

## Effect of precursor composition on the activation of pitchbased carbon fibers

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### Abstract

Pure and silver-containing carbon fibers were prepared from isotropic pitch precursors supplied by Conoco, Inc., and a Korean research team and activated in carbon dioxide to varying degrees of burn-off. The specific activation rates for the carbon fibers were measured as well as the nitrogen adsorption characteristics of the activated carbon fibers. Scanning electron microscopy was used to investigate the surface morphology and the behavior of silver particles during the activation process. Molecular composition of the two pitch precursors was determined using a gas chromatograph mass spectrometer and a MALDI TOF mass spectrometer. Results showed that specific surface area increased with the burn-off, and the trends were similar for the pure and silver-containing fibers formed from both isotropic pitch precursors. However, the catalytic behavior of silver during activation, the activation rate, and even the pore characteristics of the activated fiber were found to be dependent on the molecular composition of the precursor pitch.

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### 1. Introduction

Activated carbon fibers (ACFs) is the general term for fibrous material formed from a polyacrylonitrile PAN, rayon (regenerated cellulose), phenolic resin, or pitch precursor and subjected to a carbonization/activation processes. ACFs are characterized by their large internal surface areas and high degrees of porosity. The production of ACFs with specific pore sizes (e.g., mesopores) is of particular interest because this advance would allow the rational design of ACFs for adsorbing specific compounds from gases or liquids.

In numerous studies ACFs containing mesopores have been prepared by modifying the precursor. The addition of metal-containing compounds to the precursor appears to be a particularly promising and relatively simple approach [1–8]. ACFs have been formed from isotropic pitch precursors containing transition metal

compounds (e.g. Ag, Co, Cu ions) [1–4] and organo rare-earth metal complexes [5–8]. These metals are known to generate mesoporosity during activation. Also, depending on the metal, the resulting ACFs can exhibit antibacterial properties or serve as electrodes for lithium ion batteries.

However, past studies have shown that the optimum conditions for melt spinning and heat treatment (stabilization and carbonization) depend on the molecular composition of isotropic pitch precursor [9–11]. The reason is that heat treatment requirements are directly related to the chemical reactivity of the pitch and the deformation behavior of the pitch is directly related to the molecular structure (e.g., aromaticity and/or molecular weight) of the pitch. As a result, high molecular weight isotropic pitch melts can exhibit elastic behavior (a characteristic of solid-like structure) [11]. This solid-like behavior contributes to the development of structure as fibers are stretched during melt spinning [9]. Thus, even for isotropic pitches, the composition of the original precursor can influence the structure of the final fiber. Therefore, the objective of this study was to determine the effect of precursor composition and

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structure on the ACF production process and final properties of ACFs.

In this study silver nitrate was mixed with two isotropic pitches of widely different molecular compositions to yield pitch mixtures containing 1 wt.% of silver. Then, the two pure isotropic pitches and the two silver-containing mixtures were melt spun into fiber form, heat treated and activated in carbon dioxide. The method of preparation and activation of pure and silver-containing carbon fibers of round and trilobal shape produced from Korean isotropic pitch has already been reported [12,13]. The results discussed in this paper demonstrate that composition and structure of the isotropic pitch precursor can have major effects on the rate of activation, the surface characteristics, and the pore structure of pure and silver-containing fibers.

## 2. Experimental

### 2.1. Materials

The isotropic pitch precursors used in this study were supplied by Professor Seung Kon Ryu of Chungnam National University in Daejeon, Korea, and ConocoPhillips, Inc, located in Ponca City, Oklahoma. Galbraith Laboratories, Inc., Tennessee conducted elemental analyses of both pitch precursors. The Korean pitch contained 93.86% carbon, 5.6% hydrogen, <0.5% oxygen, <0.5% nitrogen, <0.11% ash, and had a softening point of 255 °C. The isotropic pitch supplied by ConocoPhillips contained 93.0% carbon, 4.9% hydrogen, <0.5% oxygen, <0.5% nitrogen, <0.10% ash and had a softening point of 230 °C.

### 2.2. Preparation of activated carbon fibers

Silver nitrate powder (m.p. 212 °C) was thoroughly ground and then directly mixed into the pure, molten

Korean and ConocoPhillips (hereafter referred to as Conoco) pitches using an intensive mixer, yielding isotropic pitch precursors that contained 1 wt.% of silver. The procedure is detailed in a previous paper [12].

Pure and silver-containing pitches were then melt spun into multi-filament fiber tows with round and trilobal cross-sections using a batch extrusion system at three different takeup speeds. Details of the procedure are described elsewhere [12,13]. Table 1 shows spinning temperatures used to produce the pure isotropic and silver-containing fibers. As the table shows, two trends are evident. For both the Korean and Conoco pitches, the optimum spinning temperature for the silver-containing mixtures was found to be higher than that for the pure pitches. Also, the optimum spinning temperatures for the trilobal fibers were lower than those for round fibers spun from the same pitch.

As-spun fibers were stabilized in air in a conventional oven and carbonized in a helium atmosphere. Stabilization temperatures, hold times, and heating rates are displayed in Table 1. It should be noted that high quality fibers produced from Korean pitch were obtained using an one-step stabilization program. By comparison, Conoco fibers required a much longer, three-step stabilization program. Weight gain after stabilization for the Korean and the Conoco fibers was 8–12%.

After carbonization, the carbon fiber samples were activated using a temperature-controlled Lindberg tube furnace. This involved heating the fibers at 900 °C in pure CO<sub>2</sub> at atmospheric pressure for times ranging from 10 to 540 min. The CO<sub>2</sub> flow rate for all ACFs produced in the present study was 500 ml/min.

Finally, the molecular composition, surface morphology and pore structure of the ACFs were determined in order to estimate the effect of the molecular composition of the precursor on the production process and the final properties of the ACFs.

