CARBON FIBERS AND ACTIVATED CARBON FIBERS FROM RESIDUAL SHALE OIL

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Introduction

Oil shale is one of the largest fossil fuel reserves, and an important potential source of liquid fuels and chemicals. One of the disadvantages of oil shale liquids is their high nitrogen content, which causes difficulties in their upgrading to premium quality products[1]. To accentuate the problem, the nitrogen-containing species tend to be more concentrated in the higher boiling fractions of the retorted product [2]. An alternative solution may lie in investigating the use of the residual liquids as precursors for the synthesis of high added-value advanced carbon materials. The ability to generate valuable by-products could enhance the economics of oil shale retorting.

Carbon fibers (CF) and activated carbon fibers (ACF) are commercially produced from polyacrylonitrile (PAN) and petroleum and coal-tar pitches. The PAN-based fibers have very high strength for which reason they command a higher price than pitch-based ones. Other factors that contribute to the price are the high raw material cost, and low yield [3]. Pitch-based fibers can be formed by directly processing the precursor, to produce moderate strength isotropic carbon fibers, or after heat treatment to induce mesophase formation, when the fibers can have high modulus, and high thermal and electrical conductivity [4].

Activated carbon fibers produced from PAN have several unique properties[5], including the ability to adsorb NOx, SOx and vitamin B12[6,7], and where there may be novel metal-support interactions[8]. This may be related to their nitrogen content, which can lead to the presence of basic functional groups on the adsorptive surface. For similar reasons, it is considered that carbon fibers and activated carbon fibers produced from oil shale residues might exhibit unusual properties that are not possessed by fibers from petroleum or coal tar pitches. Accordingly, a program of work has been initiated to study the synthesis of carbon fibers from residual oil shale liquids.

In the study presented here, an asphaltene fraction was isolated from a shale oil residuum produced by the Kentort II process[9]. The fraction was processed by melt spinning, oxidative stabilization, carbonization and activation to produce carbon fibers and activated carbon fibers. The products were characterized by SEM, elemental and surface area analyses.

Experimental

A shale oil residue (SOR) , produced in the Kentort II process from eastern oil shale[9], was used as the starting material. The asphaltene fraction, SOR-AS, (hexane insoluble, benzene soluble) was separated as follows. The hexane soluble fraction of the shale oil residue was removed by extraction

with boiling hexane[10]. The hexane insoluble fraction was then Soxhlet extracted with benzene, following which the benzene was removed from the extract by rotary evaporation. A petroleum-derived isotropic precursor pitch (PP) was selected for comparison.

Continuous single filament carbon fibers were produced from the shale oil asphaltenes and the petroleum pitch by melt spinning, using a spinneret (capacity about 8g, nozzle diameter 0.3 mm) that is operated under nitrogen pressure. The shale oil and petroleum precursors were spun under 150~300 kPa pressure at about 240 and 300°C, respectively. The resulting fibers were then chopped into 15~20 mm lengths and stabilized by oxidation in air for 90 minutes at 180 and 230°C for the shale oil and petroleum pitch fibers, respectively. The stabilized fibers were carbonized in nitrogen at 850°C for 30 minutes. Carbon fibers were activated by reaction at 850°C for 60 minutes in 50 vol% steam or carbon dioxide, in nitrogen. The sequence of process steps for the preparation of carbon fibers (CF) and activated carbon fibers (ACF) is shown in Figure 1.

The morphology of the carbon fibers and activated carbon fibers was studied at magnifications up to $x10^4$ by SEM (Hitachi S-2700). The BET surface area of activated fibers was measured by nitrogen adsorption at 77K , using a Quantachrome Autosorb 6.

Results and Discussion

Carbon Precursors

Analyses of the shale oil residue, its asphaltene fraction, and the petroleum pitch are shown in Table 1. The asphaltenes represent about 20 wt% of the original residue. It can be seen that the slightly higher nitrogen content of the residue (compared to the petroleum pitch) is considerably concentrated in the asphaltene fraction. The sulfur contents of the three materials are similar, but the petroleum pitch has a somewhat lower ash content. The shale oil asphaltene fraction has a softening point of 183°C, which is lower than that of the petroleum pitch, consistent with its higher hydrogen content.

