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SHALE OIL DELAYED COKING PRODUCTS UTILIZATION FOR MANUFACTURED GRAPHITES

By

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INTRODUCTION

Carbon and graphite materials are required to withstand more and more severe conditions of thermal shock, stress and reactor irradiation in the steel making, aluminum, aerospace and nuclear industries. At the same time, the sources for the precursors of these manufactured carbons are being depleted, so that other sources are needed. The aim of this work is to demonstrate the applicability of new precursors from the delayed coking products of shale oil to graphite manufacture and to determine what chemical characteristics are required for those precursors.

It is known that the microstructure and properties of graphitic materials are determined by the characteristics of an ordered fluid, termed the "carbonaceous mesophase", which forms during pyrolysis, usually between the temperatures of 370°C and 500°C (1). It is the order developed in this mesophase below 500°C that determines the properties of the final product obtained after heating to graphitizing temperatures of 2800°C. The mesophase forms an optically anisotropic microstructure and the properties expected from the graphite can be related to the mesophase microstructure. An isotropic microstructure indicates a non-graphitizing carbon with poor graphite properties, whereas a flow type or fibrous structure indicates a needle coke morphology which tends to have good thermal and tensile properties (2). So the characteristics of the final product are controlled by the mesophase formed below 500°C and these characteristics can be measured in a qualitative way from the cross polarized micrographs of the pyrolysis product residues.

In this work, graphitizing and chemical properties of the delayed coking products from a Green River shale oil were examined. Samples were pyrolyzed, solvent fractionated and analyzed using elemental analysis, cross polarized microscopy, proton nuclear magnetic resonance, infrared spectroscopy, vapor pressure osmometry and gas chromatography.

EXPERIMENTAL

The crude shale oil was distilled at 0.05 mm Hg vacuum for 6 hours at a pot temperature of 190°C. The vacuum distillate bottoms were heat treated by refluxing under N₂ gas at a temperature of 285°C for 5 hrs, 25 hrs and 74 hrs. Then all the samples including the shale oil and vacuum bottoms were Soxhlet extracted using hexane followed by benzene. The purpose was to isolate and identify the fraction(s) that is responsible for the graphitizing properties of the sample(s). Each of the above prepared samples were pyrolyzed three times under nitrogen gas at atmospheric pressure. The samples (0.5g) were placed in pyrolysis cells made of aluminum tubes with 0.5 mm pin-hole openings for vapor escape. The tubes were placed in stainless steel cells, then put in a temperature-programmed furnace and purged with nitrogen gas controlled by flow meters at 15 L/hr. The temperature was programmed at 13°C/hr to 360°C and 5°C/hr to the desired final temperature of 465°C (3). It is in this region (465°C) where the principle features of graphitic and pregraphitic microstructures are established and can be detected by polarized light (2, 4).

The residues of the pyrolyzed samples were examined under polarized light using a Leitz SM-Lux-Pol Cross Polarizing Microscope. These residues were first cast in epoxy resin and polished until the surface were optically smooth, then micrographs were obtained.

In order to determine what changes were occurring with the processing, the samples (shale oil, vacuum distillate and heat treated vacuum bottoms) and hexane solubles along with benzene solubles were investigated using the following analytical methods:

1. Elemental Analysis: Elemental analysis was done by Huffman Laboratories (Wheat Ridge, Colorado) and some earlier samples were done by the California Institute of Technology (Pasadena, California).

2. Vapor Pressure Osmometry: Molecular weights of the precursor samples were obtained using a Mechrolab 301A Vapor Pressure Osmometer (VPO). Tetrahydrofuran was used as solvent.

3. **Infrared Spectroscopy:** A double-beamed infrared spectrophotometer (IR), Model Acculab 6-Beckman Instruments, was used with sets of potassium bromide matched liquid cells of 0.025 mm thicknesses at the concentration of 2.5 g/ml in carbon tetrachloride.

4. **Proton Nuclear Magnetic Resonance:** High resolution proton nuclear magnetic resonance of samples was done on a T-60 Varian spectrometer at a concentration 10 wt/vol % in deuterated chloroform. Due to overlapping of the resonance bands, the areas were separated using the method of Brown, et al. (5).