Table 1

Fiber preparation conditions for Korean and Conoco precursors using pure isotropic pitch and silver-containing isotropic pitch

Procedure	Conoco		Korean	
	Pure pitch	Mixed pitch	Pure pitch	Mixed pitch
	Temperature/holding time/heating rate			
Mixing (AgNO <sub>3</sub> )	220 °C/0.3 h		240 °C/0.3 h	
Melt-spinning	Round 245 ± 1 °C	Round 263 ± 2 °C	Round 272 ± 1 °C	Round 278 ± 2 °C
	Trilobal 244 ± 1 °C	Trilobal 257 ± 2 °C	Trilobal 265 ± 2 °C	Trilobal 265 ± 2 °C
Stabilization		225 °C/24 h/1 °C min <sup>-1</sup> 270 °C/2 h/5 °C min <sup>-1</sup> 300 °C/3 h/5 °C min <sup>-1</sup>	265 °C/13 h/5 °C min <sup>-1</sup>	
Carbonization		1000 °C/1 h/10 °C min <sup>-1</sup>		

### 2.3. Characterization

A Hitachi FE SEM 4700, in the secondary electron mode, was used to observe the surface morphology and porosity of both the outer surface and the cross-section of selected fibers. This analysis also yielded information concerning surface pore size and silver particle distribution, both before and after the activation process. The distribution of silver particles before and after activation was also determined by inspecting selected fibers using a Hitachi 3500 SEM, in a back-scattering electron mode (BSE).

The BET surface area of the ACF samples was determined by applying the standard Brunauer–Emmet–Teller method to the nitrogen adsorption isotherm obtained at  $-196^{\circ}\text{C}$  using Coulter SA 3100 and Micromeritics ASAP 2020 instruments. The Micromeritics 2020 apparatus also was used to measure nitrogen adsorption–desorption isotherms at  $-196^{\circ}\text{C}$  and relative pressures between  $5 \times 10^{-7}$  and 1. Both BET and BJH (Barrett–Joyner–Halenda) methods were applied to the nitrogen isotherms to calculate the total and mesopore surface areas, respectively, and the ratio of these two surface areas was used as a measure of the mesopore ratio. The DFT (density functional theory) method was applied to nitrogen isotherm data to estimate the pore size distribution. All samples were outgassed at  $330^{\circ}\text{C}$  for 3 h prior to each adsorption experiment.

The molecular composition of pitch precursors was elucidated using a Bruker Daltonics Omnistar MALDI (matrix-assisted laser desorption/ionization) TOF (time of flight) MS (mass spectrometer). The details of the analysis are described elsewhere [14].

Solutions of Conoco and Korean pitch precursors in dichloromethane (dissolution was 93% and 94%, respectively) were tested by GC-FID (gas chromatography with flame ionization detection), using a Hewlett Packard 5890A Chromatograph with split injection, set to detect major peak abundance over a MW range of about 200–300. The above solutions were then analyzed by GC-MS, using a Hewlett Packard 6890 GC system with 5972 mass spectrometric detector [GC-MS] and splitless injection, focused on peaks in the MW range of 35–315.

### 3. Results and discussion

Figs. 1 and 2 show SEM images of as-spun and carbonized fibers. The average diameters of the round fibers spun from the unmixed and silver-containing Korean and Conoco pitches (Table 2) ranged from approximately 9 to  $23\text{ }\mu\text{m}$ . The notations in this table and other plots (CU, KU, CM, and KM) indicate that precursors were either Conoco isotropic pitch (C) or Korean isotropic pitch (K) and either unmixed (U) or

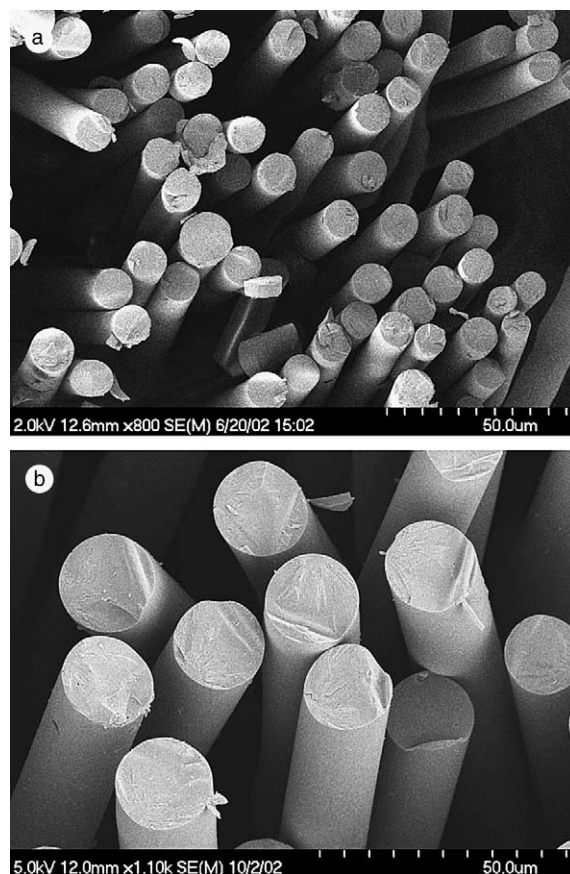


Fig. 1. SEM micrographs of as-spun round fibers: (a) Conoco, (b) Korean.

mixed with  $\text{AgNO}_3$  (M), respectively. The numerical notations indicate the relative takeup speed: 1–286 m/min, 2–457 m/min and 3–640 m/min, respectively. The notations R and T indicate that the cross-sections of the fibers were either round or trilobal, respectively. As would be expected, the diameter decreased as take-up speed increased. Also, the average diameters of the carbonized fibers were less than those of the as-spun fibers. This would be expected since carbonization eliminates many of the non-carbon elements; as a result the structure collapses and the diameter decreases.

