

## Effect of Heat Treatment on Properties of Asphaltenes from Bitumen

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### Introduction

Bitumens are recovered from tar sands by different methods depending on the accessibility of the tar sand deposits. A relatively high temperature steam stimulation process (in the 300°C range) is being used for the in situ recovery of bitumen at a depth below 300 m. One of the major components in bitumen is asphaltene and the importance of characterizing asphaltenes in the processing of heavy feedstocks has been widely recognized.

In particular, the tendency of asphaltenes to produce carbonaceous residues during processing has been investigated in some detail (1, 2). The method of recovery of a feedstock prior to processing, and most important, its thermal history plays a great role in determining the type of asphaltenes that may be present in a given feedstock.

This paper examines the asphaltenes from samples of Cold Lake bitumen that have been recovered by both steam stimulation (around 300°C) and cold-bailed techniques. Both of these bitumens were subjected to hydrocracking in a batch autoclave and the resulting asphaltenes separated and compared. The object of this work was to examine, from the limited perspective of asphaltenes, the differences between cold-bailed and steam-stimulated bitumens under hydroprocessing conditions.

### Experimental

Samples of cold-bailed and steam-stimulated Cold Lake bitumen were provided by Dr. D.S. Montgomery, Program Director, Hydrocarbon Research Centre, Chemistry Department, University of Alberta, Edmonton.

Asphaltenes were obtained from as received and hydro treated bitumen samples by exhaustive extraction with pentane followed by extraction with toluene and removal of solvent.

#### a) Hydrogenation of Bitumen

A 0.1 L stainless steel batch reactor mounted on a shaking mechanism at 45° angle to the axis of the motion was used. The re-

actor was charged with approximately 20 g of feed. It was pressurized with hydrogen to 13.8 MPa (2000 psi) then heated at a rate of 3°C/min to the desired temperature and held for 2 h. The reactor was allowed to cool to room temperature prior to workup.

#### b) FTIR Spectra

The FTIR spectra were obtained using a Bruker IFS110 Infra red Fourier spectrometer interfaced with an EG&G Princeton Applied Research Model 6003/6005 photoacoustic sample cell and amplifier system. The samples (250 µm particle size) were dried at 100°C under vacuum immediately prior to measurement.

#### c) <sup>13</sup>C nmr Spectra

<sup>13</sup>C nmr spectra were obtained for the solid asphaltenes using a Bruker CXP 180/90 spectrometer with cross-polarization and magic angle spinning. The cross polarization time was 1 ms. In the dipolar dephasing experiments a delay of 40 µs was used.

#### d) Microscopic Studies

The microscopic examination of the asphaltene coke was carried out by means of a Leitz reflected light microscope at a magnification of X600.

### Results and Discussion

An elemental analysis of the four asphaltenes considered here are shown in Table I. It is evident that the asphaltenes from the original steam-stimulated and cold-bailed

Table I

Elemental Analysis of Asphaltenes (wt %)

	C	H	O	N	H/C
CL-SS	80.32	7.64	1.66	1.10	1.13
CL-SS-H	82.34	5.75	1.69	1.79	0.83
CL-CB	80.05	8.30	1.48	0.93	1.24
CL-CB-H	81.24	5.82	1.68	1.76	0.85

CL=Cold Lake; SS=Steam Stimulated;  
H=Hydrotreated; CB=Cold Bailed. Asphaltene content of all bitumen samples 11±.5%.

bitumens are quite different: the latter contain more hydrogen and have a higher H/C atomic ratio. The analytical results for the asphaltenes from the hydrotreated bitumens are remarkably similar.

The FTIR spectra of both original asphaltenes (CL-CB and CL-SS) are given in Figure 1 along with the difference spectrum. The cold-bailed material exhibits stronger aliphatic C-H (ca. 3000  $\text{cm}^{-1}$ ) absorption and weaker aromatic C-H absorption than the corresponding asphaltene from the steam-stimulated bitumen. This is presumably a result of processing conditions. The FTIR spectra of the asphaltenes from the two hydrotreated bitumens are essentially identical; the difference spectra show no variation.

