

Structural analysis of Athabasca maltenes fractions using distortionless enhancement by polarization transfer (DEPT) related ^{13}C n.m.r. sequences⁺

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A combination of inverse-gated heteronuclear decoupling and DEPT (including DEPT-quaternary) pulse sequences has been utilized for the assignment of the different types of carbons and for the determination of their relative importance in different molecular weight (MW) fractions separated from Athabasca maltenes by gel permeation chromatography (g.p.c.). The results obtained permit the g.p.c. fractions to be divided into two classes: MW <800 ('oils') and MW >800 ('resins'). The lowest molecular weight fraction (MW = 315) had a quaternary and tertiary aromatic carbon content of more than 35%. Cyclic methylene and methine were also abundant and represented nearly 30% of the total carbon. The remaining carbons were methyls and short chain alkyls (the long chain alkyl carbon content was very low). With an increase in MW to 800 the aromatic carbon concentration decreased rapidly whereas the amount of carbon in saturated rings increased substantially. There was also a concomitant decrease in methyl carbon and an increase in long chain alkyl carbon content. In the case of Athabasca maltene g.p.c. fractions with MW greater than 800 the changes in structural parameters were slight. These results demonstrate that conventional ^{13}C n.m.r., in combination with DEPT-related sequences, is a convenient tool for characterization of the bitumen constituents. Such knowledge is essential for the conversion of bitumen into synthetic crude oil and other products.

(Keywords: carbon-13 n.m.r.; gel permeation chromatography; maltenes)

The dependence of the world oil supply upon Middle East reserves has encouraged the search for alternative sources of crude oil. More specifically, in Canada this has led to the development of processes to extract bitumen from oil sands and to convert the bitumen into synthetic crude oil. To characterize bitumen a preliminary separation into pentane insoluble asphaltenes and pentane soluble maltenes is often performed. Asphaltenes have been extensively analysed using various physico-chemical approaches¹⁻⁷ whereas investigations of maltene chemical compositions are mainly based on solvent solubility and on a different affinity to various solid supports^{1,2,8-12}. In previous work^{13,14}, Athabasca maltenes (pentane soluble portion of bitumen) were fractionated into different molecular weight fractions using gel permeation chromatography (g.p.c.) techniques. These g.p.c. fractions were characterized using analytical methods such as diffuse reflectance infrared spectrometry¹³, absorption spectrometry in the visible region, and conventional high resolution ^1H and ^{13}C n.m.r.¹⁴. The n.m.r. technique plays an important role in the characterization of petroleum in terms of structural group composition^{7,15-19}. Unfortunately, the information provided by conventional n.m.r. is rather limited. To elucidate more fully the nature of the different molecular weight Athabasca maltene fractions, the DEPT (distortionless enhancement by polarization transfer) n.m.r. pulse

sequence²⁰ was applied in this study. This method permits identification of the different types of CH_n ($n = 1-3$) multiplicities in ^{13}C n.m.r. spectra and allows a quantitative estimation of their relative distribution. In recent years the DEPT technique has been successfully applied to qualitative as well as quantitative analysis of the carbon types in complex mixtures such as coal derived oil and petroleum fractions²¹⁻²³. Since the DEPT pulse sequence, relying on polarization transfer by proton bearing carbon, does not provide the subspectra of quaternary carbon, a quaternary-only sequence (QUAT) was used for editing this type of carbon^{24,25}. The possibility of a quantitative application of the QUAT sequence applied in conjunction with the DEPT sequence for the evaluation of carbon types in complex fuel mixtures has recently been demonstrated by Netzel²³.

EXPERIMENTAL

The medium grade oil sand sample (bitumen content 9.9%) used in this work was obtained from the Suncor quarry in Fort McMurray, Alberta, Canada. Extraction and separation were performed using the Soxhlet extraction-Dean and Stark method with toluene as the solvent²⁶. The solvent was removed first at 90°C in a rotary evaporator under reduced pressure and finally in a sample concentrator at 100°C under nitrogen.

