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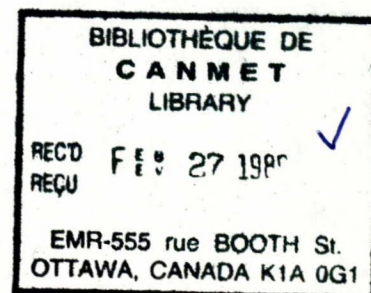
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OF ATHABASCA BITUMEN

by

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ABSTRACT

The formation of two structurally different cokes during thermal hydrocracking of Athabasca bitumen was attributed to differences in coking properties of the asphaltenes and the deasphalted heavy oils. The grain-mosaic coke structure formed from the asphaltenes may be ascribed to the presence of cross-linkage groups derived from the phenolic character of this fraction of the bitumen. The carbonization of the deasphalted heavy oils of the bitumen resulted in a flow-type coke structure, possibly indicating the absence of extensive cross-linkage in the product.

INTRODUCTION

The formation of coke during thermal and catalytic hydrocracking of bitumen has been a major concern in the petroleum refining industry. Coke formation reduces the yield of useable distillate fuels, and is also one of the primary causes of fouling of reactors during the cracking process. In view of the complexity of the chemical mechanisms leading to the formation of coke, there has been relatively little effort made to identify the origin and character of the coke obtained during the cracking process. Some workers have simply used a working definition of coke; e.g., the benzene-insoluble fraction (1). Such definitions offer little information as to the chemical

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or physical nature of the coke. For instance, a significant portion (as much as 50%) of the benzene-insoluble residue, produced during thermal hydrocracking of Athabasca bitumen, has been found to be soluble in stronger solvents such as quinoline (2). This indicates that coke is perhaps not the only constituent of the benzene-insoluble fraction obtained from thermal hydrocracking.

The assumed complex nature of coke formation originates primarily from the lack of information of the physico-chemical properties of the various constituents present in the bitumen. The subdivision of bitumen into groups such as light oil, heavy oil, resins and asphaltenes has been based predominantly upon physical properties (e.g., solubility, molecular weight, boiling points). However, little is known about the chemical structure of the various constituents. This is particularly the case of the high-molecular weight components (e.g., the heavy oils and asphaltenes) for which several conflicting structures have been proposed in the literature (3-7). These higher molecular weight compounds are most likely precursors for the formation of coke.

Speight (8) attempted to establish some basis of comparison between cokes formed from individual fractions of Athabasca bitumen. Based on analytical data, he concluded that the coke formed from thermal cracking of the deasphalted heavy oil fraction was similar to that formed from asphaltenes. However, no evidence of the physical structure was presented to substantiate this finding.

The purpose of this paper is to offer microscopic evidence to support the formation of at least two distinctly different cokes formed during thermal cracking of Athabasca bitumen. It will be shown that these cokes form independently of each other and that they correspond to coking of

specific fractions of the bitumen. Some correlation between the physical structure of the coke and the chemical structure of individual bitumen fractions will also be discussed.

EXPERIMENTAL

The studies described in this work were conducted with Athabasca bitumen supplied by Great Canadian Oil Sands (Fort McMurray, Alberta, Canada) in connection with the Canada Centre for Mineral and Energy Technology Program. The heavy oil fraction obtained from thermal hydrocracking of the bitumen was deasphalted by precipitating the asphaltenes by addition of forty volumes of pentane to one volume of oil according to the ASTM method (19). The deasphalted heavy oil was subsequently distilled under vacuum (40 mm Hg) at 260°C.

The carbonization of asphaltenes and deasphalted heavy oils was carried out under controlled rate of heating. The sample was placed in a horizontal quartz tube (15 mm diameter and 50 cm length) in a Kanthal-wound tube furnace which was heated at 10°C/min. The tube was initially evacuated and then filled with argon at atmospheric pressure.

In some experiments, samples of deasphalted heavy oil were treated with VitrideTM Reducing Agent ($\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$) (supplied by Eastman Chemicals). The reaction was conducted under reflux conditions in benzene for about 3 hours with excess reducing agent. The subsequent hydrolysis reaction was carried out with aqueous 1N NaOH solution. The benzene layer was washed with copious amounts of water and then dried with anhydrous calcium chloride. The reduced deasphalted heavy oils were recovered by distilling off the benzene.

