

EVALUATION OF RESIDUAL SHALE OILS AS FEEDSTOCKS FOR VALUABLE CARBON MATERIALS

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INTRODUCTION

Oil shale represents one of the largest fossil fuel resources in the US and in other parts of the world. Beginning in the 1970s until recently, there was considerable research and development activity directed primarily to technologies for the production of transportation fuels from oil shale. Due to the low cost of petroleum, as with other alternate fuel strategies, oil shale processing is not economically viable at present. However, future scenarios can be envisaged in which non-petroleum resources may be expected to contribute to the demand for hydrocarbon fuels and chemicals, with the expectation that process technologies can be rendered economically attractive.

There is potential to improve the economics of oil shale utilization through broadening the spectrum of products that can be derived from this resource, and producing added-value materials that are either unavailable or more difficult to produce from other sources. This concept is by no means original. The history of oil shale development shows that most attempts to commercialize oil shale technology have relied upon the marketing of by-products [1]. These have included asphalts, construction bricks, cement, soil additives, town gas, lamp oil, rock wool insulation, ammonia, sulphur, paraffin, olefins and other chemicals, and power generation.

In this context, we have conducted investigations to assess the potential for producing premium carbon materials from shale oil residues. Retorted shale oils generally contain more high-boiling fractions than petroleum crudes [2,3]. This is especially true for eastern US shale oils. These properties make shale oils very attractive as carbon sources because the heavy fractions have high carbon contents. Another characteristic of shale oils is their high nitrogen content, which presents difficulties also in upgrading these liquids to clean fuels because extensive and deep hydrogenation is required. The nitrogen-containing species are more concentrated in the higher boiling fractions and accentuate the problem [4,5]. On the other hand, the nitrogen-containing compounds can become highly valuable feedstocks or chemicals if they are separated collectively or individually from shale oils.

We have already reported the successful production of isotropic carbon fibers and activated carbon fibers from the asphaltene fraction of residual shale oil produced from eastern US shale by the Kentort process [6, 7]. While the mechanical properties of the carbon fibers have yet to be assessed, the presence of nitrogen has been shown to enhance the catalytic properties of activated carbon fibers for reactions such as the ambient-temperature oxidation of SO₂ [8], and the nitrogen content is believed to contribute to the wide pore structure that is formed in the activated fibers [7,9].

As the maltene fraction of the shale oil residue has a much lower nitrogen content than the asphaltene fraction, it may be more suitable for the synthesis of other forms of carbon. In this paper, we present the results of studies to investigate the carbonization properties of this material, and to determine the potential for generating a pitch with high mesophase (a carbonaceous liquid crystal) content that could serve as a precursor for the production of materials such as needle cokes (a highly-oriented and graphitizable carbon) for the manufacture of graphite electrodes, and high-performance carbon fibers.

EXPERIMENTAL

A shale oil residue (SOR), produced in the Kentort II process from eastern oil shale [10,11], was used in the study. This residual oil was collected in an electrostatic precipitator and comprised 70-80 wt% of the total oil products from the retort. The sample was further fractionated by extraction with boiling hexane in a Soxhlet apparatus to obtain fractions with different heteroatom contents or polarity [12], namely, hexane-soluble (HS) and hexane-insoluble fractions. The parent shale oil sample and the extracted fractions were subjected to elemental and ¹H and ¹³C-NMR analyses.

Carbonization reactions were conducted both at atmospheric pressure and elevated pressure. Atmospheric pressure carbonization was performed in a Pyrex tube. Samples were heated in the tube reactor under nitrogen flow at 440 °C for 4h, in a vertical electric furnace. Pressurized

carbonization was conducted using a stainless steel tubing bomb ($\phi 1'' \times 4''$) [13, 14]. The bomb was charged with 15-20g of sample and placed in a sand bath preheated at 440-500 °C for a reaction time of 4- 6 h. The reaction pressure was maintained at 700 kPa by pressurizing the bomb with nitrogen before the carbonization reaction and automatically releasing excess pressure through a relief nozzle over the course of the experiment. The carbonized products were weighed and further characterized by elemental analysis and optical microscopy (Leitz, MVP2), using polarized light, after mounting and polishing.