Asphaltenes were separated by a standardized

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Table 1 Conditions for preparative and analytical g.p.c. separations

	Preparative	Analytical
Pump	P.E. Series 3B	P.E. Series 3B
Solvent	Toluene (Anechemia)	Chloroform (Fisher)
Column	Waters Styragel 2.0 × 120 cm 500Å	Waters 1000, 500, 100Å Ultrastayragel Set
Flowrate	9.9 ml min ⁻¹	1 ml min ⁻¹
Temperature	22°C	40°C
Pressure	3 MPa	7 MPa
Sample loop volume	5 ml	0.2 ml
Sample loading	0.2 g (2 ml injected)	0.2 mg (5 ml injected)
Valve description	Rheodyne 7125	P.E. ISS100 Autosampler
Detector(s)	Waters R401 R.I.	P.E. LC 25 R.I.
Interface	P.E. Chromatography	Nelson Analytical 900
Computer	Model 3600 P.E.	IBM AT Compatible
Software	P.E. Chromato- graphics 2	Nelson Analytical 2600 & 2900

procedure which involved dissolution of the sample in an equal volume of benzene followed by subsequent dilution of the solution with ≈ 40 volumes of n-pentane²⁷. Maltenes were then obtained by evaporation of the filtrate.

An elemental analysis (C, H, N) was performed, and sulphur was analysed by a titrimetric oxygen flask combustion method, using a Schöniger type combustion apparatus²⁸. Preparative g.p.c. separation of the maltenes was performed under the conditions described in Table 1. All samples and the mobile phase were first filtered through 0.45 μ m membrane filters. Ten g.p.c. effluent fractions were collected on a time basis (1.5 min per sample) and evaporated in vacuo at 100°C in a sample concentrator. Analytical g.p.c. separation (Table 1) was also performed.

Number average molecular weights were determined by a vapour pressure osmometry (VPO) method. The determinations were carried out in toluene at four or five concentrations (C). The apparent molecular weights were calculated for each concentration and the results were plotted against C. The extrapolation to zero concentration gave the actual number average molecular weight (MW).

¹³C n.m.r. spectra were obtained at 75.5 MHz on a spectrometer equipped with computer in a 10 mm probe and were recorded in a solution of CDCl₃ at room temperature. General parameters for the maltene fractions were: sweepwidth 20 kHz; FT data points 16 K; line broadening 2 Hz. Using an IGATED (inverse gated heteronuclear decoupling) pulse sequence, 10 000–20 000 acquisitions were obtained with a pulse width of 45°. DEPT and QUAT sequences were run using the corresponding BRUKER microprograms with the following parameters: polarization transfer delay corresponding to $J = 140$ Hz; ¹H 90° decoupling pulse = 10 μ s; ¹³C 90° = 8.8 μ s. Relaxation delays were set to 5 s for DEPT and 15 s for QUAT experiments. Three sets of DEPT spectra corresponding to 60°, 90°, and 120° were generated. Editing of the CH_n subspectra was accomplished by the appropriate combination of these initial spectra²⁰. The number of scans (NS) for QUAT and DEPT (60° and 120°) was 8000. Twice as many NS were collected for DEPT (90°) to keep identical signal-to-noise ratios in each subspectrum. For IGATED and QUAT

experiments a small amount ($\approx 10\%$) of chromium acetyl acetonate was added to the solution to reduce the ¹³C T₁ relaxation time. To obtain completely quantitative carbon-type analyses using IGATED, DEPT and QUAT spectra, the equation proposed by Netzel²³ was used.

