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CHARACTERIZATION OF VARIOUS BITUMEN SAMPLES FROM TAR SANDS

By

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ABSTRACT

We have investigated twenty three bitumen samples obtained using different separation methods such as: ultracentrifugation, Dean-Stark extraction, solvent extraction employing vigorous agitation, hot water separation and the Solvent Extraction Spherical Agglomeration technique. These samples were extracted from oil sand feedstocks of different grades, Suncor sludge pond tailings and mineral agglomerates obtained from the Solvent Extraction Spherical Agglomeration process. All of the bitumen samples were examined on a comparative basis using various analytical techniques. These included: fractionation into asphaltenes and maltenes; elemental analyses; molecular weight determination using vapour pressure osmometry and gel permeation chromatography, infrared, proton and ^{13}C nuclear magnetic resonance spectroscopy. Proton and ^{13}C n.m.r. spectroscopic data were used to determine the distribution of various types of hydrogens and carbons in the samples. These data were also used to derive various molecular parameters in order to investigate average molecular structures of different bitumen samples and some of their asphaltene fractions.

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INTRODUCTION

Bitumen is a complex mixture of a large number of organic molecules. The composition of bitumen and the nature of their various individual components has been the subject of considerable research during the past two decades, Ignasiak et al. (1977a, 1977b), Moscopedis et al. (1976a, 1976b), Selucky et al. (1977, 1978), Speight et al. (1970, 1971, 1980), Suzuki et al. (1982) and Yoshida et al. (1983). Various modes of extraction of bitumen from oil sands such as heat, extreme mechanical force, chemical agents and solvents could significantly affect some properties of bitumen, Vorndran et al. (1980), Wallace et al. (1984). Variations in the composition of the oil sands feed stock could also affect the properties of the extracted bitumen. However, the most commonly used analytical techniques such as elemental analyses, density and viscosity cannot detect small compositional differences in the various samples of bitumen.

With developments in instrumentation and techniques the structural characterization of complex petroleum fractions employing high resolution proton and ^{13}C nuclear magnetic resonance (NMR) spectroscopy is becoming more popular. Complex hydrocarbon mixtures are characterized using structural analysis schemes, in which the results of elemental analyses, number average molecular weight determinations and hydrogen and carbon distributions from proton and ^{13}C n.m.r. are combined to yield a set of average structural Parameters, Bartle et al. (1975, 1979), Brown et al. (1960), Cantor et al. (1978), Dickinson et al. (1980), Netzel et al. (1982), Qian et al. (1984), Yokoyama et al.

(1981) and Suzuki et al. (1982). The parameters describe structural features, such as the fraction of carbon that is aromatic, the number and length of alkyl substituents in an average molecule, the percentage of aromatic carbons that are substituted and the number of aromatic rings per molecule. Given sufficient data these parameters can provide useful characterization of a hydrocarbon mixture.

In our laboratories we have collected a number of bitumen samples obtained from different feedstocks employing a variety of extraction techniques. It was of interest to investigate any differences between these samples from different sources. This paper reports a detailed investigation of average structural parameters by the combined use of elemental analyses, molecular weight determinations and proton and ^{13}C n.m.r. spectroscopy. A total of twenty three bitumen samples have been studied.

EXPERIMENTAL METHODS

Materials. Table I lists brief descriptions of all bitumen samples investigated, including source and the method of extraction, Bulmer et al. (1979), Majid et al. (1984), Sparks et al. (1979), Wallace (1983) and Wallace et al. (1984). The asphaltene fractions of the bitumens were prepared in the usual manner by precipitation with n-pentane, Mitchell et al. (1973). The precipitates were washed with pentane and vacuum dried at 80°C . Evaporation of the n-pentane from the combined filtrate and washings gave the deasphalted oil (maltenes).