5. **Gas Chromatography:** Finally, the samples were further analyzed by gas chromatography using Hewlett-Packard Model 5880 on a 30 x 0.323 mm I. D. fused silica capillary column coated with SE-54. The oven temperature was programmed to an initial value set at 100°C (hold 2 min) and a linear heating rate of 5°C/min up to 270°C (hold 2 min). 1 Microliter of each sample was injected at a concentration of 2.5 wt/vol % in toluene. The peaks were assigned quantitatively by coinjecting standard n-alkanes.

RESULTS AND DISCUSSION

After vacuum distillation, up to 71% of heavy oil residua remained. Current operational and proposed refining practices of crude shale oil in recovery of high Btu volatile matter as useful fuels (aviation fuels) quantitatively produce similar heavy ends.

The shale oil and vacuum distillate pyrolyzed residues showed isotropic microstructures under light polarizers. Heat refluxing performed was to increase the aromaticity of materials. The aromaticity did not change much. However, optically active coarse mosaic textures were observed after 5 hrs of heat treating the vacuum bottoms. Also, the examined pyrolyzed results of hexane- and benzene-soluble fractions of the samples surprisingly showed that none of the benzene-soluble materials formed any optical activity. The hexane solubles, however, were optically active with all the heat-treated fractions forming coarse mosaic structures. The optical micrographs of polished surfaces of pyrolyzed prepared samples plus their solvent fractions are shown in Figure 1.

The normalized results of solvent-fractionated samples given in Table I, show that the 5 hrs heat treated vacuum bottoms has the highest cut of hexane solubles. With excess heat treatment of 74 hrs, it appears that cracking of resin to form asphaltene and preasphaltene takes effect.

TABLE I

PARAMETERS AND DATA OBTAINED BY SOLVENT FRACTIONATION, ELEMENTAL AND ANALYSIS (EA), ¹H NMR AND VPO OF PRECURSOR SAMPLES

| Sample | Instrument and Parameter | | | | | |
|--------------------------|---------------------------|-----------------|-------------------|------|----------------|-----|
| | Soxhlet Extraction (% wt) | | | EA | H NMR | VPO |
| | Hexane-Soluble | Benzene-Soluble | Benzene-Insoluble | H/C | Aromaticity fa | MW |
| Shale oil | 96.7 | 1.4 | 1.9 | 1.81 | 0.15 | 270 |
| Vacuum distilled bottoms | 96.2 | 2.4 | 1.4 | 1.49 | 0.29 | 292 |
| Heat treated | | | | | | |
| 5 | 96.7 | 2.6 | 1.4 | 1.54 | 0.27 | 295 |
| vacuum bottoms | 25 | 95.4 | 4.4 | 1.52 | 0.29 | 353 |
| (hours) | 74 | 85.7 | 10.0 | 1.50 | 0.29 | 315 |

The atomic H/C ratios of samples and their solvent fractions, calculated from elemental analysis results, showed a decrease after vacuum distillation but heat treatment caused slight changes. It is generally known that the lower the hydrogen-to-carbon ratio, the greater the degree of ring condensation regardless of whether the rings are aromatic or naphthenic in character.

From VPO studies, the average molecular weight of the samples increased with processing up to 25 hrs of heat treatment and decreased with 74 hrs of treatment.

Results from proton NMR and IR studies of all the samples revealed that percent naphthenicity is at minimum for shale oil and at maximum for 74 hrs heat treated vacuum bottoms. This explains that these cyclic compounds are the ones which form into mesophase as it was shown by the micrographs in Figure 1. The reason that the 25 hrs and 74 hrs treated samples did not form coarse mosaic microstructures is the increased presence of non-mesophase forming materials (hexane insolubles).

Some of the results obtained from elemental analysis, proton NMR and VPO are given in Table I. From these and other results obtained so far, a possible explanation of the changes with processing is that condensation or polymerization reactions followed by cracking of molecules and/or disproportionation reactions have occurred. Also, it was observed that, with proper control of processing conditions, the coarse mosaic microstructure can be obtained.