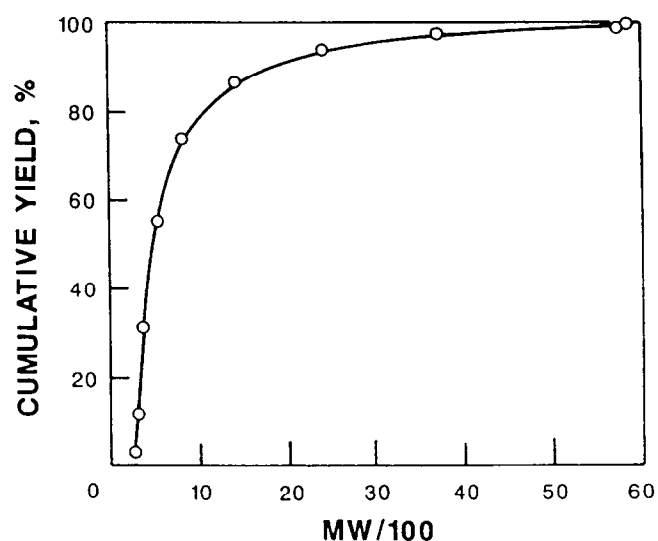
RESULTS

Yields and molecular weights

The molecular weight distributions of the maltene g.p.c. fractions are shown in Figure 1. The results are expressed as cumulative weight per cent, normalized for experimental losses, versus molecular weight. It can be seen that the MWs lie in a very broad range from 290 to 5830. About 55% of maltenes have MW lower than 600. These results are consistent with those reported previously for Athabasca bitumen²⁹.

Elemental analysis

The results of the elemental analysis of the g.p.c. fractions are given in Table 2. There was no definite trend in the distribution of sulphur and oxygen with respect to molecular weight, but these elements were more concentrated in certain fractions. The concentration of nitrogen does exhibit a trend with respect to MW and goes through a minimum at fraction 8. As the molecular weight of the fractions decreases, the H/C ratio goes

**Figure 1** Cumulative yield of g.p.c. maltenes fractions**Table 2** Elemental analysis of g.p.c. fractions

G.p.c. fraction no.	Elemental analysis (wt%)					H/C ratio
	C	H	N	S	O(diff)	
1	79.8	9.7	0.74	5.3	4.5	1.45
2	79.0	10.0	0.65	5.1	5.2	1.52
3	79.7	10.1	0.50	4.9	4.8	1.52
4	78.1	10.0	0.44	5.1	6.4	1.54
5	79.9	10.4	0.34	5.4	4.0	1.56
6	80.5	10.5	0.31	5.8	2.9	1.56
7	80.1	10.6	0.26	5.7	3.3	1.59
8	81.0	10.6	0.14	5.0	3.3	1.57
9	81.2	9.2	0.38	6.1	3.1	1.36
10	86.6	9.6	0.72	2.2	0.9	1.33