Carbon Fibers

Carbon fibers were successfully produced from the shale oil asphaltene fraction. SEM micrographs of the carbonized fibers are shown in Figure 2. Small particles (100~500 nm) were observed on the fiber surfaces: their origin is tentatively ascribed to the ash components in the precursor.

The form of the fibers was clearly retained after carbonization, indicating that the conditions chosen for stabilization were sufficient. The stabilization temperature of 180°C used here is much lower than those for conventional isotropic or mesophase pitches[11]. This suggests that the precusor have a very high oxidation reactivity.

While the freshly spun fibers had similar diameters for both precusors, the diameter of the shale oil carbonized fibers was smaller (in the range of 5~12 μm) than that of petroleum-derived ones (6-15 μm), as shown in Table 2. The greater degree of contraction of the shale oil fibers reflects their lower carbonization yield (50% versus 71%), or higher volatile matter content.

Activated Carbon Fibers

The morphology of activated carbon fibers derived from petroleum pitch and shale oil asphaltenes, and produced by activation of the respective carbonized fibers is shown in Figures 3 and 4. Ridges are apparent on the surfaces of the petroleum fibers, and they tend to follow the fiber circumference. Despite this, the surface appears relatively smooth and there are no evident cracks or pores. With the shale oil fibers, an irregular distribution of small pits or pores have developed over the fiber surfaces. In addition, particles can be observed on the surfaces of some of the pore walls. It may be that some of the ash components can have a catalytic influence on the activation or gasification of the fibers, and are instrumental in the generation of these features. The SEM micrographs also suggest that there are some differences in the internal morphology of the two types of fiber.

As shown in Table 3, under similar conditions, the shale oil carbon fibers experienced much greater burn-off during steam activation than the petroleum pitch fibers. This finding also indicates that the the former are more reactive to reactions with oxidizing gases, either due to certain inherent aspects of their composition and structure, or to the catalytic effect of ash constituents. Predictably, activation in carbon dioxide, which is known to be a slower reaction, caused lower burn-off than steam under the same conditions. Despite the different degrees of burn-off, the steam activated fibers from pitch and shale oil had very similar BET surface areas. There may be significant differences in their pore size distributions, although this has yet to be determined, as does the dependence of pore structure on burn off.

Nitrogen Content

The changes in nitrogen content (N/C atomic ratio) during carbonization and activation for both kinds of precursor are shown in Figure 5. For the petroleum pitch, the nitrogen content increased upon carbonization and then kept unchanged through steam activation. As already noted, the N/C atomic ratio was much higher in the shale oil asphaltenes. It was slightly reduced upon carbonization, and then remained at a similar level upon activation: the N/C ratio for activated carbon fibers was about 0.025.

Synopsis

Preliminary studies have been made of the feasibility of producing carbon fibers from high boiling shale oil liquids. Single filament carbon fibers and activated carbon fibers have been produced successfully from an asphaltene fraction of shale oil residuum, by spinning, oxidative stabilization, carbonization, and activation. Comparisons were made with fibers derived from a petroleum pitch.

The yield of the shale oil carbonized fibers was around 50% while that for the petroleum pitch was about 70%. Differences in yield are attributed to the different volatile contents of the precursors.

Activated carbon fibers were obtained by steam activation of the carbonized fibers at 850°C. A BET surface area of around 960 m^2/g was obtained at 63% burn off for the shale oil fibers. A similar surface area was obtained for the petroleum pitch based fiber after reaction under the same conditions but with only 38% burn off. The greater reactivity of the shale oil fibers may be due to

their inherent structure and/or to the catalytic effect of ash constituents: some evidence for catalysis is provided by microscopic observations. High reactivity of green fibers is also indicated by the low reaction temperature required for oxidative stabilization. The high nitrogen content of the activated shale oil fibers may provide unusual adsorptive or catalytic properties.