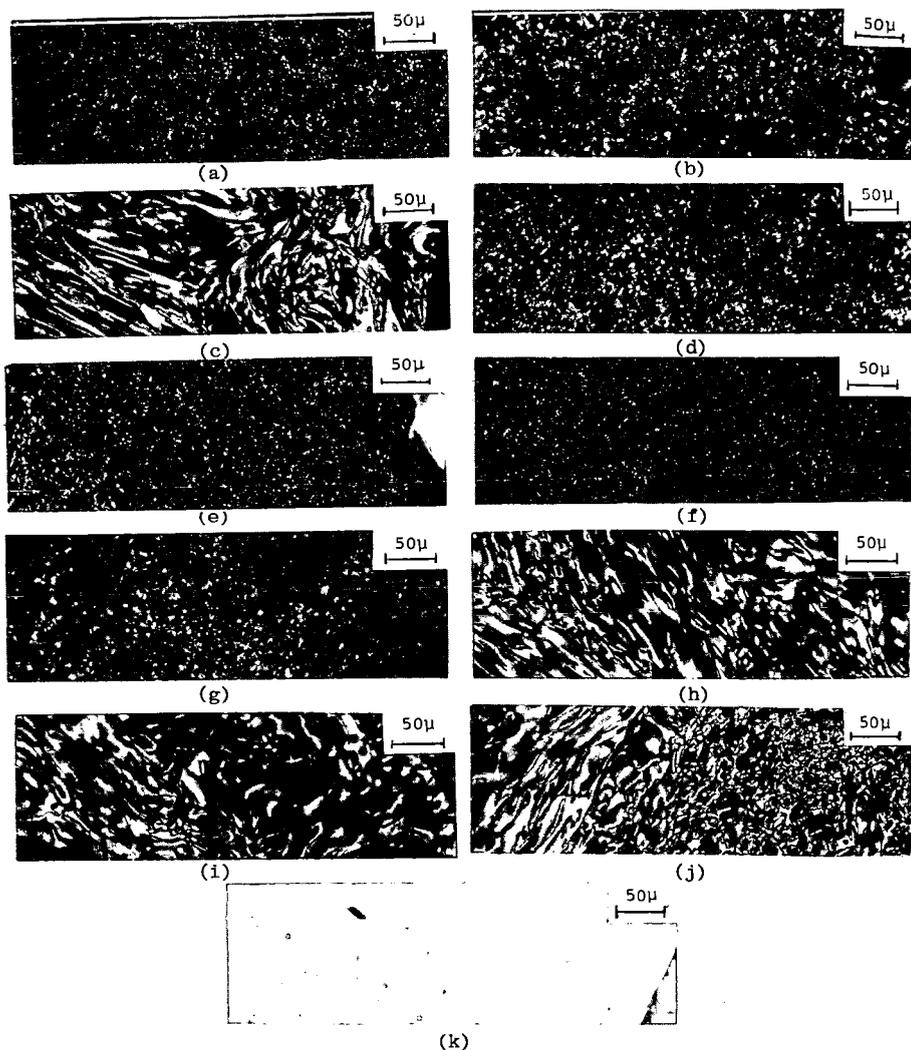
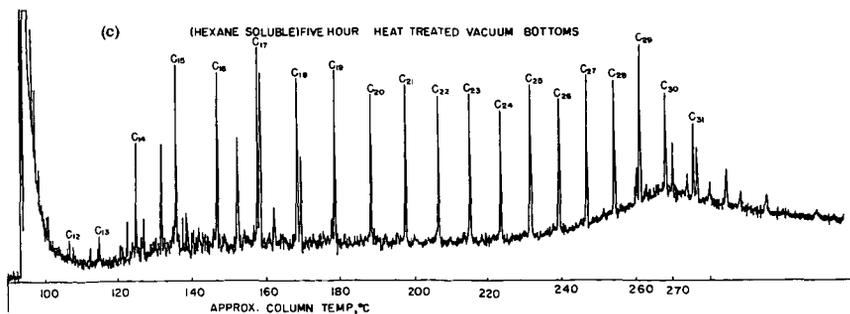
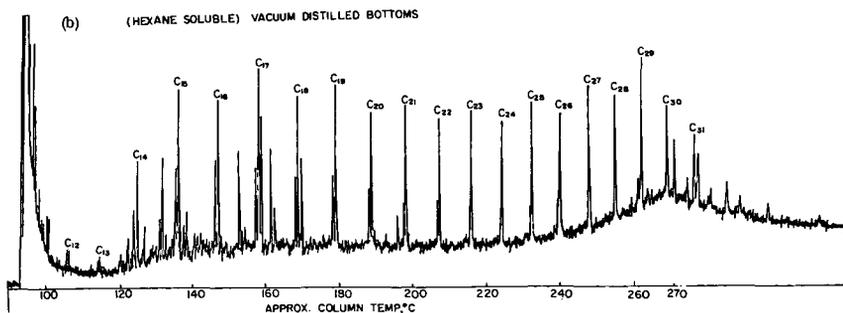
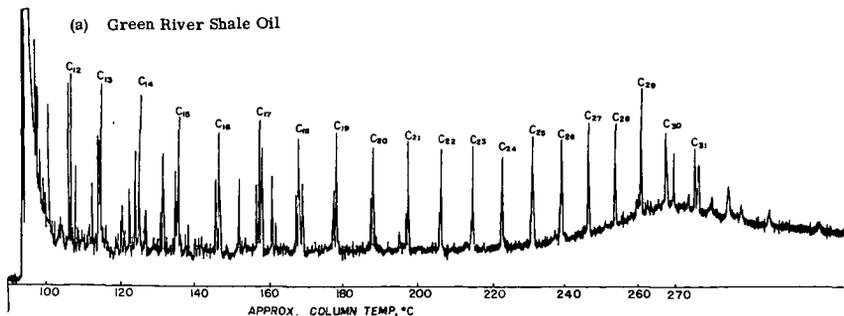


