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Introduction

Coke formation during thermal hydrocracking of bitumen from the tar sands reduces the yield of useable distillate fuels and is one of the principal causes of fouling of the reactor during the cracking process (1). The chemical complexity of the feed stocks has made difficult any attempts to relate the physical character of the coke to the various classes of compounds present.

The use of working definitions of coke, such as benzene-insolubles (2), tend to be somewhat misleading. A significant portion of the benzene-insoluble residue produced during thermal hydrocracking of Athabasca bitumen has been found to be soluble in a stronger solvent such as quinoline (3). The implication is that this "coke" may perhaps be more accurately termed a coke precursor.

This paper offers microscopic evidence to support the formation of at least two distinctly different coke structures during thermal hydrocracking of bitumen. These cokes will be shown to form independently of each other and to correspond to specific fractions of the bitumen.

Experimental

Athabasca bitumen used in these studies was supplied by Great Canadian Oil Sands of Fort McMurray Alberta. Deasphalting of the heavy oil product obtained from thermal hydrocracking of the bitumen was carried out according to the ASTM method (forty volumes of pentane to one volume of oil (4)). The deasphalted heavy oil was subsequently distilled under vacuum (40 mm Hg) at 260°C.

Carbonization of asphaltenes and deasphalted heavy oils was carried out under a controlled rate of heating. The sample was placed in a horizontal quartz tube (15 mm dia. 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.

Carbonization experiments involving deasphalted heavy oils with addition of sulphur were carried out in a vertical tube furnace. The mixture of DHO and sulphur was poured into a platinum crucible and inserted in the furnace at 400°C. The temperature in the furnace was then gradually raised to 550°C at 10°C/min. This procedure was adopted to minimize loss of sulphur during heating.

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

Typical examples of the structure of the coke formed during thermal hydrocracking of Athabasca

bitumen are shown in Figures 1 and 2. This coke was collected from the outer surface of the thermocouple sheath in the reactor subsequent to a 21-day run carried out at 460°C and 13.89 MPa (5). Two distinctly different coke structures are discernable in these photographs; a grain mosaic type and a flow type. The presence of spherical agglomerates of a grain type coke within the matrix of the flow type coke is observed in Figure 2.

In order to identify the origin of these cokes, asphaltenes and deasphalted heavy oils (DHO) from hydrocracked Athabasca bitumen were individually carbonized under conditions described in the Experimental section. The residue from carbonization of the vacuum distillation bottoms of the deasphalted heavy oils showed a characteristic flow-type anisotropic coke structure (6), Figure 3. On the other hand, carbonization of the asphaltenes at 350°C resulted in a fine-medium grain-mosaic coke structure, Figure 4. On further heating to 450°C a gradual transition to a coarse grain mosaic structure occurred, Figure 5. 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.

Based on these findings, it is evident from Figure 1 that the formation of "asphaltene-coke" on the thermocouple wall preceded the deposition of coke formed from the heavy oil. This observation is consistent with the fact that the asphaltenes polymerize more readily than the oil fractions, and tend to precipitate out of the bitumen first because of the increase in molecular weight.

In a recent publication (7) it was reported that laminar stacking of asphaltenes occurred on inert particles present in the feed stock (e.g., coal) within the liquid phase of the reactor. It is possible that these spherical agglomerates are incorporated into the matrix of the coke formed on the surface of the thermocouple sheath as shown in Figure 2.

To explain the differences in coke structure resulting from carbonization 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 (8,9) and may therefore alter the flow-type coke structure obtained from carbonization of the heavy aromatic oils.

Various quantities of sulphur were mixed with the DHO and the mixtures heated with stirring for several minutes to ensure proper homogeneity. The mixtures were then carbonized under conditions described in the Experimental section. The resulting coke structures are shown in Figures 6-9 for 5%, 7.5%, 10.2% and 20.5% sulphur, respectively. A progression from flow-type (Figure 6) to coarse-grain (Figures 7 and 8) and finally to fine-grain (Figure 9)

was apparent with increasing sulphur content in the DHO. The presence of sulphur would appear to have therefore induced cross-linkage in the heavy oil fraction during carbonization.

The addition of sulphur to samples of asphalt-
enes and subsequent carbonization at about 500°C re-
sulted in a fine grain mosaic-coke structure, Figure
10. Comparing this micrograph with Figure 3 suggests
that the presence of sulphur increased the extent of
cross-linkage in the "asphaltene-coke".

The implication of these findings is that the
difference in structure between the "asphaltene-coke"
and "heavy oil-coke" arises primarily from the extent
of cross-linkage between molecules during the carbon-
ization stage. It seems likely from the results re-
ported that the asphaltenes contain certain function-
al groups and aromatic structures which result in
cross-linkages during carbonization, whereas the
heavy oils contain fewer such groups.

Speight (10) investigated the oxygen functional
groups in bitumen by infrared spectroscopy and con-
cluded that the majority of the oxygen in the asphalt-
ene fraction existed as hydroxyl groups (mainly phen-
olic), while the majority of the oxygen within the
heavy oils occurred as carbonyl groups (primarily as
esters (11)). The pyrolysis of phenolic compounds
has been shown to induce cross-linkage (12-14). Car-
bonyl functional groups may, on the other hand, tend
to split off as carbon monoxide or carbon dioxide
under hydrocracking conditions, thereby leaving a
free radical that is quickly stabilized by reaction
with hydrogen before a cross-link can be formed.

Conclusions

The differences in the coking properties of the
asphaltenes and the heavy aromatic oils of hydrocrack-
ed 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 carbon-
ization. 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.