TABLE I

Bitumen Samples Description

Sample #	Sample Description
(1)	Bitumen recovered from medium grade oil sands (O.S.S.#1; Bitumen content $\approx 10\%$) by Ultracentrifugation, Wallace et al. (1984).
(2)	Suncor Coker Feed Bitumen used in a round robin study of bitumen analyses, Wallace (1983).
(3)	Primary production heavy oil from Husky's North Blackfoot field in the Lloydminster deposit.
(4)	Bitumen extracted from high grade oil sands (Bitumen content $\approx 15\%$) by modified Dean-Stark method using toluene, Cooley (1983).
(5)	Same as above except that the feed was a sample of medium grade oil sands (Bitumen content $\approx 12\%$).
(6)	Bitumen extracted from O.S.S.#1 by Dean-Stark method using toluene, Bulmer et al. (1979).
(7)	Same as in #5 except that the feed was a sample of low grade oil sands (Bitumen content $\approx 9\%$).
(8)	Bitumen extracted from low grade oil sands (Bitumen content $\approx 8\%$) by Dean-Stark method using toluene.
(9)	Bitumen extracted from O.S.S.#1 by Dean-Stark method using benzene-methanol (9:1).
(10)	Bitumen extracted from O.S.S.#1 by agitation with toluene on a Spex mixer, Majid et al. (1984).
(11)	As above except that extraction solvent was benzene-methanol (9:1).
(12)	Bitumen extracted from O.S.S.#1 by SESA* process using naphtha, Sparks et al. (1979).
(13)	Bitumen extracted from O.S.S.#1 in a Waring Blendor using cyclohexane.

TABLE I (Continued)

Sample #	Sample Description
(14)	Secondary extract from above in cyclohexane, Sparks et al. (1979).
(15)	Bitumen extracted in benzene from Suncor Sludge Pond Tailings.
(16)	Bitumen extracted in toluene using Dean-Stark method from sand agglomerates from experiment #12.
(17)	Bitumen extracted in toluene on a Spex mixer from sand agglomerates from sample #12.
(18)	Same as #17 except that the extraction solvent was benzene-methanol (9:1).
(19)	Same as #18 except that the extraction solvent was benzene.
(20)	Bitumen extracted from sand agglomerates from sample #14 by Dean-Stark method using toluene.
(21)	Bitumen extracted from sand agglomerates from sample #14 by agitation on a Spex mixer using toluene.
(22)	Same as #21 except that it was extracted in benzene.
(23)	Same as #20 except that it was extracted in benzene.
(24)	Bitumen extracted in toluene from aqueous tailings from EMR Solvent/Bitumen contactor.

* Solvent Extraction Spherical Agglomeration

Elemental Analyses. C, H and N analyses were performed using a Perkin Elmer model 240 CHN analyser. Sulfur was analysed as total sulfur using X-ray fluorescence spectroscopy. Oxygen was determined either by difference or directly, Culmo (1968). Asphaltene samples were also analysed using ASTM procedure D271 at

the Energy Mines and Resources laboratory. These results were comparable to those obtained from the Perkin Elmer model 240 CHN analyser. The nickel and vanadium content of the ashed bitumens were estimated, using quantitative Inductively Coupled Plasma Atomic Emission Spectroscopic methods (ICP-AES).

Ash Content. 5-10 g sample of bitumen was weighed accurately into a porcelain crucible. The crucible was placed over a low bunsen burner flame in order to burn off the low boiling point components of bitumen. This was followed by ashing in a muffle furnace at 400°C to constant weight.

Instrumental Analyses. Infrared spectra were recorded using a Perkin-Elmer model 683 i.r. spectrometer. Samples were run either as solutions in CCl_4 or as KBr pellets.

Proton n.m.r. measurements were performed on a Varian EM-360 n.m.r. spectrometer (60 MHz) in CDCl_3 . For quantitative ^{13}C n.m.r. spectra the method described by Shoolery and Budde (1976) was used. Spectra were recorded on a Bruker AM-400 NMR spectrometer. Samples were dissolved in deuteriochloroform to give approximately 10 wt% solutions; these were run in 5 mm diameter tubes. A paramagnetic relaxation agent, chromium acetylacetonate, $\text{Cr}(\text{acac})_3$, was added to the deuteriochloroform solution to give a 0.1 M solution. The FT ^{13}C n.m.r. spectrum was run using a two second delay between pulses, and the proton decoupler was gated off between pulses and on during data acquisition.

Number average molecular weights of whole bitumen samples were determined by vapour pressure osmometry in benzene at 40°C

using a Hitachi Perkin-Elmer model 115 molecular weight apparatus. Molecular weight of maltene fractions were obtained by gel permeation chromatography in tetrahydrofuran according to the procedure described elsewhere, Majid et al. (1984b).