#### 3.1. $\text{CO}_2$ activation results

As Fig. 3 shows, the initial rates of activation and the formation of surface porosities are not only highly dependent on the presence of silver, as reported by past researchers [1,3,4], they are also highly dependent on the isotropic pitch precursor itself.

Specific surface areas, as determined from nitrogen isotherms for selected ACFs with similar burnoffs, and initial specific activation rates for pure and silver-containing Conoco and Korean CFs are summarized in Table 3. The percentage burnoff (BO) and specific surface areas listed in the table represent the average values

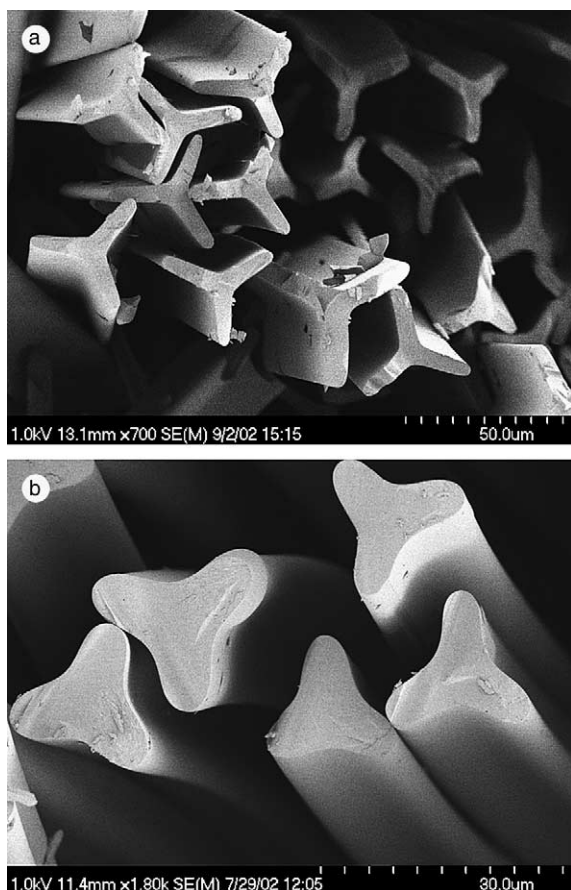


Fig. 2. SEM micrographs of as-spun trilobal fibers: (a) Conoco, (b) Korean.

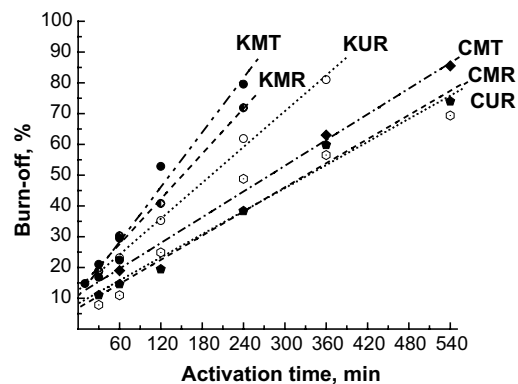


Fig. 3. Burnoff versus activation time.

for carbon fibers melt-spun at the three takeup speeds. The initial specific activation rates were calculated from data acquired during the first 30 min of activation process (when a linear relationship is observed between the extent of burn-off and time).

Apparently, the cross-sectional shape of carbon fibers does not affect the final specific surface area. However, the specific activation rate for trilobal fibers during the initial stage of activation appears to be higher than that for the round fibers. This effect is more pronounced for the silver-containing CFs. A comparison of specific surface areas listed in Table 3 shows that, to achieve similar specific surface areas, fibers produced from the silver-containing precursor require a markedly shorter activation time.

Table 2

Diameters of as-spun and carbonized round fibers

Fibers	$d$ ( $\mu\text{m}$ ) (as-spun)	$d$ ( $\mu\text{m}$ ) (carbonized)	Fibers	$d$ ( $\mu\text{m}$ ) (as-spun)	$d$ ( $\mu\text{m}$ ) (carbonized)
CUR1	13.2–16.5	9.6–14.8	KUR1	19.2–22.8	18.1–21.0
CUR2	10.0–14.0	9.3–12.3	KUR2	16.0–20.6	15.6–18.4
CUR3	8.6–11.25	8.6–8.9	KUR3	13.8–15.5	13.1–14.9
CMR1	20.3–20.9	14.9–20.0	KMR1	12.3–18.0	11.6–16.8
CMR2	14.7–20.4	14.6–18.1	KMR2	11.2–18.6	10.1–15.5
CMR3	10.2–13.5	8.6–12.2	KMR3	10.7–15.2	8.2–12.7

Table 3

Specific surface areas and specific activation rates for the pure Conoco and Korean round and trilobal fibers and fibers containing 1 wt.% of silver

Carbon fiber	Activation time (min)	BO (%)	Specific surface area ( $\text{m}^2/\text{g}$ )	Specific activation rate ( $\times 10^{-3} \text{ g/g}_{\text{carb}} \text{ min}$ )
KUR (Korean round)	360	78.1	2597	3.04
KMR (Korean round, 1 wt.% Ag)	240	73.3	2801	5.69
KUT (Korean trilobal)	360	72.2	2594	4.17
KMT (Korean trilobal, 1 wt.% Ag)	240	79.5	2762	8.72
CUR (Conoco round)	540	69.9	2519	3.01
CMR (Conoco round, 1 wt.% Ag)	540	76.2	2484	4.07
CUT (Conoco trilobal)	540	75.5	1692	3.02
CMT (Conoco trilobal, 1 wt.% Ag)	540	85.5	1915	4.56

The trends in the initial specific activation rates for the ACFs produced from the Conoco precursor are similar to those of the ACFs formed from the Korean precursor. However, actual activation rates for fibers produced from the Conoco pitch are much slower than the activation rates for fibers formed from the Korean pitch.