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Table 1 Analyses of precursor materials

Sample*	Elemental Analysis (wt%) C	H	N	S	AtomicRatio(%) H/C	N/C	Content of Ash (wt%)	Softening Point (°C)
PP	92.88	4.63	0.31	1.99	0.60	0.29	0.21	258
SOR	83.22	9.60	0.51	1.82	1.38	0.53	0.82	< 25
SOR-AS	80.98	6.64	2.54	1.96	0.98	2.69	0.97	183

* PP, petroleum-derived isotropic pitch; SOR, shale oil residue; SOR-AS, asphaltenes: hexane insoluble, benzene soluble.

Table 2 Carbonization of two kinds of green fibers

Sample Code	Precursor Type	Yield (wt%)*	Diameter of CF (mm)
CF-P1	PP	71	6 ~ 15
CF-S1	SOR-AS	50	5 ~ 12

* carbonized at 850°C for 30 min; yield as % of green fibers.

Table 3 Activation of petroleum and shale oil-derived carbon fibers

Sample Code	Precursor Type	Activating Agents	Burn-off (wt%)*	Diameter of ACF (mm)	Surface Area (m^2/g)
AF-P1	PP	H2O/N2 (50:50)	38	4 ~ 12	978
AF-S1	SOR-AS	H2O/N2 (50:50)	63	3 ~ 10	960
AF-S2	SOR-AS	CO2/N2 (50:50)	49	3 ~ 10	566

* activation at 850°C for 60 min; yield as % of carbonized fibers.

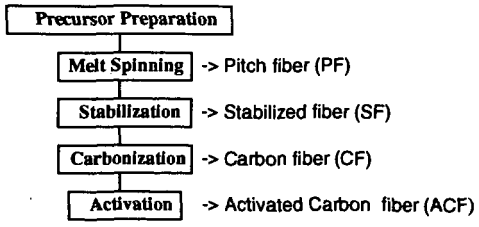

Figure 1 Flowsheet of the preparation of carbon fibers and activated carbon fibers.

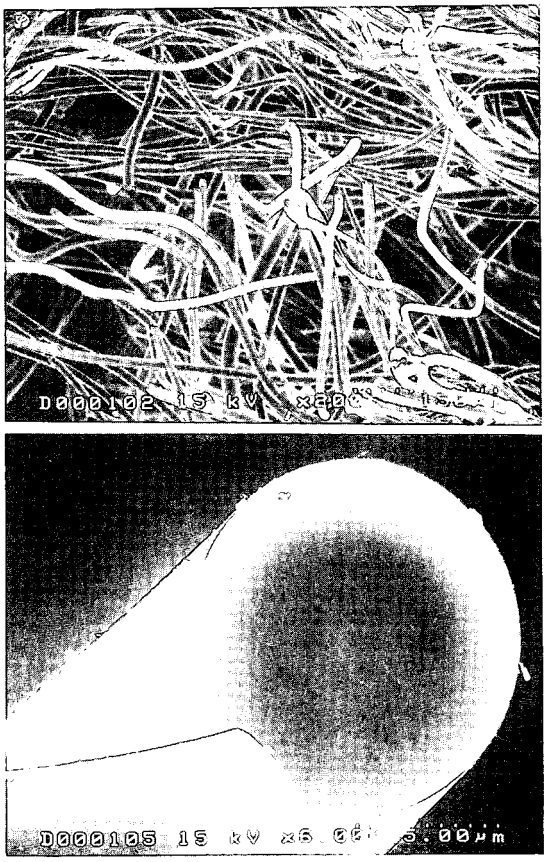

Figure 2 SEM micrographs of carbon fibers produced from shale oil.