RESULTS AND DISCUSSION

Molecular weights, ultimate analyses, and average molecular formulae. The weight percentages of the fractions, and the ultimate analyses of various bitumen samples and their asphaltene and maltene fractions are shown in Table II. Number average molecular weights and average molecular formulae of bitumen and its maltene fractions are also listed in this Table. A comparison of the asphaltene content of the various bitumen samples leads to the following observations:

1. Bitumen obtained by centrifugation had the highest asphaltene content.
2. The asphaltene content of the bitumen samples appears to be affected by the amount of mineral fines ($<44\ \mu\text{m}$ particles) in the oil sand feeds. Thus, the bitumen obtained from high grade oil sands (lowest fines content) had the highest asphaltene content. Similarly, bitumen obtained from one of the low grade ores (highest fines content) gave the lowest amount of asphaltenes. This supports our previous suggestion, Majid et al. (1982) that part of the asphaltenes are strongly adsorbed by the clay component of the oil sands, and are not removed by solvent extraction.

TABLE II

Molecular Weights, Ultimate Analyses, and Average Molecular Formulae of Bitumens and their Fractions

Samples	wt. %	M_n^a	Ultimate Analysis (wt. %) ^b						Average Molecular Formula
			C	H	N	S	O	Ash	
Bitumen #1	-	492	82.1	10.2	0.5	4.6	(0.2)	2.4	$C_{33.7}H_{50.2}N_{0.2}O_{0.1}S_{0.7}$
Asphaltenes	17.9	(412) ^d	69.6	6.9	1.2	8.60	3.4	(10.30)	$C_{28.7}H_{44.1}N_{0.09}O_{0.3}S_{0.5}$
Maltenes	82.1		83.7	10.7	0.3	4.1	(1.2)	0.0	
Bitumen #2	-	517 43	83.0	10.5	0.44	4.7	0.9	0.47	$C_{35.8}H_{54.3}N_{0.16}O_{0.3}S_{0.8}$
Asphaltenes	15.0	N.D. (433) ^d	78.6	7.8	1.2	7.8	2.2	(2.40)	$C_{30.5}H_{44.2}N_{0.1}O_{0.3}S_{0.5}$
Maltenes	85.0	479 0	84.5	10.2	0.3	3.9	(1.1)	0.0	
Bitumen #3	-	467 60	83.3	11.0	0.32	3.9	1.0	0.12	$C_{32.4}H_{51.4}N_{0.1}O_{0.3}S_{0.6}$
Asphaltenes	12.8 1	N.D.	81.5	8.0	1.1	8.0	1.7	(0.0)	—
Maltenes	87.2 1	-	-	-	-	-	-	-	
Bitumen #4	-	507 2	76.9	9.7	0.64	4.4	(7.26)	1.1	$C_{32.5}H_{49.2}N_{0.2}O_{0.2}S_{0.7}$
Asphaltenes	17.3	N.D.	74.4	7.4	1.0	8.7	2.80	(5.7)	$C_{30.9}H_{48}N_{0.16}O_{0.03}S_{0.5}$
Maltenes	82.7	(436) ^d	85.0	11.0	0.5	3.4	(0.1)	0.0	
Bitumen #5	-	561 4	79.7	9.9	0.43	4.9	(4.07)	1.0	$C_{37.3}H_{55.5}N_{0.1}O_{1.14}S_{0.9}$
Asphaltenes	15.1	N.D.	74.7	7.3	1.1	7.4	3.1	(6.4)	$C_{30.8}H_{47.8}N_{0.09}S_{0.4}$
Maltenes	84.9	(431) ^d	85.7	11.1	0.3	3.0	(0.0)	(0.0)	