Samples for petrographic examination were prepared by embedding the cokes in lucite plastic and polishing the surface. A Leitz Reflected Light microscope was used to examine the optical structures of the coke.

RESULTS AND DISCUSSION

The properties of the Athabasca bitumen used in this work are given in Table 1.

The residue obtained from vacuum distillation of the deasphalted heavy oils showed a characteristic flow-type anisotropic coke structure (21) upon carbonization (Figure 1). Carbonization of the asphaltenes at 350°C resulted in a fine-medium grain-mosaic coke structure (Figure 2). On further heating to 450°C a gradual transition to a coarse mosaic structure occurred (Figure 3). Carbonization experiments at higher temperatures (up to 1000°C) failed to alter the coarse mosaic structure of the "asphaltene-coke" to a flow-type structure.

Figures 4 and 5 demonstrate the coke deposited on the outer surface of the thermocouple sheath in the reactor during thermal hydrocracking of the bitumen at 450°C and 10.44 MPa (20). This coke was found to have representative structures of both deasphalted heavy oils and asphaltenes (cf. Figures 1 and 2, respectively). It is evident from Figure 4 that the formation of "asphaltene-coke" on the thermocouple wall preceeded the deposition of coke formed from the heavy oil. This observation is consistent with the fact that the asphaltenes precipitate out of the bitumen in the presence of low molecular weight saturated hydrocarbons (9) which are formed during the cracking process. The segregation of the "asphaltene-coke" and "heavy oil-coke", Figure 4, is an interesting phenomenon for which a satisfactory explanation cannot be offered at the present time. However, the

results strongly indicate that the chemical structure of the asphaltenes and heavy oil are sufficiently dissimilar as to prevent mixing of the two phases.

In order to elucidate the differences in coke structure resulting from coking of asphaltenes and deasphalted heavy oils, a series of experiments using elemental sulphur was carried out. The presence of sulphur is expected to induce cross-linkage between the heavy oil molecules (10,11) and may therefore alter the flow-type coke structure obtained from carbonization of the heavy aromatic oils.

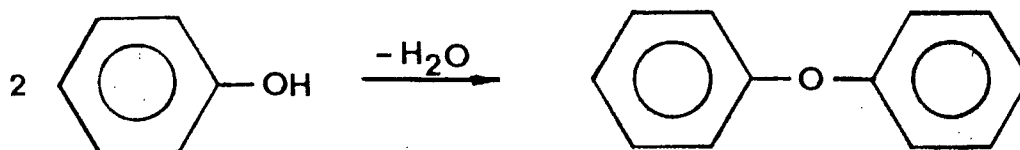
Small quantities (<5%) of sulphur were intimately mixed with the deasphalted heavy oils, and the mixtures carbonized at about 500°C. The resulting coke structure is shown in Figure 6. Three phases can be identified depending on the extent of attack by sulphur: (A) the unattacked phase, (B) the partially attacked phase and (C) the extensively attacked phase. Where sulphur had partially penetrated the deasphalted heavy oil (phase (B)), a transformation to a fine-medium grain-mosaic coke structure, similar to the "asphaltene-coke" was observed. The presence of sulphur may have, therefore, induced cross-linkage between the heavy oil molecules. The indications from these findings are that the differences in structure observed for the "asphaltene-coke" and "heavy oil-coke" arise primarily from the extent of cross-linkages in the respective cokes.

The addition of sulphur to samples of asphaltenes, and subsequent carbonization at about 500°C, resulted in a fine grain mosaic-coke structure, Figure 7. A comparison of this micrograph with Figure 3 suggests that the presence of sulphur increased the extent of cross-linkage in the "asphaltene-coke".

In areas where attack by sulphur was extensive (e.g., phase (C))

Figure 6), no visible coke structure could be discerned. This effect has been reported elsewhere (14).

It seems likely from the results reported, that the asphaltenes contain functional groups which induce cross-linkages during carbonization, whereas the heavy oils do not. Speight (12) investigated the oxygen functional groups in bitumen by infrared spectroscopy and concluded that the majority of the oxygen in the asphaltene fraction existed as hydroxyl functional groups (mainly as phenolic groups), while the majority of the oxygen within the heavy oils occurred as carbonyl groups (primarily as esters (13)). The pyrolysis of phenolic compounds has been shown to induce cross-linkage (15 - 17); e.g.,



Carbonyl functional groups may, on the other hand, not be as reactive towards formation of cross-links.