SEM measurements of the fiber cross-sections at different degrees of activation showed that the diameter of the round Conoco fibers decreased during the initial stages of activation and, then, became relatively constant as activation progressed. This same trend was reported in an earlier ACF study using fibers formed from the Korean pitch [12]. This indicates that the weight loss is caused by the formation of pore structure rather than combustion of the fiber surface.

### 3.2. Nitrogen adsorption studies

Examples of the adsorption/desorption isotherms for selected Korean and Conoco ACFs formed from silver-containing pitch and pure pitch are shown in Figs. 4 and 5. Based on their shape, the adsorption/desorption isotherms for the ACFs formed from the pure pitch are type I. This would indicate that the fibers contain mainly micropores.

By comparison, at higher activation times (at burnoff values greater than about 50–60%) the isotherms for the

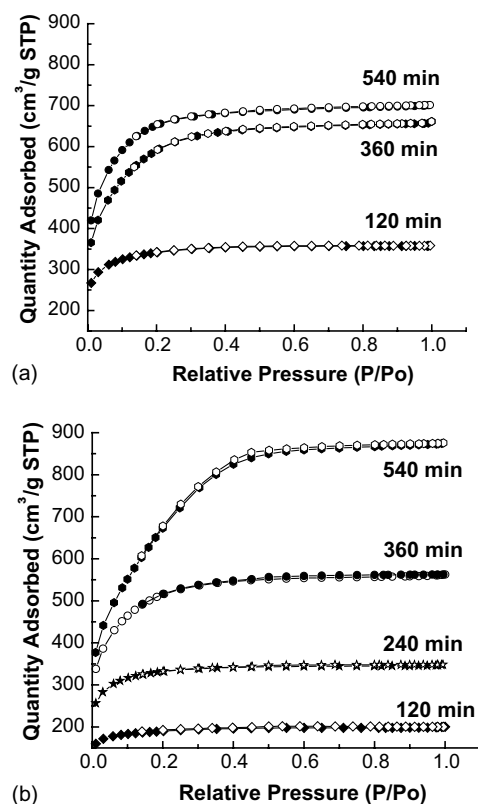


Fig. 4. Nitrogen adsorption-desorption isotherms: (a) Conoco pure, (b) Conoco Ag-containing ACFs.

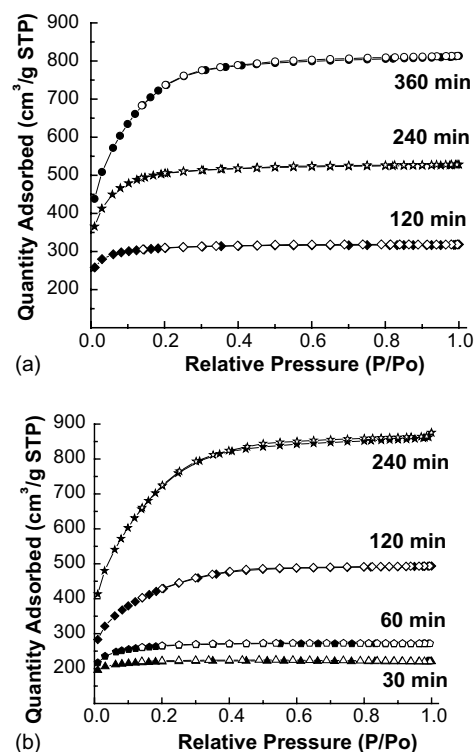


Fig. 5. Nitrogen adsorption-desorption isotherms: (a) Korean pure, (b) Korean Ag-containing ACFs.

ACFs formed from the silver-containing pitches exhibit a small hysteresis loop and show a slight increase of the amount of  $N_2$  adsorbed at relative pressures higher than 0.4 (isotherm a type IV), implying a widening of micropores and formation of supermicropores and small mesopores. The BET surface areas of the ACFs produced from both the pure and silver-containing Conoco pitch increased with burn off.

A similar trend was reported earlier for fibers produced from the pure and silver-containing Korean pitch [12,13]. However, the fibers formed from the Conoco pitch required a much longer activation times to achieve a given specific surface area than similar fibers formed from the Korean pitch. This was true for both pure and silver-containing Conoco and Korean pitches.

Pore size distribution curves for selected samples with a BO of about 70% are shown in Fig. 6. The mesopore volume was higher for the ACFs formed from both silver-containing pitches than that for the ACFs formed from the corresponding pure pitch. Interestingly, this increase was confined to a relatively narrow region (20–50 Å) of pore width.

### 3.3. SEM observations

Further differences between Conoco and Korean ACFs become apparent when their external surfaces are examined using scanning electron microscopy. The

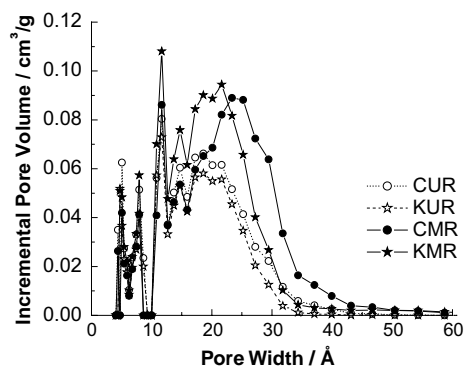


Fig. 6. Pore size distribution curves of Korean and Conoco ACFs, BO ~70%.

silver particle distribution and porous structure were imaged at both the fiber surface and the fiber cross-section.

### 3.3.1. SEM of carbonized fibers

Fig. 7 shows typical SEM images of carbonized fibers produced from the silver-containing Conoco and Korean pitches. The silver particles could be easily detected as bright spots in the SEM images. The silver particles are uniformly distributed, both throughout the core and on the surface of the carbonized fibers. The average particle size is less than 100 nm.

### 3.3.2. SEM of activated fibers

In general, SEM analyses of carbon fibers at different degrees of activation showed that, as the burn-off increases, fiber morphology changes and mesoporosity develops on the fiber surface (Fig. 8). As was described in our previous study [12], during activation the silver particles remain evenly distributed, both throughout the fiber core and on the fiber surface.