Bitumen #6	-	659 19	79.1	9.8	0.60	4.6	(5.5)	0.4	$C_{43} \cdot 4H_{64} \cdot 6N_0 \cdot 3O_2 \cdot 3S_1 \cdot 0$
Asphaltenes	14.6	N.D (307) ^d	78.5	7.7	1.8	8.8	3.4	(0.0)	
Maltenes	85.4	464 11	84.1	11.1	0.3	4.1	0.4	(0.0)	$C_{21} \cdot 5H_{34} \cdot 1N_0 \cdot 07O_0 \cdot 08S_0 \cdot 4$
Bitumen #7	-	559 5	81.1	10.2	0.6	5.0	(1.8)	1.3	$C_{37} \cdot 8H_{57}N_0 \cdot 2O_0 \cdot 6S_0 \cdot 9$
Asphaltenes	13.4	N.D (414) ^d	72.2	7.2	1.0	8.6	3.5	(7.5)	
Maltenes	86.6		84.7	10.9	0.5	3.4	(0.5)	0.0	$C_{29} \cdot 2H_{45} \cdot 1N_0 \cdot 15O_0 \cdot 1S_0 \cdot 4$
Bitumen #8	-	534 1	80.4	10.5	1.0	6.7	(0.6)	0.8	$C_{35} \cdot 8H_{56}N_0 \cdot 4S_0 \cdot 2S_1 \cdot 1$
Asphaltenes	17.0	N.D (437) ^d	76.7	7.6	1.3	8.3	3.0	(3.1)	
Maltenes	83.0		84.2	11.4	0.4	3.8	(0.2)	0.0	$C_{30} \cdot 7H_{49} \cdot 8N_0 \cdot 1O_0 \cdot 05S_0 \cdot 5$
Bitumen #9	-	589 15	77.8	9.5	0.63	4.5	(7.4)	0.2	$C_{38} \cdot 2H_{56}N_0 \cdot 3O_2 \cdot 7S_0 \cdot 8$
Asphaltenes	14.2	N.D (388) ^d	77.3	7.1	1.3	8.4	5.8	(0.1)	
Maltenes	85.8		83.8	10.4	0.4	3.6	(1.8)	0.0	$C_{27} \cdot 1H_{40} \cdot 4N_0 \cdot 1O_0 \cdot 4S_0 \cdot 4$
Bitumen #10	-	647 20	78.7	9.7	0.5	4.7	(6.0)	0.4	$C_{42} \cdot 4H_{62} \cdot 8N_0 \cdot 2O_2 \cdot 4S_1 \cdot 0$
Asphaltenes	15.7	N.D (315) ^d	79.1	7.7	1.5	7.7	2.9	(1.9)	
Maltenes	84.3		84.2	11.2	0.3	3.7	(0.6)	0.0	$C_{22} \cdot 1H_{35} \cdot 3N_0 \cdot 07O_0 \cdot 1S_0 \cdot 4$

cont'd

TABLE II. (Continued)

Samples	wt. %	M_n^a	Ultimate Analyses (wt. %) ^b						Average Molecular Formula
			C	H	N	S	O	Ash	
Bitumen #11 Asphaltenes Maltenes	-	681 24	82.7	9.9	0.5	5.5	(1.25)	0.15	$C_{46.9}H_{67.4}N_{0.2}O_{0.5}S_{1.2}$
	15.9	N.D.	76.9	6.9	1.2	7.6	6.8	(0.6)	
	84.1	(395) ^d	83.4	10.9	0.4	4.1	(1.2)	0.0	$C_{27.5}H_{43.1}N_{0.1}O_{0.3}S_{0.5}$
Bitumen #12 Asphaltenes Maltenes	-	600 34	79.8	9.9	0.4	4.8	(4.65)	0.45	$C_{39.9}H_{59.4}N_{0.2}O_{1.7}S_{0.9}$
	15.5	N.D.	78.3	7.6	1.5	8.9	2.8	(0.90)	
	84.5	(326) ^d	82.2	11.0	0.3	4.1	(2.4)	0.0	$C_{22.3}H_{35.9}N_{0.07}O_{0.5}S_{0.4}$
Bitumen #13 Asphaltenes Maltenes	-	626 25	82.2	10.2	0.3	4.8	(2.3)	0.2	$C_{42.9}H_{62.6}N_{0.1}O_{0.9}S_{0.9}$
	16.1	N.D.	80.7	8.0	0.7	9.0	3.0	(0.0)	
	83.9	(410) ^d	84.6	11.0	0.2	3.9	(0.3)	0.0	$C_{34.3}H_{53.3}N_{0.07}O_{0.09}S_{0.6}$
Bitumen #14 Asphaltenes Maltenes	-	650 31	80.4	10.0	0.4	4.6	(4.35)	0.25	$C_{43.6}H_{65}N_{0.2}O_{1.8}S_{0.9}$
	14.9	N.D.	80.0	7.8	0.9	9.1	2.70	(0.0)	
	85.1	489 12	84.2	11.3	0.4	4.0	(0.1)	0.0	$C_{34.3}H_{56.3}N_{0.14}O_{0.03}S_{0.6}$
Bitumen #15 Asphaltenes Maltenes	-	404 6	83.8	10.0	0.35	4.4	(1.25)	0.2	$C_{28.2}H_{40.4}N_{0.1}O_{0.3}S_{0.6}$
	11.0	N.D.	75.5	6.6	1.0	7.4	7.9	(1.6)	
	89.0	(269) ^d	84.1	10.9	0.2	3.2	(1.6)	0.0	$C_{18.9}H_{29.3}N_{0.04}O_{0.13}S_{0.3}$