RESULTS AND DISCUSSIONS

Almost the same yields of hexane-soluble (SOR-HS) and hexane-insoluble (SOR-HI) fractions were obtained upon extraction. This means that the eastern crude shale oil contains 30-40 wt% of asphaltenes, in comparison with western shale oils which have less than 5 wt% [2,3]. Table 1 shows some analytical data for the parent shale oil and the extracted fractions. In the order of SOR-HS, parent SOR and SOR-HI, the aromaticity increased and the H/C atomic ratio decreased. Aliphatic components are concentrated in the maltene (SOR-HS) fraction which has correspondingly low aromaticity. Sulfur is distributed evenly in both extracted fractions although it is to be noted that the sulfur concentration is much higher than found in other shale oils [2,3]. About 85% of the total nitrogen in the parent shale oil is concentrated in the SOR-HI fraction, where nitrogen content is about six times higher than that of SOR-HS.

Figure 1 shows the optical texture of products obtained by atmospheric pressure carbonization of the parent shale oil and the hexane soluble fraction. Both feeds produced mosaic texture cokes. The product from the parent shale oil has a fine mosaic texture (about 5 μm in size), while larger isochromatic units ($\sim 20 \mu\text{m}$ size) were observed in the SOR-HS coke. The hexane insoluble fraction (SOR-HI) also gave a fine mosaic texture very similar to that of the parent shale oil, possibly because the presence of the HI fraction dominates the carbonization progress, as indicated by carbonization yield in Table 2. The hexane soluble fraction alone gave a yield of only 8 wt %, whereas it was 46 wt% for the hexane-insoluble fraction. The yield for the parent shale oil was 26 wt%, essentially following the additive rule.

The optical micrographs of products obtained by pressurized carbonization of the shale oil and the hexane-soluble fraction are shown in Figure 2. Under these conditions, excellent flow domain textures were formed from the SOR-HS fraction. The full-range shale oil gave a mosaic texture, $\sim 20 \mu\text{m}$, larger than that obtained under atmospheric pressure. The effects of using elevated carbonization pressure have been reported to be favorable for anisotropy development for many other heavy oils, and it has been employed commercially to produce needle cokes [14]. It has been reported that a western shale oil and its maltene fraction also produce mosaic texture cokes upon the atmospheric carbonization, even after various preheat treatments [15, 16]. These results are consistent with the experiment results described above, although there may be differences in composition, structure and reactivity between the eastern and western shale oils. The experiment results indicates the importance of both solvent fractionation and overpressure to the carbonization of shale oil products. The results of the present study further suggest that the maltene fraction of eastern shale oil may be used to produce mesophase pitches for the synthesis of high-performance carbon fibers, or for premium coke production if sulfur and nitrogen contents are acceptable. Elemental analyses of green cokes shows that much lower nitrogen cokes are produced by using the maltene fractions rather than the full-range shale oil, Table 3.

The influence of carbonization conditions on coke yield can also be seen in Table 2. Pressurized carbonization can substantially increase the yield. Notably, the yield from the maltene fraction was increased by a factor of about four at 700 kPa. The effects of high pressure and a closed system will be to prevent the escape of volatile components and cracked products and retain a higher proportion of the precursor in the liquid phase. The coke yield also reflects the high reactivity of the SOR-HI fraction: there was only a 20% increase in yield upon going to pressurized carbonization.

Based upon previous findings [6,7] and the results of the present investigation, at least one scheme can be proposed for the more effective use of residual shale oils, Figure 3. The first step involves solvent separation into maltene and asphaltene fractions. Deasphalting processes have been used to prepare feedstocks for delayed coking in order to produce high grade cokes from petroleum heavy oils and lower the impurity contents (basically metals, such Ni and V) of the coke products. The same step seems necessary to render shale oils suitable for premium coke production, although the reasons appear to be somewhat different.

The asphaltene fraction from shale oil contains a high concentration of nitrogen species and has a high coking reactivity that can inhibit mesophase development [5]. The nitrogen-containing species also tend to be retained in the resultant cokes, and could cause puffing problems at graphitization. Although the sulfurs in the SOR-HS may also result in puffing, desulphurization can be achieved relatively easily by mild hydrogenation [17]. Thus, by removing asphaltenes, a material can be obtained that would be a suitable precursor for the production of needle cokes, or a mesophase pitch for the manufacture of high performance carbon fibers. Alternatively, maltene fractions may be completely refined to produce liquid fuels by conventional catalytic upgrading, since most of problematic nitrogen-containing species are removed.

The asphaltene fractions can be used as a source of specialty carbons with high nitrogen content. The combustion of such high nitrogen-content fuels could result in unacceptable emission of nitrogen oxides [18]. The production of isotropic carbon fibers and activated carbon fibers with unique properties may be an example of their practical utilization. Thus, starting with a heavy shale oil, we may produce a variety of valuable carbon materials in the form of pitch, coke and carbon fibers, with optical texture ranging from isotropic, fine mosaic to flow domain.