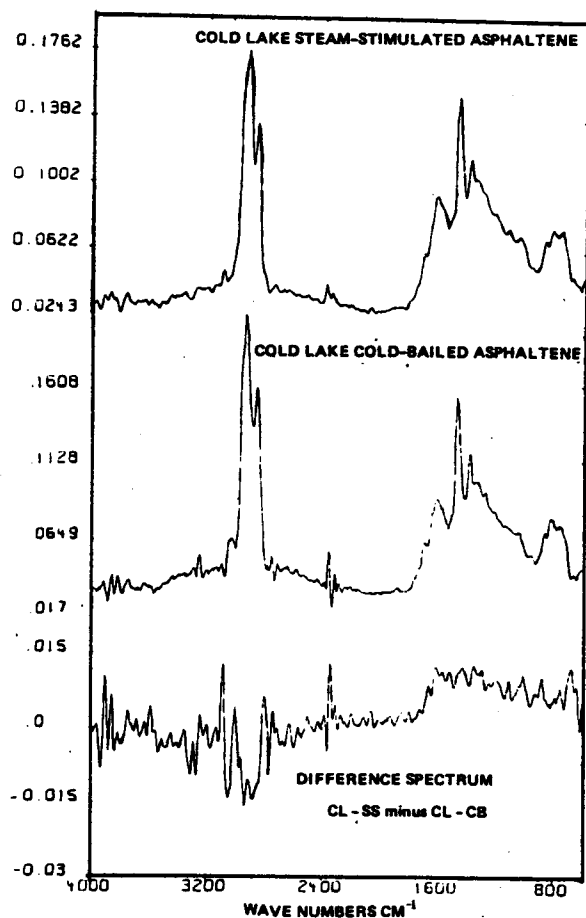


Fig.1 FT-IR spectra of original asphaltenes.

Solid state  $^{13}\text{C}$  nmr spectra with cross polarization and magic-angle spinning were obtained for all four asphaltenes ( $f_a$  values, CL-SS = 41.6%; CL-SS-H = 61.0%; CL-CB = 39.2%; CL-CB-H = 61.7%). On the basis of the aromaticity values alone the cold-bailed and steam-stimulated asphaltenes are quite similar, the cold-bailed asphaltene being slightly less aromatic (2). The dipolar dephasing results, however, show that the ratio of non-protonated to protonated aromatic carbons is higher (3.2) for the cold-bailed asphaltene than for the steam-stimulated asphaltene, (1.6) indicating

important structural differences. After hydrotreatment the asphaltenes from both bitumens were considerably more aromatic than the asphaltenes from the original bitumens, as was anticipated due to loss of alkyl groups. However, the dipolar dephasing results show no detectable differences between the asphaltenes from the hydrotreated bitumens.

#### Microscopic Evaluation

Coke samples were prepared for microscopic examination by heating the asphaltenes in the RUHR dilatometer up to 550°C with a constant heating rate of 3°C/min. The samples were mounted in epoxy resin, polished and examined under a reflected light Leitz microscope.

Cold-bailed asphaltene: Coke from cold bailed asphaltene shows fine mosaic structure (Figure 2) indicating low aromaticity and high aliphatic side chains consistent with nmr results. On hydrogenation, the structure in Figure 3 shows coarse mosaic to coalescence of small spheres probably owing to the removal of alkyl groups.

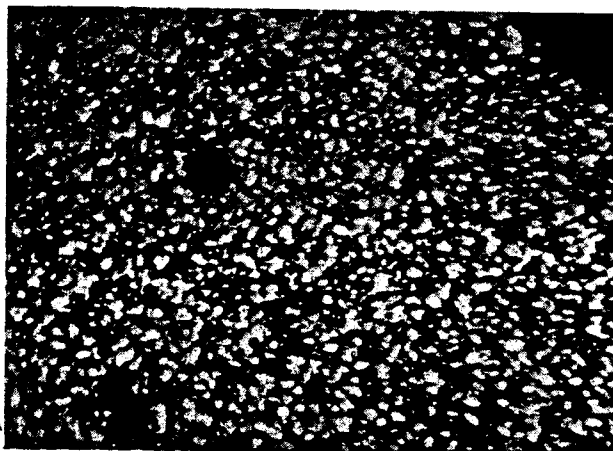


Fig.2 Fine mosaic structure of cold bailed asphaltene (CL-CB).