Bitumen #16 Asphaltenes Maltenes	-	454 12	79.9	9.9	0.5	5.6	(4.0)	0.1	$C_{30} \cdot 2H_{45}N_0 \cdot 2O_1 \cdot 1S_0 \cdot 8$
	6.2	N.D	78.4	7.8	0.8	8.6	3.6	(0.8)	
	93.8	(350) ^d 472 18	81.3	10.8	0.4	3.9	(3.6)	0.0	$C_{23} \cdot 7H_{37} \cdot 8N_0 \cdot 1O_0 \cdot 8S_0 \cdot 4$
Bitumen #17 Asphaltenes Maltenes	-	468 7	83.2	9.6	0.4	5.2	(1.3)	0.3	$C_{32} \cdot 4H_{44} \cdot 9N_0 \cdot 1O_0 \cdot 4S_0 \cdot 8$
	15.8	N.D	79.6	7.8	1.5	7.8	3.3	(0.0)	
	84.2	(393) ^d 425 17	82.5	11.0	0.3	4.2	2.0	0.0	$C_{27}H_{43} \cdot 2N_0 \cdot 08O_0 \cdot 5S_0 \cdot 5$
Bitumen #18 Asphaltenes Maltenes	-	480 10	82.7	10.2	0.5	4.3	(2.2)	0.1	$C_{33} \cdot 1H_{49}N_0 \cdot 17O_0 \cdot 65S_0 \cdot 65$
	11.5	N.D	76.6	7.0	1.2	8.1	6.2	(0.9)	
	88.5	(269) ^d	82.8	10.5	0.4	4.0	(2.3)	0.0	$C_{18} \cdot 6H_{28} \cdot 3N_0 \cdot 08O_0 \cdot 4S_0 \cdot 3$
Bitumen #19 Asphaltenes Maltenes	-	502 2	80.7	9.8	0.3	4.7	(4.5)	0.25	$C_{33} \cdot 8H_{49} \cdot 2N_0 \cdot 1O_1 \cdot 4S_0 \cdot 7$
	15.8	N.D	78.7	7.7	1.2	7.7	3.2	(1.5)	
	84.2	(391) ^d	82.8	10.1	0.2	4.0	(2.9)	0.0	$C_{27}H_{39} \cdot 5N_0 \cdot 06O_0 \cdot 7S_0 \cdot 5$
Bitumen #20 Asphaltenes Maltenes	-	517 13	83.7	10.3	0.4	4.7	(0.8)	0.1	$C_{36} \cdot 1H_{53} \cdot 3N_0 \cdot 15O_0 \cdot 3S_0 \cdot 8$
	6.7	N.D	79.8	7.6	0.9	8.9	3.2	(0.0)	
	93.3	(344) ^d	84.3	10.5	0.3	4.2	(0.7)	0.0	$C_{24} \cdot 2H_{36} \cdot 1N_0 \cdot 07O_0 \cdot 15S_0 \cdot 45$

(Cont..)

TABLE II. (Continued)

Samples	wt. %	M_n^a	Ultimate Analyses (wt. %) ^b						Average Molecular Formula
			C	H	N	S	O	Ash	
Bitumen #21	-	583 16	78.8	9.7	0.7	4.9	(5.45)	0.45	$C_{38} \cdot 3H_{56} \cdot 6N_0 \cdot 3O_2 \cdot 0S_0 \cdot 9$
Asphaltenes	16.0	N.D.	77.6	7.8	1.2	7.8	3.3	(2.3)	
Maltenes	84.0	(408) ^d	83.5	11.0	0.6	4.6	0.3	(0.0)	
Bitumen #22	-	463 8	82.9	10.0	0.4	4.8	(1.8)	0.1	$C_{32}H_{46} \cdot 3N_0 \cdot 1O_0 \cdot 5S_0 \cdot 7$
Asphaltenes	7.0	N.D.	79.5	7.8	1.0	7.4	3.4	(0.9)	
Maltenes	93.0	(337) ^d	84.3	11.0	0.4	3.9	0.4	0.0	
Bitumen #23	-	522 5	78.0	9.6	0.6	4.4	(6.7)	0.7	$C_{33} \cdot 9H_{50} \cdot 1N_0 \cdot 2O_2 \cdot 2S_0 \cdot 7$
Asphaltenes	18.4	N.D.	78.0	7.9	1.2	7.7	3.4	(1.8)	
Maltenes	81.6	(387) ^d	83.6	10.9	0.5	4.3	(0.7)	0.0	