In order to substantiate this hypothesis, samples of deasphalted heavy oils were reduced with VitrideTM reducing agent under conditions given in the Experimental section. Vitride is used specifically for reducing carbonyl groups to hydroxyl groups (18). Carbonization of the reduced heavy oil gave rise to a grain-coke structure, similar to that observed for the "asphaltene-coke" (Figure 8).

It is difficult to determine the chemical structure of the asphaltenes and heavy oils solely on the basis of microscopic evidence of their respective cokes. However, it appears that the structure of the coke formed

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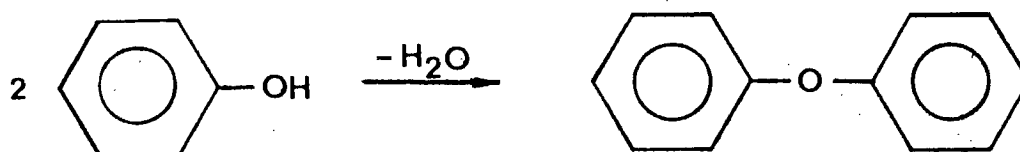
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It is difficult to determine the chemical structure of the asphaltenes and heavy oils solely on the basis of microscopic evidence of their respective cokes. However, it appears that the structure of the coke formed

during carbonization depends on the degree of cross-linkage in the product.

CONCLUSIONS

The differences in the coking properties of the asphaltenes and the heavy aromatic oils of bitumen may be attributed to the extent of cross-linkage formed during carbonization. Asphaltenes give a fine mosaic grain structure on coking which transforms to a coarse grain structure as the coking temperature is increased. Deasphalted heavy oils on the other hand, give a flow-type structure on carbonization. The flow-type structure obtained from the deasphalted heavy oils could be transformed to a grain-type structure by inducing cross-linkages by addition of sulphur prior to carbonization.

ACKNOWLEDGEMENTS

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TABLE 1

Properties of Athabasca Bitumen

Specific gravity	60/60°F	1.009
Sulphur	wt %	4.48
Ash	wt %	0.59
Conradson Carbon Residue	wt %	13.3
Pentane Insolubles	wt %	15.5
Benzene Insolubles	wt %	0.72
Vanadium content	ppm	213
Nickel content	ppm	67
Total Acid number		2.77
Total Base number		1.89
Carbon	wt %	83.36
Hydrogen	wt %	10.52
Nitrogen	wt %	0.43
Viscosity	cst at 210°F	133.3

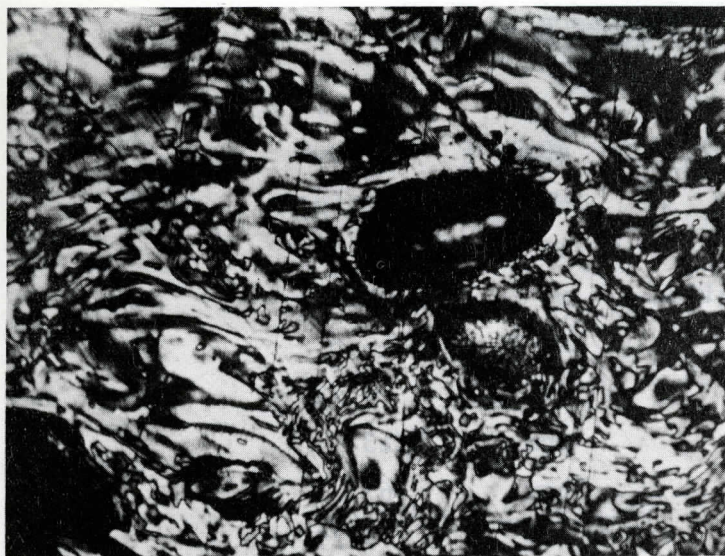


FIGURE 1 - Coke Formed from Deasphalted Heavy Oils Carbonized at 500°C (x 600)

