

## POROUS STRUCTURE OF POLYARYLAMIDE-BASED ACTIVATED CARBON FIBRES

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**Abstract**—Activated carbons were prepared from two polyarylamide fibres (Kevlar and Nomex) by carbonization and subsequent steam activation to 25 and 50% burn-off. The porous structure of the carbons has been investigated by physical adsorption of  $\text{CH}_2\text{Cl}_2$  and  $\text{N}_2\text{O}$  at 293 K and immersion calorimetry into liquids of different molecular dimensions.

The activated fibres have good sorptive capacities and relatively narrow micropores. The materials resulting from activation at low degrees of burn-off could therefore be of great interest in gas separation, owing to their molecular sieve properties. Compared to industrial activated carbons, the fibres are hydrophilic and have small external surface areas. Copyright

**Key Words**—Activated fibres, microporosity, molecular-sieve properties.

### 1. INTRODUCTION

The use of carbon molecular sieves (CMS) in gas separation—in particular oxygen and nitrogen—has grown steadily over the past years [1]. These carbons are characterized by a high adsorption capacity and by dimensions of their micropore openings, which must be close to those of the potential adsorptives. The latter is of great importance in the separation of gases since molecules with a kinetic diameter smaller than the average opening rapidly diffuse into the micropore volume, while the adsorption of larger molecules is much reduced or excluded. Depending on the respective dimensions, a small change in the size of the constrictions can affect considerably the rate of diffusion of a given gas molecule. As a consequence, gas mixtures can be separated efficiently.

At present, the classical manufacture of carbon molecular sieves requires the development of a sufficiently large sorptive capacity in the precursor, which is achieved by physical or chemical activation. This process often leads to relatively wide micropores and requires a subsequent reduction of their width. This is usually achieved by the deposition of carbon resulting from the cracking of hydrocarbons adsorbed in the micropores [2], by varying the degree of heat treatment, or through mild gasification [3]. As a result, the pore size decreases, as well as the pore volume, and a substantial fraction of the initial adsorption capacity is lost.

From a practical point of view, the use of activated carbon fibres as selective molecular adsorbents presents many advantages over activated carbons, in view of their unique characteristics [4]: Activated carbon fibres often have a greater adsorption rate and a

larger adsorption capacity than typical granular activated carbons used in gas filtration. They can also be converted into a wide variety of forms to be used in thin layers for treatment of high gas flow rates. Fibres are also easy to handle and the problems arising from the packing of the granules or powders can be avoided. All these features increase the efficiency of the adsorption bed and lead to simplifications in the design and in the size of regeneration units used for environmental pollution control.

In the present work we describe the preparation and the properties of activated carbon fibres obtained from polyarylamide chars activated with steam. The adsorption capacity and molecular-sieve properties of the activated carbons were examined by techniques based on gas adsorption and on immersion calorimetry with probes of various molecular dimensions.

As before, the theoretical background is provided by Dubinin's theory for the volume filling of micropores [5] and its extension to immersion calorimetry [6,7]. In the case of adsorption by typical microporous carbons, the fundamental relation is the Dubinin-Radushkevich equation

$$N_a = N_{a0} \exp[-(A/\beta E_0)^2] \quad (1)$$

where  $N_a$  represents the amount adsorbed at temperature  $T$  and relative pressure  $p/p_0$ ,  $N_{a0}$  is the limiting amount adsorbed in the micropores and  $A = RT \ln(p_0/p)$ ;  $\beta$  and  $E_0$  are specific parameters depending on the adsorptive and on the adsorbent. The latter is related to the average micropore-width [8]. An important characteristic of the micropore system is the micropore volume  $W_0 = N_{a0} V_m$ , where  $V_m$  is the molar volume of the adsorbate (it is usually taken equal to the volume of the liquid at the same temperature).  $W_0$  may vary with the size of the adsorptive, depending on the distribution of the

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micropore sizes and/or on the presence of constrictions at the entrance of the pores. The latter corresponds to so-called gate- or molecular-sieve effects, which will be considered in this study.