^a Number-average molecular weight determined by vapour pressure osmometry in benzene at 40°C^b (): by difference^c N.D.: Not determined^d Number-average molecular weight determined by gel permeation chromatography in THF

3. Bitumen obtained from a second sample of low grade ore (high fines content) had a high asphaltene content comparable to that of the bitumen obtained from a high grade ore. This second sample of low grade ore was unique in that it was amenable to hot water extraction, Hamilton (1985). The mineral composition of the ores appears to be more important in determining the quality of the ore than the actual fines content. It is obvious from these results that the asphaltene content of various bitumen samples is dependent on the absorptive capacity of the mineral constituents of the oil sand feed.
4. Bitumen extracted from Suncor sludge Pond tailings has a lower asphaltene content than the bitumen obtained from oil sand feeds (11% vs 13.4 - 17.3%). This could be due to the adsorption of the asphaltenes to the clay minerals present in the sludge pond tailings.
5. Asphaltene content of the bitumen samples; extracted from mineral agglomerates, is dependent on the mode of extraction of bitumen. Bitumen extracted using the Dean-Stark method, Bulmer et al. (1979) has substantially lower asphaltene content compared with the samples extracted using a Spex mixer (6.2 - 7.0% vs 11.5 - 18.4%). This can be explained on the basis of the entrapment of high molecular weight asphaltenes inside the pores of compact mineral agglomerates. Diffusion of the high molecular weight asphaltenes through the small pores of mineral agglomerates will be more difficult than the low molecular weight components of bitumen. On the Spex mixer, agglomerates are constantly being

broken and reformed because of the vigorous agitation. This resulted in the release of all bitumen components thus explaining the higher asphaltene content of this bitumen compared with the bitumen extracted using Dean-Stark method.

6. Asphaltene content of the bitumen extracted from sand agglomerates on the Spex mixer using benzene-methanol (4:1) is low compared to bitumen from the same sample but extracted with toluene or benzene. This is difficult to explain particularly in view of the fact that no significant solvent effect was noted when the bitumen was extracted from the oil sand feed.

Number average molecular weights of various bitumen samples were determined in benzene using vapour pressure osmometry. There was a considerable variation in the data for various bitumen samples. The bitumen extracted from Suncor sludge pond tailings had the lowest molecular weight. This might be due to the fractionation of bitumen by clay minerals present in the sludge. It is probable that the higher molecular weight components of bitumen are strongly associated with the clay component of tailings either by adsorption or by clay organic interactions, Majid et al. (1986).

Bitumen samples extracted from sand agglomerates have relatively lower molecular weights than the samples extracted directly from bituminous feed-stocks. Again this can be explained on the basis of entrapment of high molecular weight components of bitumen inside the pores of sand agglomerates.

The Bitumen sample prepared using centrifugation had a considerably lower molecular weight compared with the solvent

extracted samples in spite of the fact that it had the highest asphaltenes content. Bitumen samples prepared using centrifugation are known to have a greater proportion of low boiling components, Wallace et al. (1984). It is possible that the greater proportion of low boiling components offsets the higher asphaltenes content thus accounting for lower molecular weight.

Molecular weights of maltenes were not as meaningful as those for bitumen for the following reasons:

- (1) These molecular weights were determined using a gel permeation chromatographic method which has been shown to give different results to vapour pressure osmometry, Philip et al (1982), Bartle et al. (1984).
- (2) The molecular weights were determined in THF, which has been shown to give anomalous results with bitumen and maltenes, Majid et al. (1984b).
- (3) Complete removal of the last traces of solvent from bitumen and maltenes is very difficult. However, the effect of residual solvent will be more pronounced for the low molecular weight maltenes compared with bitumen.