The silver particles are particularly reactive and act as active sites for the reaction with carbon dioxide. As a result, the surface of the carbon fiber near the silver particles appears to be partially eaten away, creating holes which are larger than the silver particle (Fig. 8b and d).

Most of the surface on the fibers formed from the Korean pitch remains relatively smooth during activation (Fig. 8a). By comparison, activation appears to roughen the entire surface of the fibers formed from the Conoco pitch (Fig. 8c). SEM images of fibers formed from the Korean pitch show that small silver particles remain evenly distributed along the fiber surface during activation (Fig. 8a). Submicron-sized particles can also be seen in the interior of these fibers (Fig. 8b). By comparison, for the fibers formed from Conoco pitch, the particles appear to have coalesced into larger particles. These coalesced particles appear to create larger surface cavities during burn-off (Fig. 8c and d).

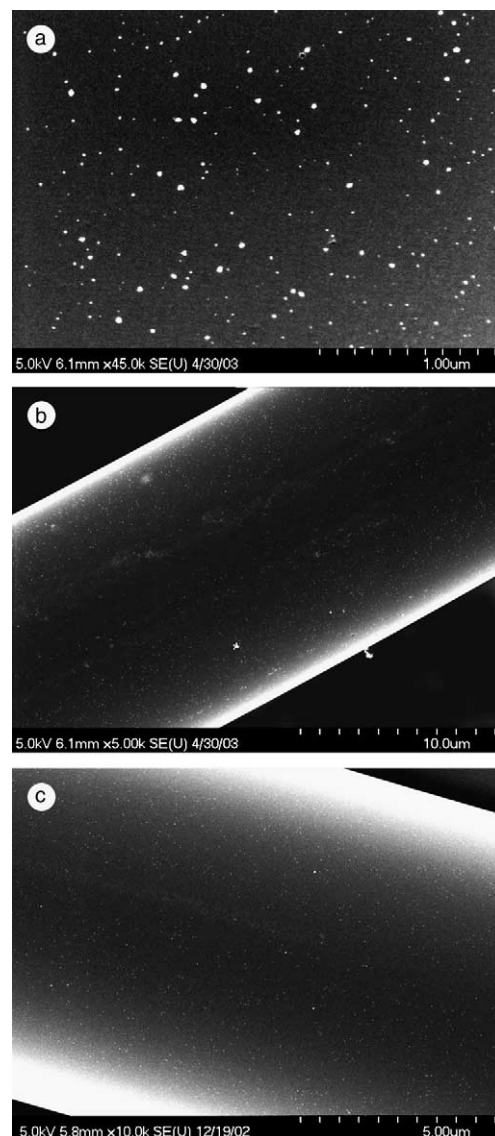


Fig. 7. SEM micrographs of carbonized silver-containing Korean (a), (b) and Conoco fibers (c): (a) fracture surface and (b), (c) fiber surface.

This difference in particle behavior, as well as in activation rate, may be caused by density differences in the two pitch precursors which, in turn, could affect the diffusion of CO<sub>2</sub> molecules during activation. However, it is more likely that the differences are related to the chemical nature and composition of the precursor pitch (molecular structure, interaction with silver particles, etc.).

### 3.4. Molecular composition

Generally speaking, petroleum pitches are composed of key building blocks, such as benzene, naphthalene, anthracene, phenanthrene, pyrene, perylene units and their derivatives [15]. The molecular composition, i.e. molecular weight distribution (MWD) and the molecu-

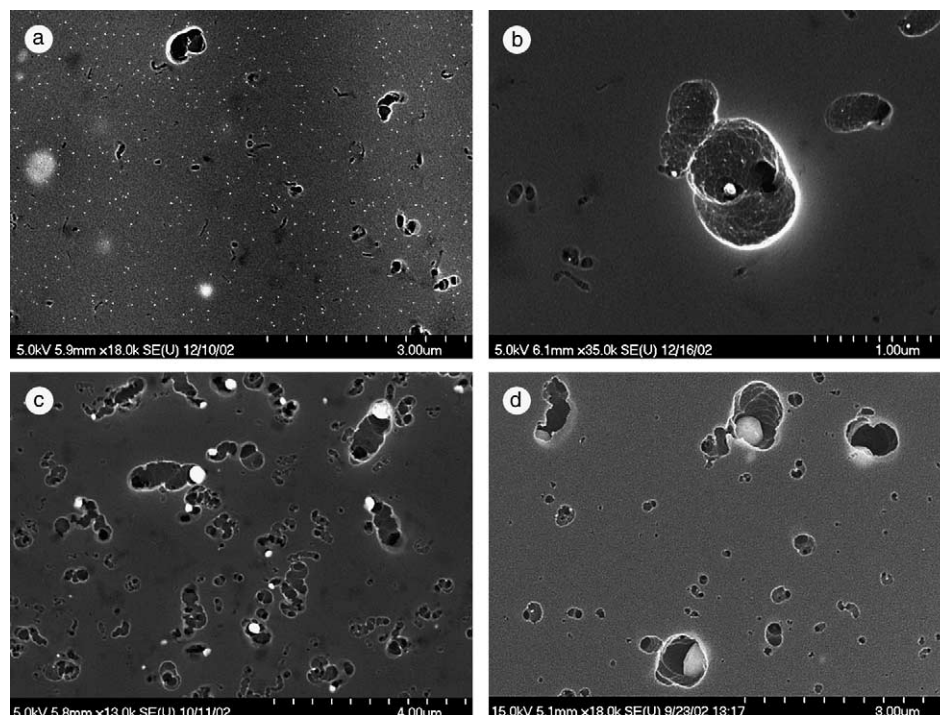


Fig. 8. SEM micrographs of silver-containing ACFs surfaces: Korean (a), (b) and Conoco fibers (c), (d). BO 76–79%.

lar structures, as well as the relative quantity of these structures, may affect properties of the resultant fibers.