## 2. EXPERIMENTAL

### 2.1 Raw materials

Two types of polyarylamide fibres were used as starting materials, Nomex III T-455 (poly(m-phenylene isophthalamide)) and Kevlar (poly(p-phenylene terephthalamide)). Both materials are registered trademarks of E.I. DuPont de Nemours, Inc. The average diameters of the fibres were around 10  $\mu\text{m}$ .

### 2.2 Sample preparation

**2.2.1 Carbonization.** 2 g of polyarylamide fibres were placed in a tubular quartz reactor (3 cm i.d.) and heated under a stream of nitrogen (1500  $\text{cm}^3/\text{minutes}$ ) up to 850°C. The heating rate was 10°C/minute, with a soaking time of 1 hour at the final temperature. After treatment, the samples were cooled in  $\text{N}_2$  to room temperature. The carbonized Nomex and Kevlar fibres will be designated here as N-0 and K-0, respectively.

**2.2.2 Activation.** The activated carbon fibres were obtained by gasification of the carbonized fibres in a 28% w/w steam/nitrogen gas mixture (gas flow rate: 500  $\text{cm}^3/\text{minute}$ ) at 700°C. The reaction was carried out in a quartz reactor (2 cm internal diameter) placed in a vertical furnace. Samples activated to burn-offs of 25% (K-25 and N-25) and 50% (K-50 and N-50) were produced by this technique.

### 2.3 Sample characterization

The microporosity of the activated carbon fibres was characterized by techniques based on Dubinin's theory and on its extensions. They have been described in detail elsewhere [7]. The techniques used in this study include the adsorption of  $\text{CH}_2\text{Cl}_2$  and  $\text{N}_2\text{O}$  vapours at 293 K and immersion calorimetry at the same temperature, using molecular probes of different critical dimensions such as dichloromethane, benzene, cyclohexane, carbon tetrachloride, 1,5,9-cyclododecatriene (CDDT) and tri-2,4-xylylphosphate (see Table 1). Complementary information on the hydrophilic/hydrophobic character of the

carbon surface was obtained from immersion into water.

The  $\text{CH}_2\text{Cl}_2$  and  $\text{N}_2\text{O}$  adsorption isotherms were determined gravimetrically, using a quartz spring balance of the McBain type. All samples were out-gassed at 400°C for 12 hours to a residual pressure around  $10^{-5}$  Torr prior to adsorption and immersion experiments. The enthalpies of immersion were measured in a calorimeter of the Calvet type, described elsewhere [9].

As discussed elsewhere [7], the micropore volume  $W_0(L_c)$  filled by a liquid of critical molecular dimension  $L_c$ , can be calculated by using the expression derived from eqn (1)

$$W_0(L_c) = (\Delta h_i(\text{exp}) - h_i S_e) 2V_m / \beta E_0 (1 + \alpha T) (\pi)^{1/2} \quad (2)$$

where  $\Delta h_i(\text{exp})$  is the experimental enthalpy of immersion of the carbon into the liquid,  $\alpha$  and  $V_m$  are the thermal expansion coefficient and the molar volume of the liquid and  $h_i$  is the specific enthalpy of wetting of the external (non-microporous) surface  $S_e$  of the carbon.

For carbons with relatively small external surface areas, the quantity  $h_i S_e$  can be neglected in the calculation of  $W_0(L_c)/W_0(\text{CH}_2\text{Cl}_2)$ , the ratio between the limiting volumes filled by the different probes and the micropore volume accessible to a small molecule (in our case,  $\text{CH}_2\text{Cl}_2$ ). This ratio can be estimated with a good approximation from the enthalpies of immersion alone, without considering  $h_i S_e$  in eqn (2). Examples are provided in the following section (Figs 6 and 7)

This approach shows that immersion calorimetry alone can already provide a reasonable picture of the accessibility of the micropores. By comparing the profiles obtained for the different samples within an activation series, it is possible to follow the evolution of the microporosity. However, the absolute values of the volumes  $W_0$  require at least one isotherm for every sample (usually  $\text{CH}_2\text{Cl}_2$  or benzene at 293 K or nitrogen at 77 K).

