



Energy, Mines and
Resources Canada

Énergie, Mines et
Ressources Canada

CANMET

Canada Centre
for Mineral
and Energy
Technology

Centre canadien
de la technologie
des minéraux
et de l'énergie

CHARACTERIZATION OF ATHABASCA BITUMEN FRACTION
DERIVED BY GEL PERMEATION CHROMATOGRAPHY

P.J. Champagne and E. Furimsky

May 1981

ENERGY RESEARCH PROGRAM

ENERGY RESEARCH LABORATORIES

ERP/ERL 81-38(J)

ERP/ERL 81-38(J)
0.2

01-0003582 0.2

INTRODUCTION

Athabasca bitumen has been the subject of numerous investigations, attention, usually focussing on the structure and chemical composition. Effects of various technological parameters on the changes occurring in the bitumen have been of great interest as well.

Separation of bitumen into a number of fractions is always the first step in these studies. Subsequently, the fractions are characterized by chemical and spectroscopic techniques. In most published works the separations are based on different solubilities of bitumen fractions in various solvents. Combinations of solubility effects, and different affinities of the bitumen constituents to certain solid supports, are also used frequently.

In the present work the bitumen fractionation was performed by gel permeation chromatography (GPC), which separates molecules on the basis of their molecular size. The technique is generally applied to the determination of molecular weight distribution. Because the GPC column material is inert, the technique should be indifferent to various polar groups containing S, N and O heteroatoms and to various species containing transition metals. Structure and chemical composition of fractions investigated in the present work will be different than those obtained by some other separation methods, for example, the one used by Speight (1). The outlined approach therefore, provides additional information on the properties of the Athabasca bitumen.

EXPERIMENTAL

The sample of the Athabasca bitumen was obtained from Suncor Ltd. of Fort McMurray, Alberta. The properties of the bitumen are listed in Table 1.

GPC separations were carried out on a Waters Association ALCGPC 244 instrument equipped with refractive index and dual channel UV detectors and four μ - styrogel columns, 10^4 , 10^3 , 500 and 100A°. Detailed description of the procedure applied and separation conditions are published elsewhere (2).

Average molecular weight (AMW) determinations of the fractions were performed by vapor pressure osmometry technique using the Model 301A instru-

ment manufactured by Mechrolab Inc.

Tetrahydrofuran (THF), product of Burdick & Jackson Laboratories, used as received, was the solvent used for the GPC separations as well as the AMW determinations.

Carbon, hydrogen and nitrogen analyses were performed on the CHN 240 Perkin Elmer analyzer and sulphur analyses on the Leco Sulphur analyzer.

Metals were analyzed on the Jarrell-Ash Model 850 AA spectrophotometer. A low temperature wet ashing procedure was applied in sample preparations for this analysis.

NMR analyses were performed on a Varian CFT-20 pulse Fourier transform spectrometer. For the ^1H NMR evaluations CDCl_3 was used as a solvent and internal lock. In the ^{13}C NMR analysis, chromium (tris) acetylacetonate was added to the sample to give a concentration of 0.08 to 0.15M in the final solution, and CDCl_3 was used as solvent and internal lock as well as secondary reference compound. NMR procedures applied in the present study were described in detail by Ozubko and co-workers (3).

Gas chromatography-mass spectroscopy (GC/MS) evaluations were performed on the GC/MS Finnigan 4000 instrument with INCOS data system attached. The samples were injected onto a 1.83 m column packed with 3% dexil 300 on acid washed chromosorb W and a temperature programmed from 40-300°C at 10°C/min.

RESULTS AND DISCUSSIONS

Yields of the fractions and their important characteristics are summarized in Table 2. Because fractions 13 to 16 account for more than 70% of the characterized bitumen, the bitumen properties depend considerably on their composition. High H/C ratios combined with low contents of heteroatoms suggest that these fractions contain the main portion of hydrogen donating components; this was confirmed during the bitumen and coal liquefaction studies (4).

Trends which follow from the H/C ratios are in line with the NMR results, i.e., content of aromatic carbon (C_{AR}) and aromatic hydrogen (H_{AR}) are low for the low ratios. The lowest aromaticity was observed for fractions 14 and 15 which account for more than 40% of the bitumen. The aromaticity then increases towards both the high and low AMW fractions.

The accuracy of the NMR results was affected by transition metals the presence of which in fractions resulted in a broadening of the peaks. These effects were most visible during the ^1H NMR evaluations. Further, because of the limited amounts of fractions available, the ^{13}C NMR analysis could be performed only on the four fractions. The NMR results therefore reflect trends in chemical composition of the fractions rather than exact carbon and hydrogen distribution.

Considering the size of fractions and arrangements of the GC/MS system used in the present study, only qualitative information could be obtained on fractions 18 and 19. Thus, the presence of polynuclear structures with molecular weights ranging between anthracene and benzophenanthrene, benzofluoranthene, chrysene, pyrene, perylene or their alkylated species were major components. Methyl appears to be the main substituent in the rings. Partially hydrogenated rings were also detected with dihydro-saturation being predominant. No definite evidence on the presence of saturates was found, suggesting that in these fractions a substantial portion of non-aromatic carbon and hydrogen is associated with alkyl substituents and partially hydrogenated part of rings.

From the fraction 15 to 18, H_{AR} content increases markedly while AMW changes slightly, suggesting a decrease in the extent of ring hydrogenation or ring alkylation. These effects can be better illustrated on the tentatively chosen example of model compounds such as 9, 10-dihydroanthracene and anthracene. These two compounds have very similar molecular weights but markedly different H_{AR} contents. Similarly, removing two methyl groups from a molecule such as, for example, 9, 10-dihyrodimethyl anthracene will result in a noticeable increase of the H_{AR} content. The presence of these compounds was confirmed by the GC/MS analysis. The marked increase of the AMW from fractions 14 to 11 indicates an increasing content of asphaltene molecules in the fractions. On the basis of the outlined trends, the highest hydrogen donating capabilities may be assigned to the bitumen molecules having molecular weight of about 500. This conclusion is supported by the small numbers of S and N atoms per molecule in this range of the AMW.