#### 3.4.1. MALDI TOF mass spectrometry

The molecular weight distribution of the original Conoco and Korean pitches is shown in Fig. 9. While the Korean pitch shows a broad molecular weight distribution of carbonaceous compounds, monomers through pentamer groups are visible in the spectrum of Conoco pitch indicating a polymeric-like structure.

#### 3.4.2. Gas chromatograph mass spectrometry (GC-MS)

Since 93% of the Conoco and 94% of the Korean pitches can be dissolved in  $\text{CH}_2\text{Cl}_2$ , a major portion of the compounds contained in both pitches can be analyzed by a GC-MS method focusing on a MW range, 35–315, which is difficult to analyze by MALDI [14].

Identification of peaks and a comparison of peak abundances provide a clue to the difference in the behavior of fibers formed from the two pitches. The Korean pitch contained many compounds that could be generally classified as polycyclic aromatic hydrocarbons, PAH's (Table 4). There was a much greater concentration of PAH's in the Korean (K) as compared to the Conoco (C) pitch (Fig. 10, Table 4). The average ratio (K/C) of GC-MS peaks for compounds which are common in both pitches (or of very similar structure) is over 5.9:1. The majority of these compounds are fused super rings made up of benzene rings arranged in an almost circular pattern (disc-shaped), such as benzopy-

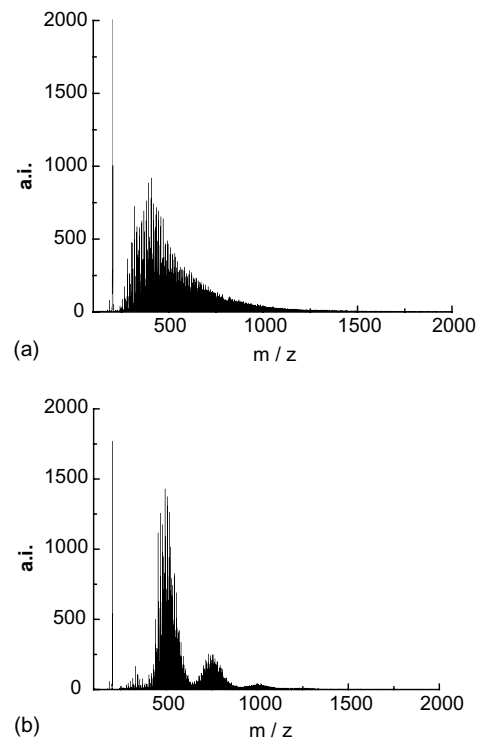


Fig. 9. MALDI spectra of Korean and Conoco pitch precursors: Korean (a), Conoco (b).

renes, perylenes, phenanthrenes (Table 4). In other words, these compounds are found in great abundance in the Korean pitch, and the Conoco pitch contains

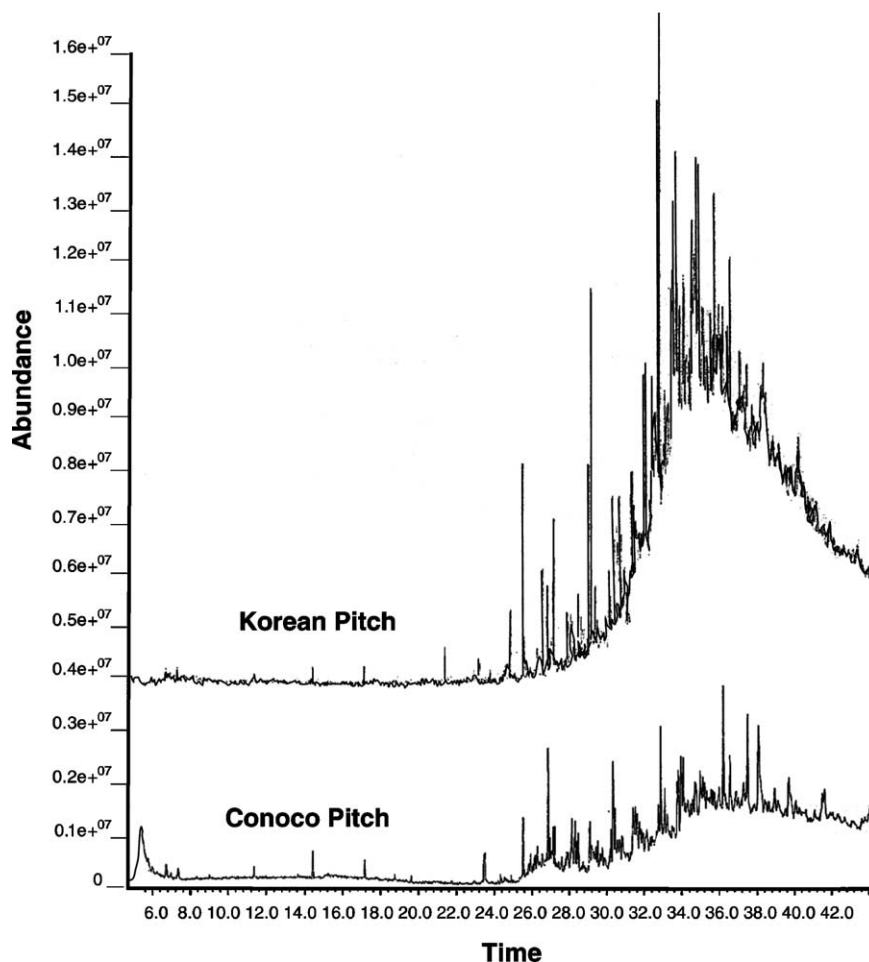


Fig. 10. GC-MS chromatograms of Korean and Conoco pitches.

much less of these compounds. The major compounds detected in the Conoco pitch are mainly chrysene, anthracene and their derivatives. These compounds are straight fused benzenes (Table 5).