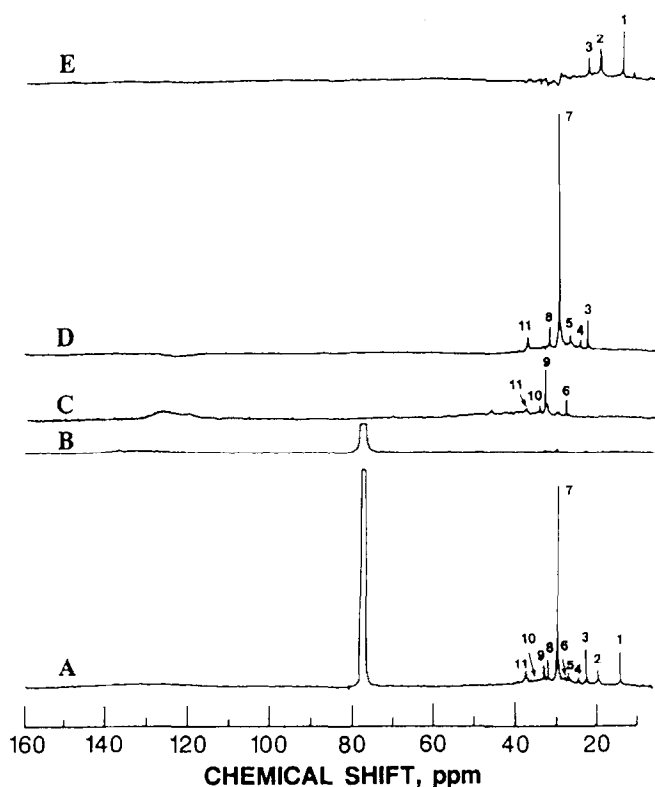


Figure 2 ^{13}C n.m.r. spectra of fraction 4, separated from Athabasca maltenes by g.p.c. A, IGATED; B, QUAT; C, DEPT CH; D, DEPT CH_2 ; E, DEPT CH_3

through a maximum value of 1.59 corresponding to fraction 7.

^{13}C n.m.r.

Maltene g.p.c. fractions 4–9 with molecular weights from 2385 to 315 were analysed using a combination of IGATED, DEPT and QUAT pulse sequences. Typical spectra obtained are shown in Figure 2 (results for fraction 4). The degree of suppression of the unwanted lines for each subspectrum is reasonably good, except for some spectral artefacts with a dispersion mode as can be seen in spectra B, C and E. Their presence can be attributed to several factors, such as inexact calibration of the ^1H 90° pulse length and the inhomogeneity of the RF fields²². The chemical shifts of the aliphatic peaks (numbered 1 to 11) in the spectra presented in Figure 2 and the corresponding structural assignments^{30–32} are listed in Table 3. The CH_3 resonances (Figure 2E) are displayed between 10 and 23 ppm. The chemical shifts in the 10–17 ppm range mainly include resonances from CH_3 in $\geq \text{C}_2$ alkyls. The major CH_3 peak (1) at 14.1 ppm is due to terminal CH_3 in straight chain alkyl groups of $\geq \text{C}_3$ alkyl chains. The area from 17 to 23 ppm is characteristic of methyls attached to aromatic or hydroaromatic rings. This range of chemical shifts also includes characteristic iso-alkyl peaks at 19.7 ppm (2) and 22.7 ppm (3). The latter resonance is overlapped by methylene signals in the normal (IGATED) spectrum. The CH_2 DEPT subspectrum (Figure 2D) demonstrates that the bulk of the 20–40 ppm range in the IGATED spectrum is due to CH_2 groups. It is also obvious that a wide variety of CH_2 environments exists in this range. Major peaks (3, 7, 8) are those at 22.7, 29.7 and 31.9 ppm, which are attributed to long chain alkyls. The CH_2 peaks

between 21 and 31 ppm are mainly due to unsubstituted (six-membered) hydroaromatic rings. Peaks at lower field than 31 ppm and the remainder of the 21–31 ppm band are due to alkyl substituted rings and to naphthenic rings in compounds such as 1–4, 4a, 9, 10, 10a-octahydrophenanthrene.

Aliphatic CH resonances (DEPT subspectrum, Figure 2C) occur mainly over the range 28–48 ppm due to alkyl-substituted rings and iso-alkyl groups. Most of these resonances are hidden by methylene resonances in the IGATED spectra. From 32 to 45 ppm the resonances of interior carbons are found which are at, or immediately adjacent to, a branching point. Branched centres near the end of a chain generally occur in the region around 28–30 ppm. Aromatic CH resonances are represented by a broad peak in the area from 110 to 130 ppm. The QUAT spectrum (Figure 2B) displays broad resonances for aromatic quaternary carbons (130–150 ppm region). This spectrum did not point to the presence of any detectable amount of aliphatic quaternary carbons.

The n.m.r. spectra obtained for each g.p.c. fraction by the IGATED, DEPT and QUAT sequences allowed the estimation of both the aromatic (C and CH) and aliphatic (CH_3 , CH_2 and CH) carbon contents per total carbon²³. The results obtained are shown in Table 4. It can be seen that both the aromatic CH and aromatic C concentrations apparently decrease with an increase in MW from 315 (fraction 9) to 800 (fraction 6). For higher MW fractions the aromatic C concentration increases slightly with increasing MW, whereas the content of aromatic CH remains nearly constant. Proportions of aliphatic CH_2 and CH tend to increase, whereas the CH_3 concentration tends to decrease with increasing MW.