## 3. RESULTS AND DISCUSSION

### 3.1 Carbonized fibres

The two original polymers differ only in the position of substitution of the aromatic rings. However, this leads to differences in a number of physical and mechanical properties (density, thermal behaviour, tenacity, etc. [10]). As a consequence, the polymers undergo different transformations during pyrolysis. A first indication is provided by the chars obtained under identical conditions: After heating in nitrogen at 10°C/minute, up to 850°C, Nomex and Kevlar yielded respectively 51 and 39% of solid residues (samples N-0 and K-0). These results are in agreement with those obtained by other authors [11,12]. Freeman *et al.* [12] suggest that the much higher

Table 1. Characteristics of the liquids at 293 K [7]

Liquid	$L_c$ (nm)	$\alpha$ [ $10^{-3}$ ] ( $\text{K}^{-1}$ )	$V_m$ ( $\text{cm}^3/\text{g}$ )	$\beta$
Dichloromethane	0.33	1.34	64.02	0.66
Benzene	0.41	1.24	88.91	1.00
Cyclohexane	0.54	0.96	108.10	1.04
Carbon tetrachloride	0.63	1.22	96.50	1.05
1,5,9-Cyclododecatriene	0.76	0.76	182.02	1.90
Tri-2,4-xylylphosphate	1.50	0.66	360.04	4.05

crystallinity of Kevlar fibres favours the formation of volatile compounds by depolymerization reactions.

The difference in the original polymer structures is also reflected, to some extent, by the adsorption characteristics of the corresponding chars. For example, the enthalpies of immersion of the carbonized samples into a series of liquids with different molecular sizes, as shown in Table 2. The low enthalpies obtained with the Kevlar char K-0 suggest a poorly developed or inaccessible porous structure. On the other hand, for the Nomex char N-0 one observes a relatively high enthalpy of immersion into  $\text{CH}_2\text{Cl}_2$  (43 J/g, as opposed to 9 J/g for K-0), followed by a significant drop for the liquids with larger critical dimensions. This evolution clearly indicates the presence of a relatively important microporosity in sample N-0, but with molecular-sieve properties around 0.4–0.5 nm. On the other hand, the parameters  $E_o$  and  $W_o$  obtained for the activated fibres (Table 2) suggest that the sample K-0 probably has a small system of narrow micropores, rather than a "gate" effect.

The higher enthalpies of immersion of both samples into CDDT and TXP suggest that the structure of the samples is not rigid and that very large molecules may induce deformations in the micropore system.

Both chars appear to be relatively hydrophilic, as indicated by the high enthalpies of immersion into water,  $\Delta h_1 = -62$  J/g. Usually, this enthalpy is smaller than that obtained with typical organic liquids such as  $\text{CH}_2\text{Cl}_2$  or benzene (see Table 2). Therefore, one may assume the presence of a high concentration of oxygen-containing groups or of residual nitrogen [13,14] on the walls of the micropores of our chars.

At this stage, it is also interesting to point out that the activation rate of the Nomex char N-0 (3.1% hour<sup>-1</sup>) is five times slower than that of Kevlar char K-0 (15.5% hour<sup>-1</sup>). This evolution cannot be explained by taking into account the crystallinity of the original precursor alone: Kevlar is more crystalline than Nomex [15] and the corresponding carbonized materials should be less reactive, due to the presence of fewer highly reactive centres. Tomlinson

*et al.* [15] suggest that the higher reactivity of Kevlar char may be a consequence of the presence of metallic residues. However, scanning electron microscopy studies of the external surface of the fibres did not show the existence of detectable foreign residues. The surfaces of activated fibres and chars are smooth and do not show the existence of pitting. On the other hand, the difference in the elemental composition of carbonized samples reported by other authors [15,16], does not suggest great differences in the reactivity. Under these circumstances, the high reactivity of Kevlar char could be related to the existence of a more disordered structure than in the Nomex char.

### 3.2 Activated carbon fibres

The steam activation of the Kevlar and Nomex chars K-0 and N-0 to burn-offs of 25 and 50% leads to samples K-25, K-50, N-25 and N-50, respectively.

