carbon fibers with respect to activation time at 900 °C. Under the same activation time, burn-off levels differed from one another depending on the shapes, which meant that the external surface area affected burn-off levels. The burn-off level of X-CF was larger than that of carbon fibers of other shapes and was particularly about 1.3 times larger than that of R-CF because of the larger external surface area. Activation time of X-CF for the

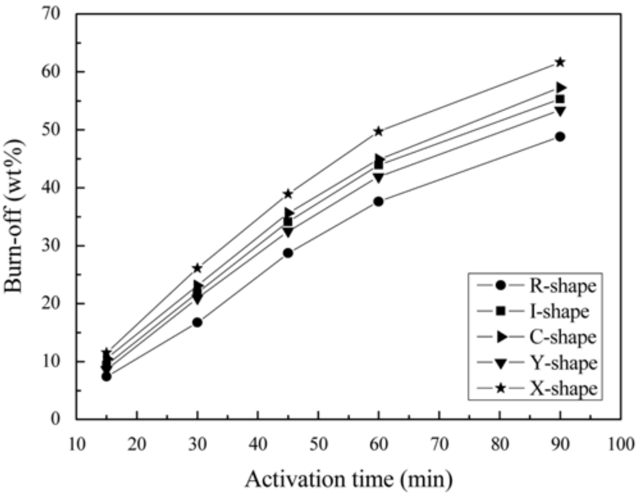

Fig. 3. Burn-offs of differently shaped carbon fibers with respect to activation time at 900 °C.

same burn-off level could be shorter than that of carbon fiber of other shapes. Actually, the activation time of X-CF was about 1.43 times shorter than that of R-CF at 40 wt% burn-off. The activation rate of X-CF (6.85 mg/g·min) was also approximately 1.3 times larger than that of R-CF (5.42 mg/g·min). Especially, for 0-30 min, the activation rate of X-CF (8.70 mg/g·min) was approximately 1.6 times larger than that of R-CF (5.57 mg/g·min).

3. Adsorption Capacity

Fig. 4 shows the changes in cross-sectional shape of carbon fibers and ACFs during the activation. Despite the 37.6-49.7 wt% weight loss by burn-off, the shapes of fibers were not changed during the activation, which means that the development of micropores progressed all over the fibers.

Table 2 shows the pore properties of differently shaped ACFs obtained from adsorption isotherm. The BET surface area, total pore volume and pore diameter were in inverse proportion to the hydraulic radius. The average pore diameters of ACFs ranged from 14.2 Å to 16.4 Å. The specific surface area of non-R-ACFs was larger than