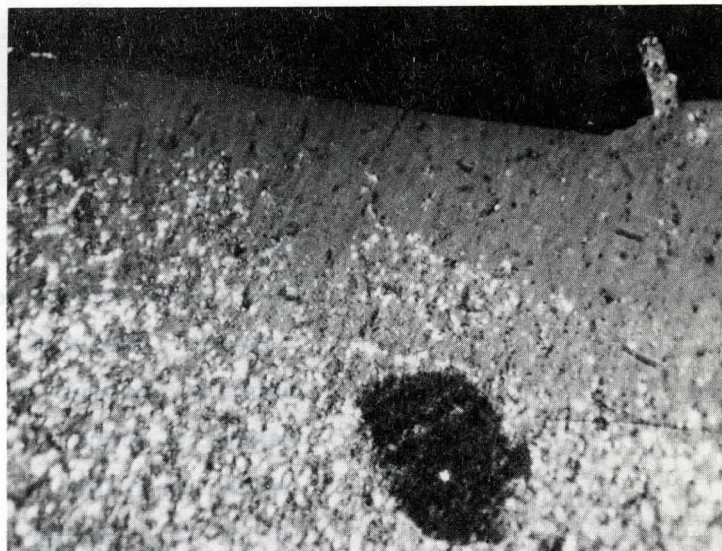


FIGURE 2 - Initial Stages of Coke Formation from Asphaltenes at 350°C (x 600)
Upper part - fine grain
Lower part - medium grain

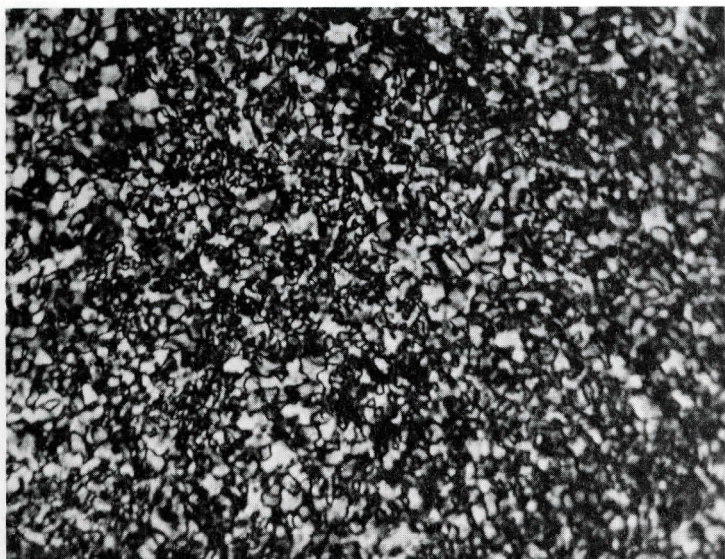


FIGURE 3 - Coke Formed from Asphaltenes Carbonized at 450°C, showing a coarse-grain structure (x 600)



FIGURE 4 - Coke Deposited on the surface of the Thermocouple Sheath in the Reactor During Thermal Hydrocracking of Athabasca Bitumen; 450°C, 10.44 MPa (x 600)
A - grain-mosaic structure
B - flow-type structure