As illustrated by Fig. 1, the  $\text{CH}_2\text{Cl}_2$  adsorption isotherms are all of type I. This indicates that the activated fibres are essentially microporous, the meso- and macroporosity being negligible. The structural

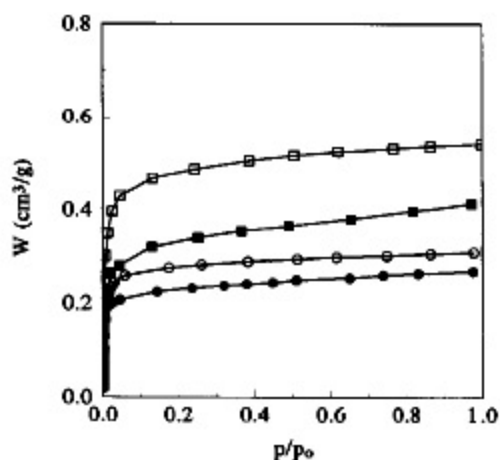


Fig. 1. Adsorption isotherms of  $\text{CH}_2\text{Cl}_2$  at 293 K on activated carbon fibres K-25 (●), N-25 (○), K-50 (■) and N-50 (□).

Table 2. Characteristics of porous structure of fibres and enthalpies of immersion into different carbons

Sample	K-0	K-25	K-50	N-0	N-25	N-50
$W_o$ (cm <sup>3</sup> /g)	—	0.24	0.34	—	0.29	0.54
$E_o$ (kJ/mol)	—	34.5	26.0	—	30.6	22.5
$L$ (nm)	—	0.47	0.74	—	0.56	0.97
$S_{mi}$ (m <sup>2</sup> /g)	—	1021	919	—	1036	1114
$S_{ext}$ (m <sup>2</sup> /g)	—	8	34	—	4	9
$S_{int}$ (m <sup>2</sup> /g)	—	1029	953	—	1040	1123
$\Delta h_1[\text{CH}_2\text{Cl}_2]$ (J/g)	9.1	131.7	131.5	43.0	140.0	155.9
$\Delta h_1[\text{C}_6\text{H}_6]$ (J/g)	10.8	117.9	133.6	7.2	134.6	155.9
$\Delta h_1[\text{C}_6\text{H}_{12}]$ (J/g)	4.0	74.0	97.8	5.9	96.1	116.9
$\Delta h_1[\text{CCl}_4]$ (J/g)	4.1	59.3	99.4	8.2	102.4	119.3
$\Delta h_1[\text{CDDT}]$ (J/g)	13.8	39.6	83.5	8.2	15.0	86.2
$\Delta h_1[\text{TXP}]$ (J/g)	28.5	51.8	44.0	30.1	24.7	37.9
$\Delta h_1[\text{H}_2\text{O}]$ (J/g)	61.6	98.3	92.0	62.4	70.1	93.3
$-h_1[\text{H}_2\text{O}]$ (mJ/m <sup>2</sup> )	—	95.5	96.5	—	67.4	83.1

data, derived from the Dubinin eqn (1) and from the logarithmic plots of the isotherms (Figs 2-5), is given in Table 2. It appears that the micropore volume  $W_0$

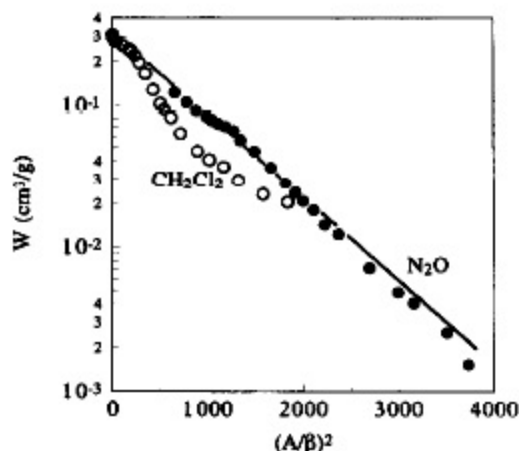


Fig. 2. D-R plot for the adsorption of  $N_2O$  and  $CH_2Cl_2$  at 293 K by Nomex fibre activated to 25% burn-off.