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Table 1 Analytical data for the parent shale oil and fractions

Sample ID	Yield (wt%)	Elemental Analysis(wt%)				Atomic Ratio		fa
		C	H	N	S	H/C	N/C(x100)	
SOR	–	82.02	8.58	1.38	1.84	1.26	1.47	0.57
SOR-HS	52	82.55	10.21	0.41	1.85	1.48	0.43	0.45
SOR-HI	48	81.39	6.88	2.49	1.81	1.01	2.62	0.71

* SOR, parent shale oil; HS, hexane-soluble fraction; HI, hexane-insoluble fraction; fa, fraction of aromatic carbon

Table 2 Carbonization yield (wt%) of parent shale oil and fractions

Feedstock	Atmospheric pressure	Pressurized (700 kPa)
SOR	26	40
SOR-HS	8	31
SOR-HI	46	57

* SOR, parent shale oil; HS, hexane-soluble fraction; HI, hexane-insoluble fraction

Table 3 Properties of green cokes obtained from parent residual shale oil and HS fraction

Feedstock	SOR	SOR-HS
Carbonization condition	440 °C-700 kPa	440 °C-700 kPa
Optical texture	Mosaic	Flow
N content (wt%)	3.22	1.08

* SOR, parent shale oil; HS, hexane-soluble fraction.

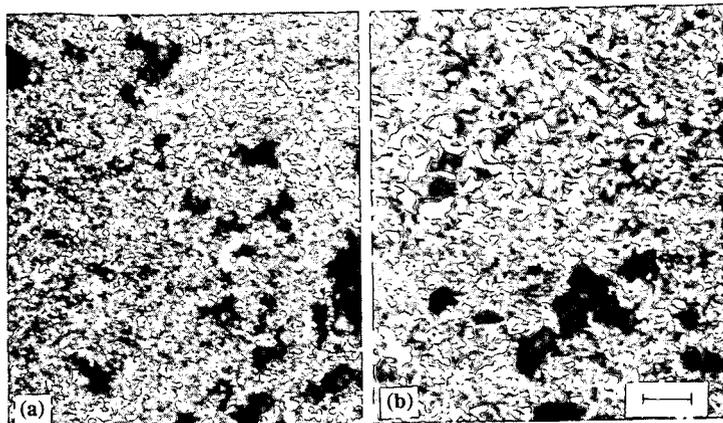


Figure 1 Optical texture of products carbonized at atmospheric pressure from: (a) Parent SOR, (b) Hexane-soluble fraction of SOR

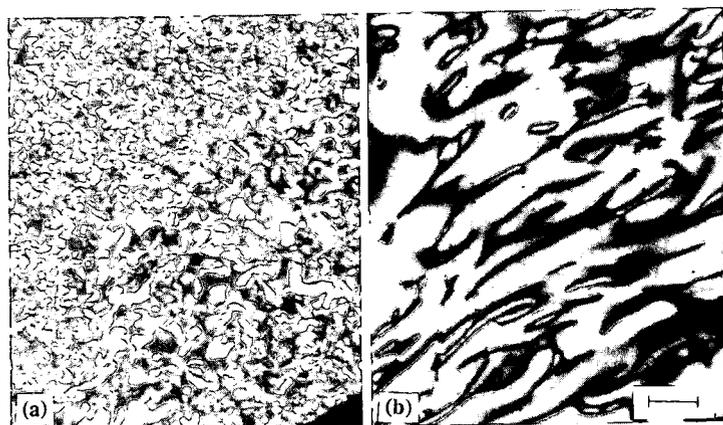


Figure 2 Optical texture of products carbonized under pressure (700 kPa) from: (a) Parent SOR, (b) Hexane-soluble fraction of SOR

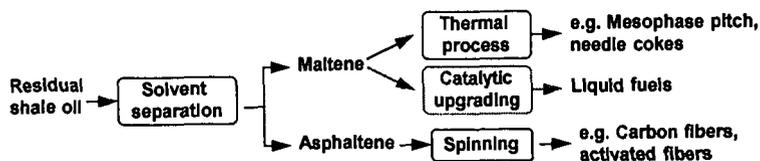


Figure 3 Illustration of a value-adding route for utilization of residual shale oils and resultant intermediate and final products