The H/C ratios for the different samples were of almost the same magnitude: 1.48 ± 0.04 for bitumen, 1.17 ± 0.04 for asphaltenes and 1.55 ± 0.05 for maltenes.

Trace metal analyses of crude oils usually leads to information of geochemical significance, Abu-Elgheit et al. (1980). The V/Ni index in particular has been extensively studied

in relation to oil maturation, Hodgson (1954), Ball et al. (1960), oil migration, Al-Shakristani et al. (1972), or depth and age of reservoir rocks, Katchenkov (1977). There is substantial variation in the nickel and vanadium content of the various bitumen samples. The bitumen sample extracted from Suncor sludge pond tailings had the lowest concentration of both nickel and vanadium. This suggests that the nickel and vanadium containing components of bitumen in the sludge, have become strongly associated with the clay components and cannot be easily extracted.

Bitumen obtained using cyclohexane in a blender has the highest nickel and vanadium content. This is consistent with our previous findings, Majid et al. (1985). In that investigation it was demonstrated that heavy metals can be concentrated in a blender due to an effect similar to flotation.

Although the absolute concentration values for vanadium and nickel show considerable variations, the V/Ni index is fairly uniform (3.6 ± 0.3). This suggests that the V/Ni index is independent of any compositional differences. The uniformity of the index suggests that vanadium and nickel might have been incorporated during the genesis of bitumen. The uniformity of the V/Ni index also suggests that all bitumen samples are genetically related, that is they are all of the same origin. The V/Ni concentration ratios of various bitumen samples suggests that these are middle cretaceous oils.

Figures 1 and 2 illustrate the correlation between the asphaltene content of various bitumen samples and their vanadium

Figure 1. Correlation between Vanadium and Asphaltene Content of Bitumens.

and nickel content. Except for a few cases there is a fairly good correlation between the asphaltene content and the metal content of various bitumen samples. This suggests that in most cases Ni and V complexes are associated with the asphaltene fraction of the bitumen. Since the petroleum asphaltenes are known to have the capacity to complex heavy metals, Erdman et al. (1963), it is probable that at least a part of vanadium and nickel are associated with the asphaltenes.

Figure 2. Correlation between Nickel and Asphaltene Content of Bitumens.

The V/Ni index for the Loyminster heavy oil suggests that it is a lot more mature oil than the oil sand bitumen.

Infrared spectra. Because of the difficulty of removing the last traces of solvent from bitumen and its maltene fractions the differences in the infrared spectra of these samples were difficult to interpret. The infrared spectra of various asphaltene samples were remarkably similar resembling the typical infrared spectra for petroleum asphaltenes.

Figure 3. Typical Proton n.m.r. spectra of (a) Bitumen, (b) Asphaltenes, (c) Maltenes.

Interpretation of N.M.R. Spectra. Figure 3 and 4 illustrate typical proton and ^{13}C n.m.r. spectra for bitumen and its asphaltene and maltene fractions. All spectra were essentially similar. Proton n.m.r. spectrum of asphaltenes consists of two broad resonances. The strongest band, centered around 1.0 ppm, is due to various types of methyl and methylene hydrogens; and the

Figure 4. Typical ^{13}C n.m.r. spectra of (a) Bitumen, (b) Asphaltenes, (c) Maltenes.

weak band centered at 7.0 ppm results from aromatic hydrogens. Bitumen and maltene samples show proton n.m.r. spectra with at least 4 well defined regions. Two sharp peaks at 1.3 and 0.9 ppm correspond to the saturated alkyl and naphthenic hydrogens, and γ and further methyl hydrogens, respectively. A broad band centered

around 7.0 ppm represent aromatic hydrogens and a broad region extending from 2 to 3.5 ppm is due to the hydrogens attached to the α carbon bonded to aromatic rings.

^{13}C n.m.r. spectra of all samples had a sharp peak around 29 ppm which indicates the presence of interior methylene groups, $-(\text{CH}_2)-$, of long straight-chain side chains. Other peaks such as those at 14, 22 and 32 ppm are all characteristic of long alkyl side chains, Takegami (1980). A peak at 19 ppm may be assigned to branched methyl groups in long alkyl substituents. The region between 37 and 50 ppm has a number of peaks in addition to a broad envelop. This region contains resonances from bridgehead and other CH naphthenic carbons, some methylene bridge carbon (between site, where one has no adjacent ring or group), alkyl CH, other than in isoalkyl groups, and alkyl CH_2 adjacent to alkyl CH, Ladmer et al. (1978). Precise assignments in this region are difficult, but it appears that most of the above groups could be present.