### 3.5. Porosity

Fig. 11 shows that the mesopore ratio increases with activation time for round and trilobal ACFs. The degree of mesoporosity of the Korean ACFs is comparable to that of the Conoco fibers, but this mesoporosity is achieved in a shorter time. For the silver-containing ACFs, the mesopore ratio was determined to be 38–42%. By comparison, even when the fibers formed from the pure Korean and Conoco pitches were activated for much longer times they developed lower mesopore ratios (27–34%), even though the BET specific surface areas of these fibers were similar to those of the silver-containing fibers (see Table 3). Thus, during the activation process the rate of mesopore formation is higher for the silver-containing fibers, indicating that silver catalyzes mesopore formation.

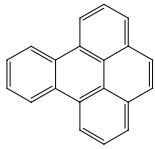
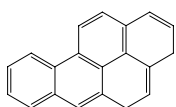
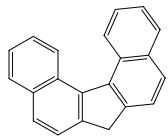
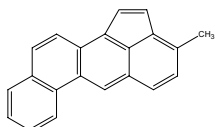
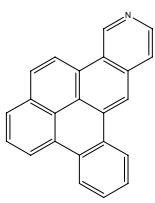
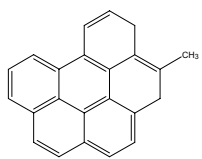
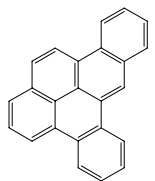
Our data on chemical structure and mesopore ratio correlate well with the findings of Tamai et al. [16], who studied the activation of mixtures of rare metal complexes and condensed polynuclear aromatic resins prepared from individual compounds. They mixed disc-shaped aromatics, such as pyrene, phenanthrene, and perylene, with rare-earth metal compounds and then activated the mixtures to produce activated carbon with a high percent of mesoporosity. However, when linear-shaped aromatic compounds like naphthalene and anthracene were mixed with the same rare-earth metal compounds and activated, little or no mesoporosity developed. Also, negligible mesopore ratios were detected in activated mixtures formed from polymeric-type skeletons, such as polydivinylbenzene and polystyrene.

It should be noted that the molecules in Conoco pitch are more linear-shaped in nature (Table 5) and the Korean pitch is more disc-shaped (Table 4). Past studies have shown that isotropic pitches can exhibit significant visco-elasticity [10]. This solid-like behavior is likely the result of larger molecules interacting and entangling during deformation and flow. Thus, differences in molecular structure of the isotropic pitch precursors



Table 4

GC-MS analysis of the chemical composition of Korean pitch (major polycyclic aromatic hydrocarbons detected and Korean/Conoco (K/C) abundance ratio, for compounds found in both GC-MS patterns)

Compound	Peak abundance, area counts	Structure	Ratio (K/C), if the same peak found in both GC-MS patterns
Benzo(e)pyrene	1 150 000		5.90
Benzo(a)pyrene	1 300 000		4.70
13H-Dibenzo[a,h]fluorene	950 000		Detected only in Korean pitch
3-Methylbenzo(j)aceanthrylene	1 050 000		4.12
Azadibenzopyrene	980 000		Detected only in Korean pitch
4-Methylbenzo(ghi)perylene	870 000		3.41
1,2,4,5-Dibenzopyrene	650 000		Detected only in Korean pitch

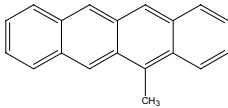
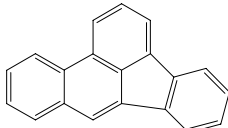
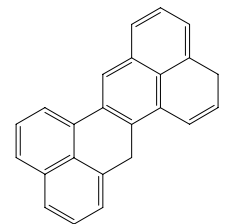
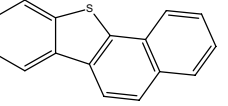
could lead to slight differences in the molecular orientation and structure of the as-spun fibers. These structural variations could contribute to the observed differences in fiber reactivity during activation.

### 3.6. Effect of silver ion additive

Even though similar size salt particles were mixed into both pitches, the average silver particle size in the Korean ACFs, was much smaller than that in the Co-

noco fibers (Fig. 8). Washburn et al. [17] has reported that silver ions form complexes with olefin and aromatic compounds. The stability of such complexes depends on the silver-containing compound and the aromatic or olefin substrates. These findings are based on the principle that the  $\text{Ag}^+$  ion from  $\text{AgNO}_3$  interacts with the conjugated  $\pi$ -electrons of the polycyclic aromatic hydrocarbons and bind as a complex. The bonding is a result of two events: (i) the extended conjugation acts as an electron donor and transfers electrons to the unfilled

Table 5  
GC-MS analysis of the composition of Conoco pitch (major polycyclic aromatic hydrocarbons not detected in Korean pitch)

Compound	Peak abundance, area counts	Structure
12-Methylbenzo(a)anthracene	245 000	
Benzo(e)acephenanthrylene	315 000	
Dibenzo(def,mno)chrysene	390 000	
Benzo[2,1-b:3,4-b']bis[1]benzothiophene	340 000	

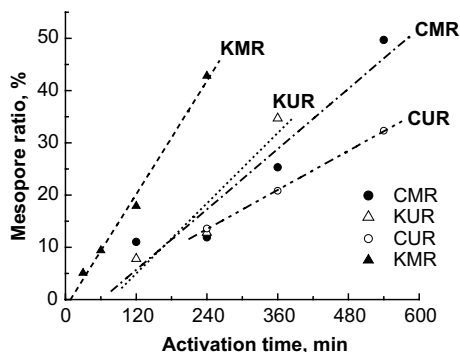


Fig. 11. Mesopore ratio versus activation time.

metal orbitals, and (ii) the resulting filled metal orbitals interact with the empty  $\pi$ -antiorbitals of PAH's. This information lends support to our arguments. The Korean pitch consists mainly of PAHs (benzenoid disc-shaped structures, such as pyrene, perylene, phenanthrene compounds and their derivatives). Thus, the  $\text{Ag}^+$  ions and the benzenoid compounds most likely form stable organometallic complexes during the preparation of the silver-containing pitch precursors. These stable complexes would be expected to improve particle distribution, prevent silver coalescence, and increase the reactivity of the PAHs contained in the Korean pitch.