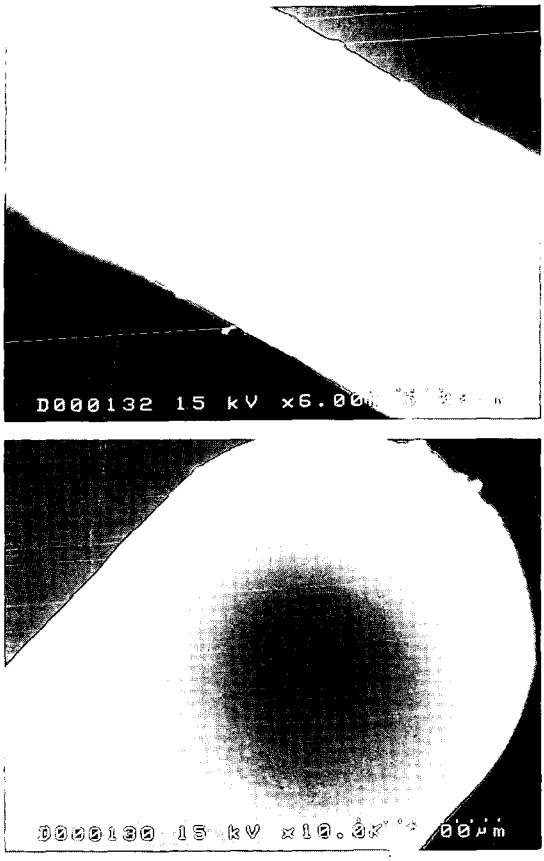

Figure 3 SEM micrographs of activated carbon fibers from petroleum pitch by steam activation.

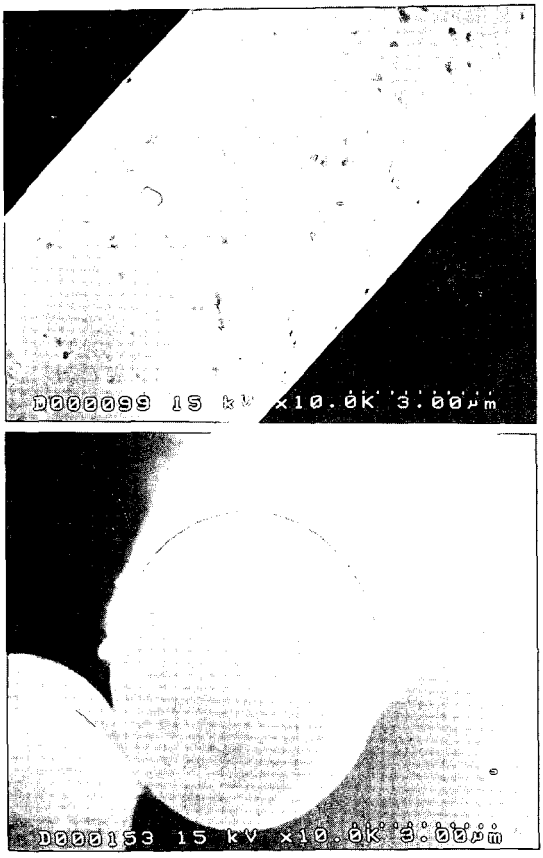

Figure 4 SEM micrographs of activated carbon fibers from shale oil by steam activation.

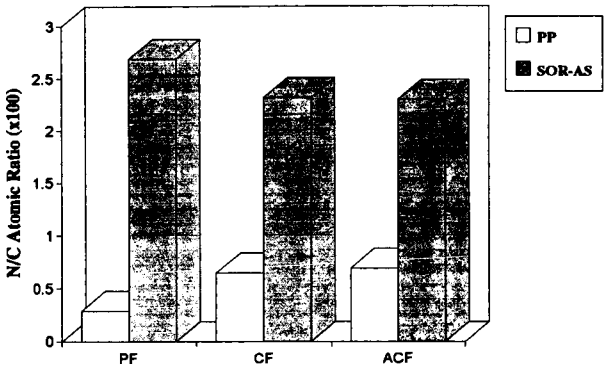

Figure 5 Changes in nitrogen content during the preparation of carbon fibers and activated carbon fibers from shale oil (SOR-AS) and petroleum (PP) precursors.