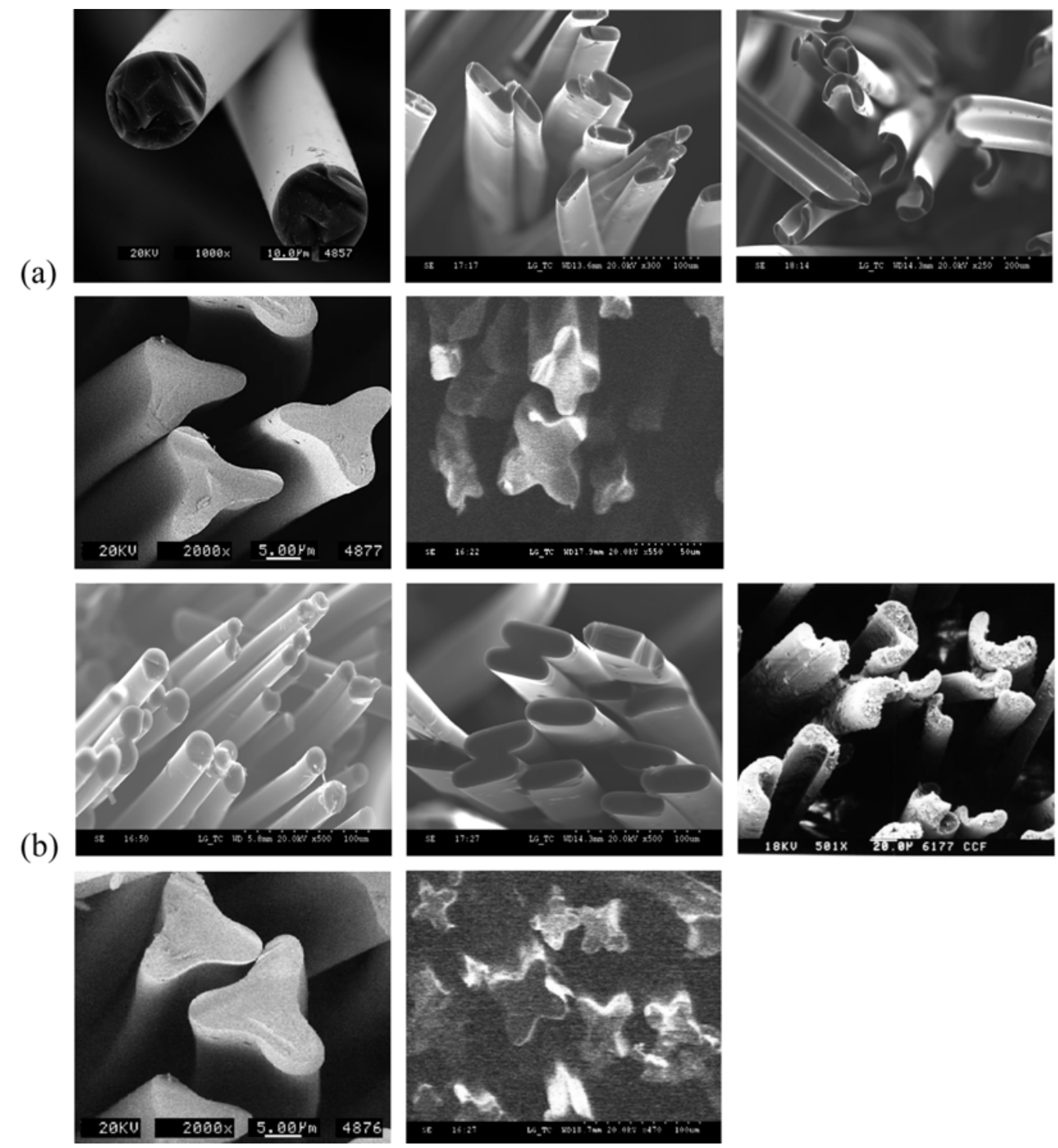

Fig. 4. SEM images of differently shaped carbon fibers (a) before and (b) after activation.

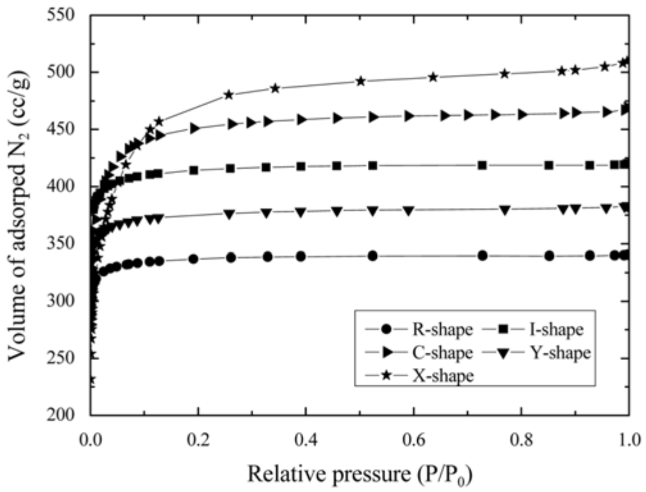

Fig. 5. Adsorption isotherms of N_2 on differently shaped ACFs.

Table 2. Pore properties of differently shaped ACFs obtained from adsorption isotherm

Shape	S_{BET} (m^2/g)	V_T (cc/g)	V_{micro} (cc/g)	V_{meso} (cc/g)	D_p (Å)
R	1195	0.43	0.40	0.02	14.2
I	1290	0.51	0.47	0.03	15.8
C	1398	0.57	0.54	0.03	16.3
Y	1272	0.48	0.43	0.05	15.1
X	1498	0.61	0.61	0.01	16.4

* Activated at 900 °C for 1 h

that of R-ACF. Particularly, the specific surface area of X-ACF was approximately 1498 m^2/g, which is 1.1-1.3 times larger than that of ACFs with other shapes.

Fig. 5 shows the N_2 adsorption isotherms of differently shaped ACFs produced in this research. The isotherms exhibit Type-I, which indicates that the pores developed in these ACFs show pore size less than 20 Å. The trend of pore development in non-R-ACFs was very similar to that in R-ACF. The only difference was the amount of adsorption. The amount of adsorbed N_2 of X-ACF was larger than that of ACFs of other shapes, which is due to the larger surface area.

CONCLUSIONS

The activation energy and rate of carbon fibers were affected by external surface area, and adsorption properties of ACFs also depend on the external surface area. The external surface area was increased by decreasing the hydraulic radius of carbon fiber, and hydraulic radius was in this order: X-, C-, I-, Y-, and R-type. At the same burn-off level, the activation time of X-CF was shorter than that of carbon fiber in other shapes, and the activation energy of X-CF was approximately 1.3 times lower than that of R-CF. The shapes of carbon fibers were maintained during the steam activation, but the specific surface area and total pore volume of X-ACF were larger than those of ACFs in other shapes. Therefore, we can produce ACFs that have more effective activation and adsorption properties by applying non-round spinneret such as X-shaped spinneret.

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