Carbon and Hydrogen Distribution from N.M.R. Data. Carbon and hydrogen distributions in the bitumen and some of its asphaltene fractions were calculated from the integrated areas of various regions as shown in Table III. Considering the accuracy of nmr measurements, there was not much variation in the data for the distribution of carbon and hydrogens in bitumen and asphaltenes. Ca, the ratio of aromatic carbon to total carbon (carbon aromaticity) for different samples were of almost the same magnitude: 0.24 ± 0.02 for bitumen and 0.39 ± 0.03 for

TABLE III

Assignments of Proton and Carbon-13 n.m.r. Spectra

Proton: Symbol	Definition	Chemical Shift Range (PPM from TMS)
H_a	Aromatic protons	6.00 to 9.00
H_α	Hydrogen in saturated groups α to aromatic rings	2.00 to 4.00
H_β	Hydrogen in saturated groups β to aromatic rings	1.00 to 2.00
H_γ	γ -CH ₃ to aromatic ring and straight-chain or branch alkane methyl hydrogens	0.50 to 1.00
<u>C-13</u>		
C_a	Aromatic carbon atoms	100.00 to 150.00
C_{al}	Saturated carbon atoms	0.00 to 70.00

asphaltenes. This suggests that $\frac{1}{4}$ of the total carbons in bitumen and $\frac{2}{5}$ of the total carbons in asphaltenes are in aromatic locations. Data for the distribution of various types of hydrogens suggests that H_β , the saturated alkyl and naphthenic hydrogens and H_γ the γ and further methyl hydrogens together constitute about 80% of the total hydrogens. Aromatic hydrogens constitute only 6.4% of the total hydrogens. However, the proportion of aromatic hydrogens in asphaltenes is greater than in bitumens (9.3% vs 6.4%). This is consistent with the higher carbon aromaticity of asphaltenes compared with bitumens. The ratio of H_α to total hydrogens in asphaltenes is also considerably higher than in bitumens (0.27 ± 0.015 vs 0.14 ± 0.014). Subsequently, the proportion of H_β and H_γ hydrogens is lower in asphaltenes than in bitumens (0.798 ± 0.016 vs 0.639 ± 0.016).

The Average Molecular Structural Parameters. Average molecular structural parameters of various bitumen samples and some of its asphaltene fractions were calculated using data obtained from the integration of the areas of the various carbons and hydrogen regions in the respective n.m.r. spectra. The equations used to calculate average molecular parameters were similar to those used by Knight (1967), Dickinson (1980), Takegami et al (1980), Suzuki et al. (1982) and Seshadri et al. (1982). Heteroatoms, such as sulfur, oxygen and nitrogen were neglected in the calculations in order to simplify the average structures. The absolute accuracy of calculated average molecular parameters is probably not high. However, these differences were small, and consequently it was deduced that the various samples bear a close resemblance to each other in terms of their chemical nature.

CONCLUSIONS

- 1) In a previous publication we demonstrated that the bitumen extraction efficiency of the Clark hot water process depends mainly on the mineral fines (<44 μm particles) content of the bituminous feedstock, Majid et al. (1982). However, the data in this report suggests that the composition of the mineral fines also plays a significant role in determining the efficiency of extraction of a process.
- 2) There appears to be a correlation between the asphaltene content of bitumens and the grade of the bituminous feedstock.
- 3) High molecular weight asphaltenes are entrapped in the pores of mineral agglomerates and are not easily removed, using simple solvent extraction such as the Dean-Stark method.

- 4) Clay minerals fractionate bitumen. High molecular weight components of bitumen appear to be associated with clay minerals either by adsorption or by clay-organic interactions.
- 5) V/Ni index for various bitumen samples is fairly uniform suggesting that it is independent of any compositional differences. The uniformity of V/Ni index suggests that all bitumen samples are genetically related. The value of the V/Ni index is characteristic of middle cretaceous oils.
- 6) Average molecular parameters calculated from proton and ^{13}C n.m.r. spectroscopic data do not differ significantly for different bitumen samples.
- 7) An average bitumen molecule appears to contain 1.5 to 2 aromatic rings and 4-5 naphthenic rings with 4-5 alkyl substituents of chain length ranging from 6-7 carbon atoms.

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