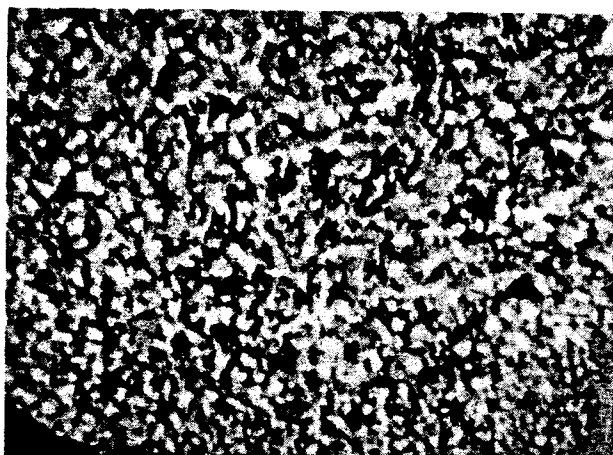


Fig.3 Coarse mosaic to coalesced spheres of hydrogenated cold lake asphaltene (CL-CB-H).

Steam stimulated asphaltenes: Asphaltenes from Cold Lake bitumen obtained from steam stimulation process are chemically different from cold-bailed asphaltenes. The coarse mosaic structure of semi-coke in Figure 4 indicates that the asphaltenes possibly may have lost alkyl groups due to heat treatment. On hydrogenation, the coalesced mosaic sphere in Figure 5 confirms the higher aromaticity and further loss of aliphatic side chains.

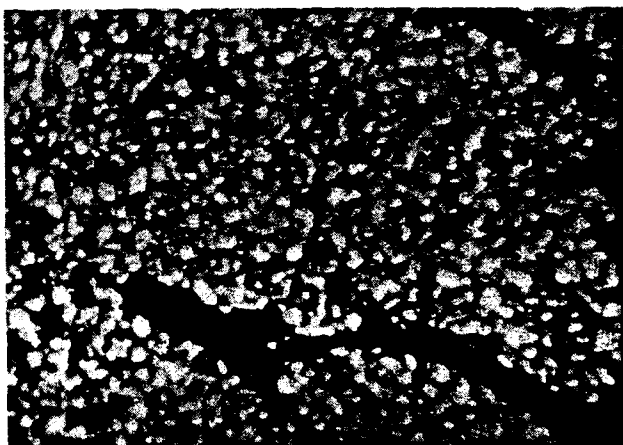


Fig.4 Coarse mosaic structure of asphaltene from steam-stimulated bitumen (CL-SS).

#### Observations and Conclusions

1. The chemical and microscopic coke structures of the asphaltenes from cold-bailed and steam-stimulation bitumens are quite different due to different processing conditions.
2. The asphaltenes from the hydrotreated cold-bailed and steam-stimulated bitumens appear to be quite similar on

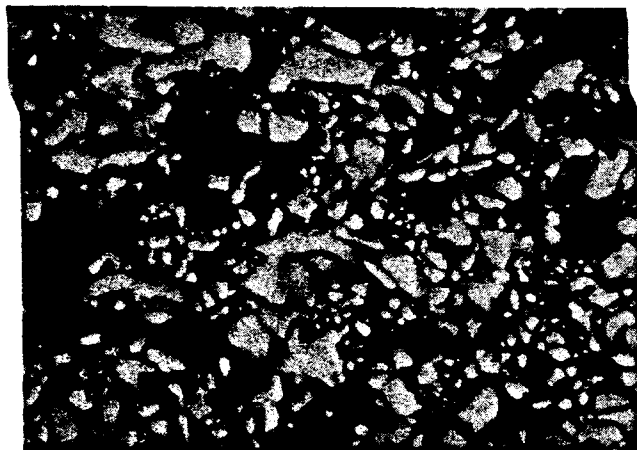


Fig.5 Coalesced mosaic spheres of asphaltene from hydrogenated steam-stimulated bitumen (CL-SS-H).

the basis of chemical and spectroscopic evidence. However, microscopic examination of the corresponding cokes reveals unexpected and important differences (3).

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