Figure 1. The Optical Micrographs of Polished Surfaces of Pyrolyzed Samples (a) Shale Oil, (b) Vacuum Distilled Bottoms and Heat Treated Vacuum Bottoms for (c) 5hrs., (d) 25 hrs. and (e) 74 hrs. Samples (f) to (j) are Hexane Solubles of Samples (a) to (e). And (k) Shale Oil Benzene Soluble Fraction. (Magnification is 200 Times).

Figure 2.
HEXANE SOLUBLE FRACTIONS OF SHALE OIL
ON 30Mx0.323 MM FUSED SILICA CAPILLARY COLUMN



Gas chromatograms of hexane-soluble matter of the shale oil, vacuum distillates and 5 hrs-heat-treated vacuum bottoms are shown in Figure 2. The chromatograms show the presence of certain branched aliphatic compounds attached to the left of most peaks in (a) shale oil and (b) vacuum distillates. These isocompounds disappeared with heat treatment as shown in (c) 5 hrs thermal treated sample. From the micrographs of Figure 1 (f-j), it can be concluded that the presence of such isocompounds act as suppressors to mesophase formation. This could be due to cracking of these highly unstable isocompounds at the branch level into smaller volatile molecules which, in turn, may interfere with the free radical aromatics that construct the matrix of the "Carbonaceous Mesophase".

CONCLUSIONS

The following conclusions may be drawn from the results of this preliminary research.

1. With 5 hrs of heat refluxing of shale oil vacuum distillate bottoms, coarse mosaic microstructures can be achieved. This shows that controlled processing will enhance the graphitizing properties of these organic products.

2. It is known that a good precursor for mesophase formation is a highly condensed organic compound with a large aromatic core and few and short aliphatic molecules. However, contrary to other precursors, proton NMR and IR studies revealed that the naphthenics are most likely responsible for mesophase formation. This phenomena was also shown by solvent fractionation of the samples. Only the hexane solubles which are of low aromaticity formed mesophase during the carbonization process.

3. Gas chromatography of the hexane-soluble fractions from shale oil and vacuum distillate bottoms indicates the existence of certain branched compounds. These isocompounds disappeared with heat treatments of 5 hrs, 25 hrs and 74 hrs. The micrographs of polished surfaces for these pyrolyzed hexane-soluble samples reveal that only the heat treated vacuum bottoms show anisotropic microstructures. Therefore, the presence of these branched compounds act as inhibitors to mesophase formation.

4. Shale oil delayed coking products utilization is indeed possible for manufactured graphites. However, scale-up procedures are required so that the cost of these carbon and graphite composites could be compared with those derived from petroleum and coal.

ACKNOWLEDGMENTS

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