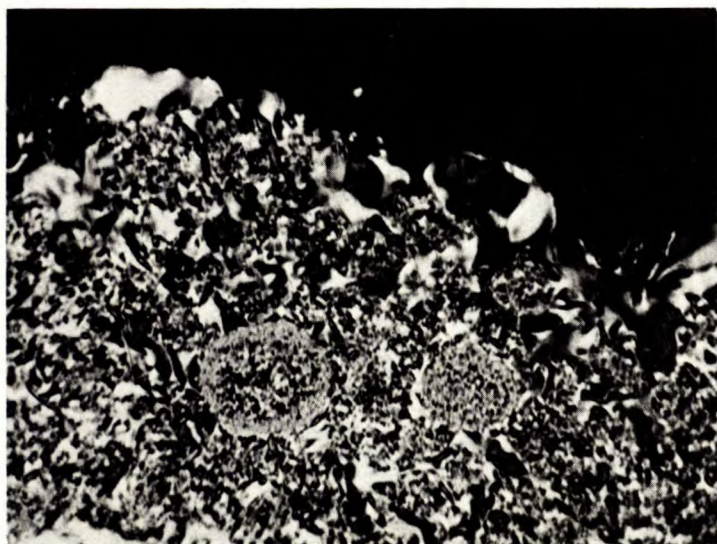


FIGURE 5 - Same as Figure 4.
Continuation of Upper Part
(B) of Previous Figure

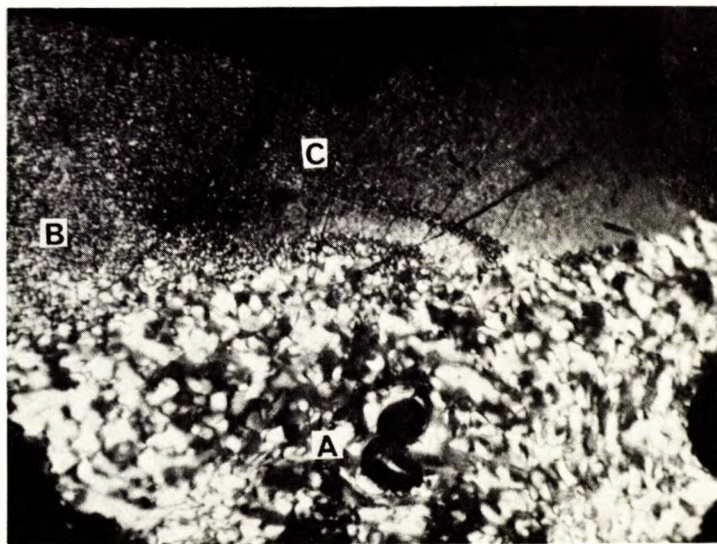


FIGURE 6 - Coke Formed by Carbonizing a
Mixture of Deasphalted
Heavy Oils and Elemental
Sulphur at 500°C (x 600)
A - unattacked phase
B - partially attacked phase
C - extensively attacked
phase

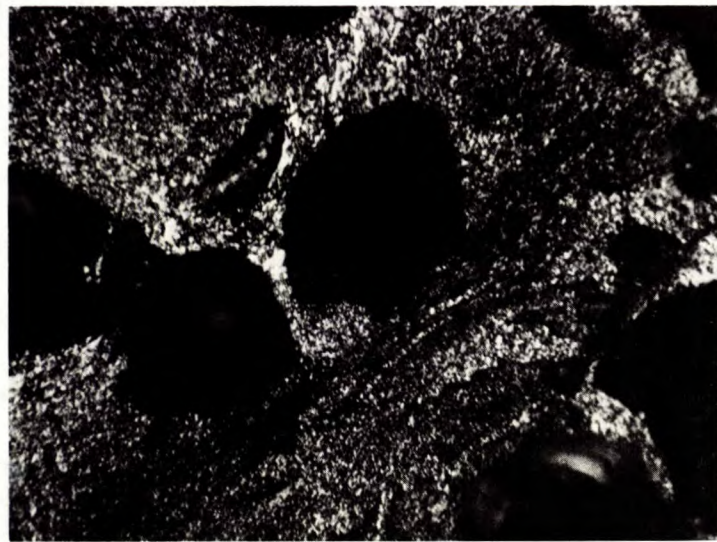


FIGURE 7 - Coke Formed by Carbonizing
a Mixture of Asphaltenes &
Elemental Sulphur at 500°C,
Showing a very Fine-grain
Structure (x 600)

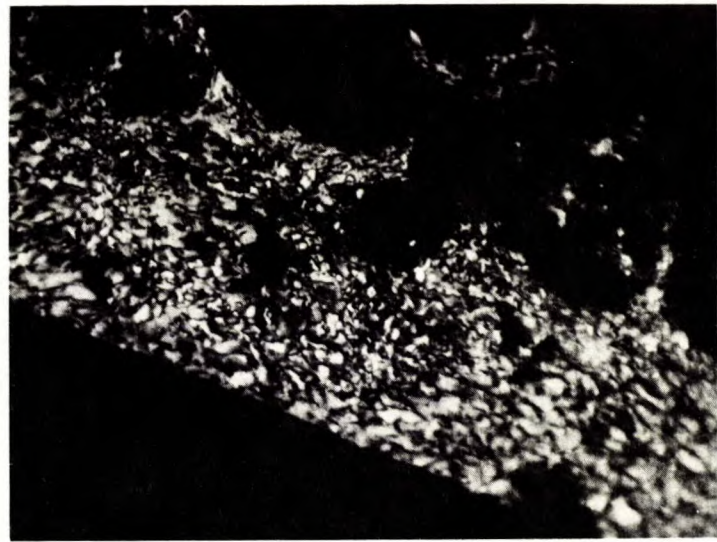


FIGURE 8 - Coke formed from Deasphalted
Heavy Oils Chemically Pre-
treated with Vitride Car-
bonized at 500°C, Showing
Transformation from a Flow-
Type to a Coarse-Grain Coke
Structure.