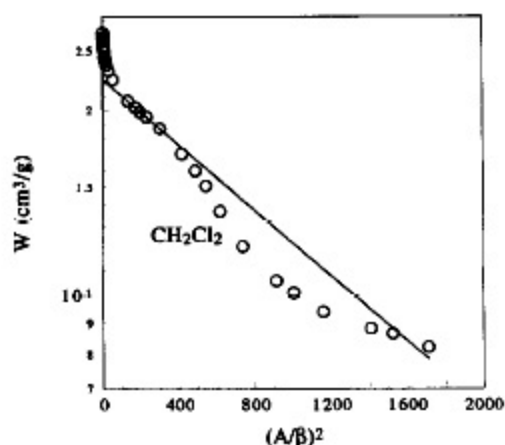


Fig. 3. D-R plot for the adsorption of  $CH_2Cl_2$  at 293 K by Kevlar fibre activated to 25% burn-off.

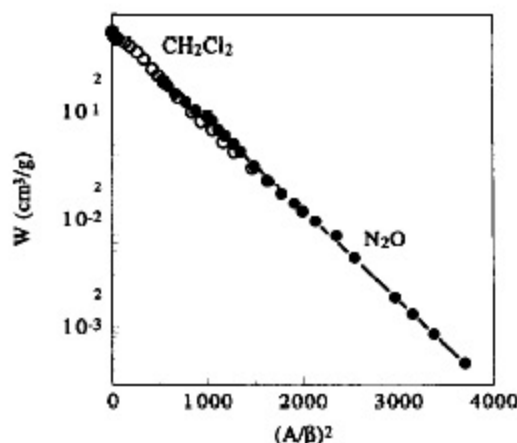


Fig. 4. D-R plot for the adsorption of  $N_2O$  and  $CH_2Cl_2$  at 293 K by Nomex fibre activated to 50% burn-off.

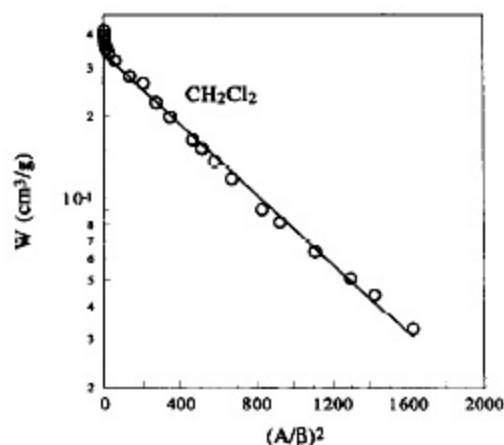


Fig. 5. D-R plot for the adsorption of  $CH_2Cl_2$  at 293 K by Kevlar fibre activated to 50% burn-off.

and the average pore-width  $L$  of the activated fibres both increase with the degree of burn-off, as expected. However, the yield is systematically higher for the Nomex series than for Kevlar.

For 50% activation, the Kevlar-based fibres shows a micropore volume of  $0.34 \text{ cm}^3/\text{g}$  against  $0.54 \text{ cm}^3/\text{g}$  obtained by activation of the Nomex char. The latter value is high and compares favourably with typical active carbons. One may also expect further activation to increase  $W_0$  up to 0.6 or  $0.7 \text{ cm}^3/\text{g}$ , before the fibre loses its mechanical properties. The difference between the two types of active fibres is significant and it is probably related to the pore structure of the precursors. As observed previously, the pore system is more developed in the Nomex char than in the Kevlar char. Moreover and, according to Tomlinson *et al* [15], the slower reaction observed between steam and the Nomex fibre char may reduce the diffusion limitations and favour a larger pore volume formation. The balance between the formation and the destruction of micropores during the activation process can be illustrated by the ratio of the micropore volume to the weight of initial char (Table 3). It is clear that the ratio is much more favourable in the case of the Nomex-based activated fibre.