Distribution of V and Ni in fractions 10 to 16 are shown in Table 3. Analysis of Fe was also performed but the results were too inconsistent to draw any conclusion. Limited amounts of samples prevented the evaluations of the lighter fractions. The results show that the metal contents increase

with increasing AMW. Fractions 10 and 11 which account for about 10 wt % of the bitumen contain more than 30% of all V and almost 40% of all Ni contained in the bitumen. Fractions of metals on total amount of metals contained in the bitumen do not change from fraction to fraction. This results from higher yields of lighter fractions which compensate for decreasing metal contents.

Fractions 10, 11 and 12 together, account for 16.9 wt %, while the pentane insolubles for 15.9 wt % of the bitumen. The metal contents in the insolubles is, however, noticeably larger than in the three fractions together. This suggests, that the solubility of metal containing species in pentane is lower than that of other hydrocarbon molecules. In other words, organometallic components of smaller size (or AMW) than those in the first three fractions are included in the insolubles. At the same time, the pentane soluble portion of the bitumen may include non-metal containing molecules of larger size than those in fraction 13 and up. This is an example of differences between fractions derived from the bitumen by different methods of separation.

According to Constantides and Arich (5) the V concentration should show more pronounced increase towards the highest AMW fraction than does the Ni. Separation of asphaltenes, for example, should result in the removal of a substantial portion of V. Present results do not support this view as both Ni and V seem to follow the same concentration trends. In addition, the amount of Ni removed from the bitumen via separation of pentane insolubles was larger than that of V, contrary to the views of the authors.

Contents of metals and N in fractions 15 to 10 show similar incremental increases. In particular six fold increases in V and N content is interesting. This is an indication of some form of association between N and metals. Structures containing the transition metals, usually identified in materials such as bitumen, are those of porphyrine type. It is believed that the 4/1 ratios of N/metals is maintained also in N and the metals containing structures other than porphyrines (6). Despite this the amount of N necessary to account for all metals, Fe included, is at the most 25% of total N. This suggests that also in the heaviest fractions of the bitumen a substantial portion of N is in other than organometallic structures, most likely in a heterocyclic form.

REFERENCES

1. Speight, J.G. Fuel, 49, 1, 76; (1970).
2. Champagne, P.J., Ternan, M. and Manolakis, E. Manuscript in preparation.
3. Ozubko, R., Clugston, D.M. and Furimsky, E. Anal Chem; 53, 183; (1981).
4. Nandi, B.N., Ternan, M., Parsons, B.I. and Montgomery, D.S. Fuel, 54, 197; (1975).
5. Constantinides, G. and Arich, G. Proceedings Sixth World Petroleum Congress; Sect. III, p 297; (1964).
6. Riediger, B. Int Chem Eng; 16, 2, 203; (1976).

Table 1 - Properties of Athabasca bitumen

Average mol. weight	1200
Pitch (+525°C), wt %	52.0
Carbon residue (Conradson), wt %	12.6
Insolubles, pentane, wt %	15.8
benzene, wt %	0.9
Carbon, total, wt %	83.0
aromatic, wt %	30.6
Hydrogen, total, wt %	10.5
aromatic, wt %	
Sulphur, wt %	4.7
Nitrogen, wt %	0.4
Oxygen, wt %	0.8
Vanadium, ppm	190
Nickel, pp,	70

Table 2 - Chemical composition of the fractions

Fraction No.	Yield wt %	AMW	C wt %	H wt %	H/C	C _{AR}	H _{AR}	H _{AR} /C _{AR}	S wt %	N wt %	No of S and N atoms per one molecule	
											S	N
10	4.5	6680	77.6	8.1	1.2	-	-	-	6.5	1.2	13.6	5.74
11	5.5	5470	76.6	8.5	1.3	-	6.8	-	6.3	1.0	10.8	4.06
12	6.9	1680	77.1	9.4	1.5	-	5.0	-	5.3	0.7	2.8	0.84
13	12.2	1420	80.4	10.4	1.6	28.7	5.5	2.3	-	0.6	-	0.56
14	19.4	710	81.7	11.0	1.6	22.1	3.4	1.9	3.7	0.3	0.8	0.16
15	23.1	500	82.6	11.2	1.6	20.9	3.8	2.2	3.0	0.2	0.5	0.07
16	16.8	370	83.2	10.7	1.5	28.7	7.1	3.0	3.7	0.3	0.4	0.08
17	7.8	370	79.0	8.9	1.4	-	11.5	-	6.3	0.4	0.7	0.11
18	3.0	280	72.7	8.3	1.4	-	17.9	-	-	0.5	-	0.09
19	0.5	270	71.3	7.7	1.3	-	17.9	-	-	0.6	-	0.11
20	0.3	250	72.3	8.2	1.4	-	-	-	-	0.6	-	0.11

* The amounts in per cent of total carbon and hydrogen, respectively

Table 3 - Distribution of vanadium and nickel in fractions

Fraction	V		Ni	
	ppm	wt % *	ppm	wt % '
Pentane insol.	820	69	340	78
10	621	15	292	19
11	543	16	256	20
12	346	13	184	17
13	191	12	91	16
14	125	12	55	15
15	100	12	32	10
16	76	7	-	-

*Weight per cent of total metal content in the bitumen