The uniform particle distribution, combined with the higher catalytic reactivity of the particles with the PAHs contained in the Korean pitch results in enhanced pore formation, when Korean and Conoco fibers with similar burnoffs are compared.

The results clearly demonstrate that the activation behavior of isotropic pitch fibers is highly dependent on the chemical composition and structure of the pitch itself. Structure can influence the rate of activation of the carbonized fiber and chemical composition can affect the coalescence of metal-additives. These findings are significant and may well explain many of the conflicting results reported in the literature.

#### 4. Conclusions

The exact procedure used for melt-spinning and stabilization of fibers depends on the composition of precursor, silver additive and the cross section of spinneret capillary. The activation rates of Conoco and Korean CFs were found to depend on the composition of the original pitch precursor, the presence of silver particles, and shape of carbon fibers. In all cases, the rate of activation was significantly higher for fibers formed from the Korean isotropic pitch. The carbon skeleton of the Korean pitch, composed of multi-benzenoid ring structures, comprising pyrene, perylene, phenanthrene compounds and their derivatives, appears to enhance the activation process and mesoporosity formation. The  $\text{Ag}^+$  ion from  $\text{AgNO}_3$  interacts with the conjugated  $\pi$ -electrons of the polyaromatic hydrocarbons, major compounds in Korean pitch, improving particle distribution and preventing of Ag particles from coalescence. This, combined with the enhanced reactivity of the disc-shaped aromatics, leads to enhanced activation and mesopore formation. By selecting the proper precursor and controlling time of exposure, the desired surface area and porosity can be achieved. The Korean pitch was found to be a much better precursor for producing mesoporous ACFs.

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## References

- [1] Oya A, Wakahara T, Yoshida S. Preparation of pitch-based antibacterial activated carbon fiber. *Carbon* 1993;31(8):1243–7.
- [2] Ryu SK, Kim SY, Gallego N, Edie DD. Physical properties of silver-containing activated pitch-based carbon fibers. *Carbon* 1999;37(10):1619–25.
- [3] Ryu SK, Kim SY, Li ZJ, Jaroniec M. Characterization of silver-containing pitch-based activated carbon fibers. *J Coll Interf Sci* 1999;220:157–62.
- [4] Yim KS, Ryu SK, Edie DD. Characterization of metal(Ag, Cu, Co)-containing pitch-based activated carbon fibers. Extended abstracts, International Conference on Carbon, Beijing, China. 2002.
- [5] Tamai H, Kouzu M, Yasuda H. Extremely large mesoporous carbon fibers synthesized by the addition of rare earth metal complexes and their unique adsorption behaviors. *Adv Mater* 1997;9:155–8.
- [6] El-Merraoui M, Tamai H, Yasuda H, Kanata T, Mondori J, Nadai K, et al. Pore structure of activated carbon fibers from organometallics/pitch composites by nitrogen adsorption. *Carbon* 1998;36(12):1769–76.
- [7] Tamai H, Yoshida T, Sasaki M, Yasuda H. Dye adsorption on mesoporous activated carbon fibers obtained from pitch containing yttrium complex. *Carbon* 1999;37(6):983–9.
- [8] Hong I, Jiang H, Park YD, Kim JY, Ha BH. Metal dispersed activated carbon fibers and their application for removal of  $\text{SO}_x$ . *Chem Phys Lett* 2002;366:572–7.
- [9] Edie DD. The effect of processing on the structure and properties of carbon fibers. *Carbon* 1998;36(4):345–62.
- [10] Blanco C, Fleurot O, Menendez R, Santamaria R, Bermejo J, Edie DD. Contribution of the isotropic phase to the rheology of partially anisotropic coal-tar pitches. *Carbon* 1999;37:1059–64.
- [11] Menendez R, Fleurot O, Blanco C, Santamaria R, Bermejo J, Edie DD. Chemical and rheological characterization of air-blown coal-tar pitches. *Carbon* 1998;36(7–8):973–9.
- [12] Lee YS, Basova YV, Edie DD, Reid LK, Newcombe SR, Ryu SK. Preparation and characterization of trilobal activated carbon fibers. *Carbon* 2003;41(13):2573–84.
- [13] Lee YS, Basova YV, Carneiro V, Huggins L, Lee C, Harris J, et al. Non-Circular activated carbon fibers, Extended abstracts, Carbon 2003, Oviedo, Spain. 6–10 July 2003.
- [14] Edwards WF, Jin L, Thies MC. MALDI-TOF Mass Spectrometry: obtaining reliable mass spectra for insoluble carbonaceous pitches. *Carbon* 2003;41(14):2761–8.
- [15] Dickinson EM. Average structures of petroleum pitch fractions by  $^1\text{H}/^{13}\text{C}$  NMR spectroscopy. *Fuel* 1985;(64):704–6.
- [16] Tamai H, Kakii T, Hirota Y, Kumamoto T, Yasuda H. Synthesis of extremely large mesoporous activated carbon and its unique adsorption for giant molecules. *Chem Mater* 1996;8(2):454–62.
- [17] Washburn K, Huebner H, Safe S, Phillips T, Donnelly KC. Development of an instrumental fractionation and quantitation scheme for selected polynuclear aromatic hydrocarbons present in extracts from wood-preserving waste. Proceedings of the HSRC/WERC Joint Conference on the Environment, Albuquerque, NM. 21–23 May 1996. p. 400–7.