References

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FIGURE 1 - Coke collected from the thermal hydrocracker; A-grain-mosaic; B-flow-type

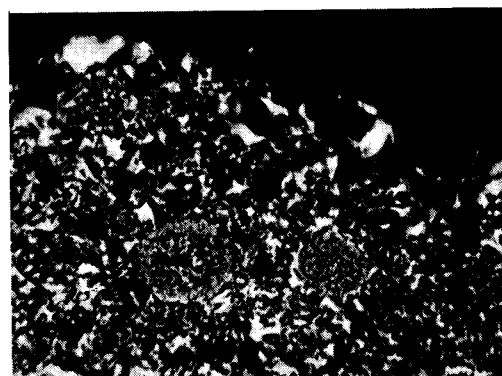


FIGURE 2 - Same as Figure 1; continuation of upper part (B) of previous figure

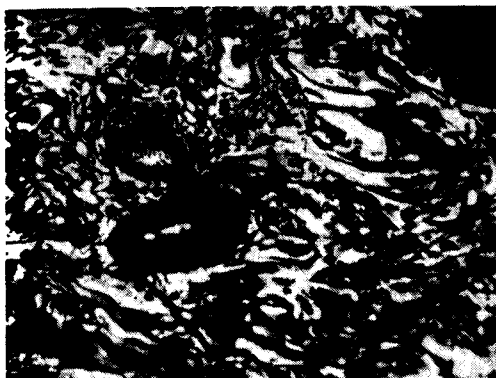


FIGURE 3 - Coke formed from DHO carbonized at 500°C

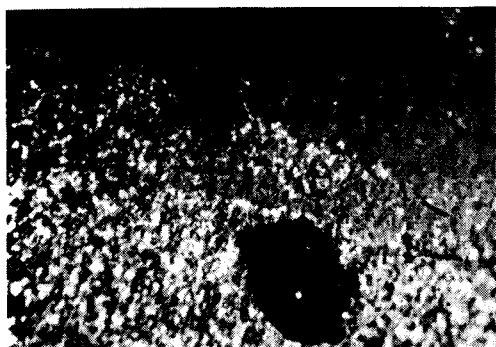


FIGURE 4 - Initial stages of coke formation from asphaltenes at 350°C; upper part-fine grain; lower part-medium grain

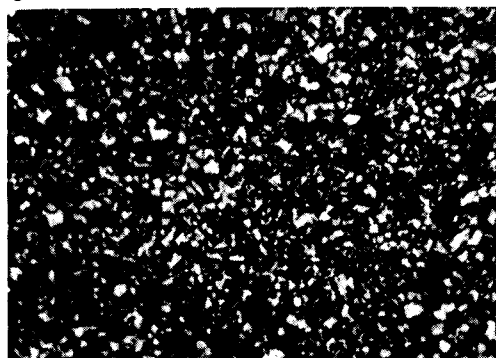


FIGURE 5 - Coke formed from asphaltenes carbonized at 450°C; coarse-grain

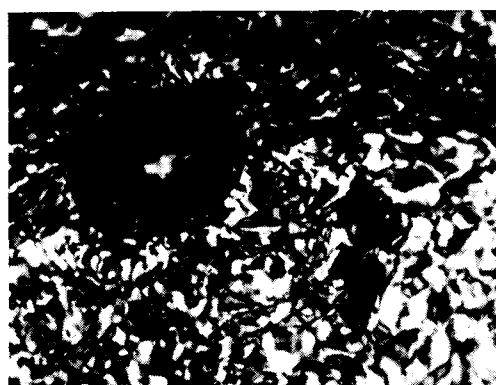


FIGURE 6 - Coke formed from DHO and 5.0% sulphur

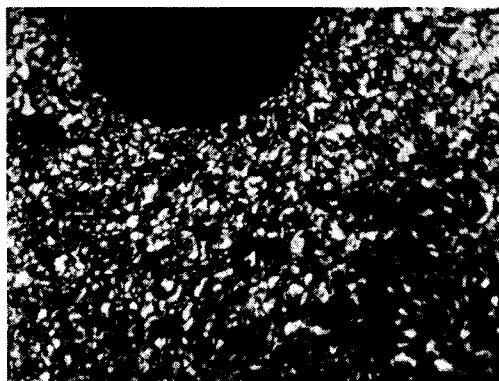


FIGURE 7 - Coke formed from DHO and 7.5% sulphur

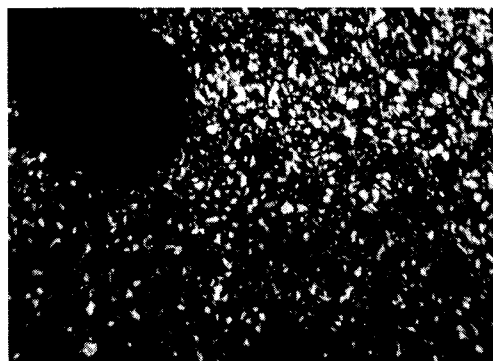


FIGURE 8 - Coke formed from DHO and 10.2% sulphur

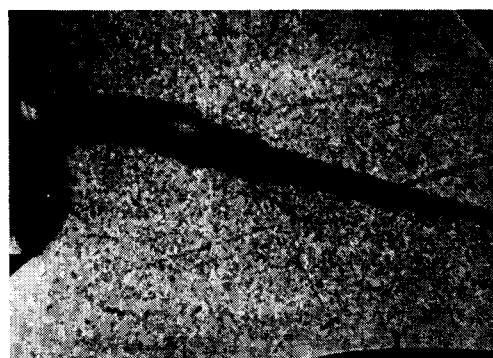


FIGURE 9 - Coke formed from DHO and 20.5% sulphur



FIGURE 10 - Coke formed from asphaltenes at 5% sulphur; fine-grain structure