The evolution of the microporosity itself is illustrated by the profiles of the relative micropore volumes  $W_0(L_0)/W_0(CH_2Cl_2)$  shown in Figs 6 and 7 and based on immersion calorimetry. It appears that for both types of fibres the apparent micropore distributions become wider as the degree of burn-off

Table 3. Micropore volume of samples expressed by unit weight of carbonized fibres as a function of weight loss

Weight loss (%)	Micropore volume ( $\text{cm}^3/\text{g}$ char)	
	Kevlar	Nomex
25	0.18	0.22
50	0.17	0.27

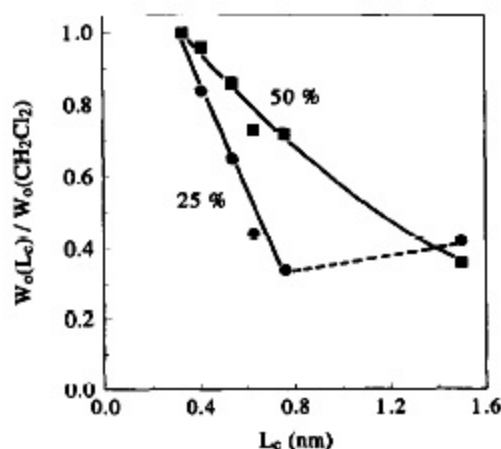


Fig. 6. Ratio between the micropore volume  $W_0(L_c)$  accessible to liquids with different molecular sizes and the total micropore volume  $W_0(\text{CH}_2\text{Cl}_2)$  for Kevlar fibre activated to 25 and 50% burn-off.

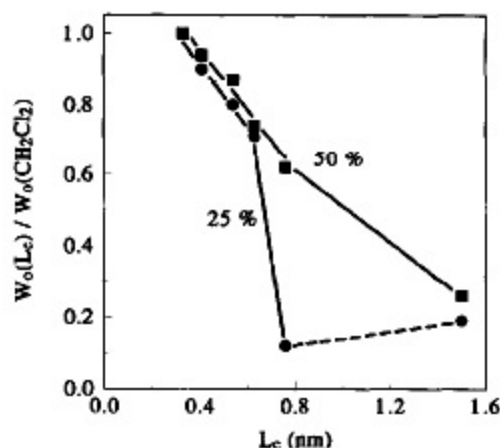


Fig. 7. Ratio between the micropore volume  $W_0(L_c)$  accessible to liquids with different molecular sizes and the total micropore volume  $W_0(\text{CH}_2\text{Cl}_2)$  for Nomex fibre activated to 25 and 50% burn-off.

increases. The average pore-widths  $L_c$  derived from the characteristic energies  $E_0$  of the  $\text{CH}_2\text{Cl}_2$  isotherms, are in agreement with the values suggested by the profiles, in particular at 50% burn-off. On the other hand, at 25% burn-off the pore systems are still narrow (averages of 0.45 and 0.56 nm for the K-25 and N-25 samples, respectively). Experimental evidence (time needed to reach adsorption equilibrium) and the deviations in classical Dubinin plots of the isotherms (Figs 2 and 3) suggest the presence of constrictions in sample K-25. This is clearly illustrated in the case of  $\text{CH}_2\text{Cl}_2$  adsorption, as opposed to  $\text{N}_2\text{O}$ , a somewhat smaller molecule (Fig. 2). Such constrictions have been observed previously in chars and activated carbons obtained from a bituminous coal [17], as well as in carbons prepared from phenolic resin [18]. On the other hand,  $\text{CH}_2\text{Cl}_2$  and  $\text{N}_2\text{O}$  show identical patterns for the fibres activated to 50% burn-off (Figs 4 and 5). This

means that the constrictions have been eliminated by further activation from 25 to 50% burn-off.

It is well known, that the materials obtained by steam activation have wider micropores than those obtained with  $\text{CO}_2$  [19]. However, in the present case, steam activation also leads to relatively narrow micropores, even at 50% burn-off. The comparison shows that the textural properties of our samples (micropore volume and average pore-widths) are similar to those obtained by  $\text{CO}_2$  activation of phenolic- and pitch-based carbon fibres [19].

#### 4. CONCLUSIONS

Steam activation of polyarylamide fibres leads to materials with a large adsorption capacity, but relatively narrow micropores, which makes them attractive for selective adsorption. Thus, by controlling the conditions of manufacture of the chars and the subsequent activation (essentially the activating agent, the degree of burn-off and its rate), activated carbon fibres with molecular-sieve properties can be produced from polyarylamide fibres. Such adsorbents could be of great interest in gas separation processes, where the physical properties of the fibres present a number of advantages over granular active carbons. However, it must be taking into account that these fibres are relatively hydrophilic, as opposed to typical active carbons, and that they have small external surface areas.

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