Knowledge of the concentrations of C, CH, CH_2 and CH_3 groups allows further structural characterization of the maltene g.p.c. fractions. Subdivision of the aliphatic groups needed for this type of analysis³³ as well as the results of structural analysis are shown in Table 5. Although several assumptions have been made, most of these parameters were derived directly from the ^{13}C n.m.r. spectra. It can be seen that in the case of the lowest MW fraction (no. 9) 29% of total carbon is present in saturated (naphthenic/hydroaromatic) rings listed in Table 5 as $(\text{CH} + \text{CH}_2)$ cyclic. Cyclic methylenes (including ring-joining $\text{Ar}(\text{CH}_2)_n\text{Ar}$) and methines each account for 15% of the carbon atoms. The aromatic

Table 3 Aliphatic carbon types present in the Athabasca maltene g.p.c. fractions

Peak no.	Chemical shift (ppm)		Assignment
	Observed	Reported ³¹	
1	14.1	14.1–14.2	CH_3 in $\text{R}-\text{CH}_2-\text{CH}_2-\text{CH}_3$
2	19.7	19.8	CH_3 in $\text{R}-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{R}$
3	22.7	22.7–23.1	CH_2 in $\text{R}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{R}$
4	24.5	24.7	CH_2 in $\text{R}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{R}$
5	27.2	27.4	CH_2 in $\text{R}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{R}$
6	28.0	28.1	CH_2 in $\text{R}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{R}$
7	29.7	29.9–30.0	CH_2 in $\text{R}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{R}$
8	31.9	32.1–32.4	CH_2 in $\text{R}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{R}$
9	32.7	32.7	CH_2 in $\text{R}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{R}$
10	34.7	34.8	CH_2 in $\text{R}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{R}$
11	37.3	37.3	CH_2 in $\text{R}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{R}$
	37.4	37.7	CH_2 in $\text{R}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{R}$

* = Carbon responsible for n.m.r. signal
R = Alkyl group

carbon content (C + CH) of 36% (Table 4) is greater than the carbon content in saturated rings. The presence of a high proportion of mono-, di- and tri-aromatics could be responsible for the high carbon aromaticity and consequently the low H/C atomic ratios (Table 2) of this fraction. The aromatic rings are relatively highly protonated, as aromatic CH represent 55% of total aromatic carbon (Table 5). The naphthenic rings may be fused to 1–3 aromatic rings, and also present as a saturate class with 1–5 saturated rings^{8–10}. Main substituents on aromatic and saturated rings are methyls (7%) and short chain alkyls (α and β to rings, 15%). The percentage of long chain alkyls present in this fraction is very low (<3%).

With increasing MW there was an apparent change in the hydrocarbon structural parameters, with the most significant changes taking place in the range of molecular weights from 315 to 800. For example, the concentration of cyclic methylene and methine carbon in naphthenic/

hydroaromatic rings increases from 29% for fraction 9 (MW = 315) to 50% for fraction 6 (MW = 800). At the same time the aromatic carbon content decreases by more than a factor of 2 (Table 4). The decrease in the carbon aromaticity is accompanied by an increase in the atomic H/C ratios (Table 2). This fact, taking into account the work of Payzant *et al.*^{8–10}, suggests that a substantial proportion of the saturate class is concentrated in the fractions with MW around 800, thus reducing the concentration of aromatic carbon. This is not surprising, as any g.p.c. type separation by molecular weight causes a separation by chemical type, because the saturates, aromatic and polar classes of compounds all have different molecular weight distributions. Each molecular weight fraction therefore contains a different proportion of the various classes of compounds. As can be seen from Table 5 in the case of fractions 6–8, the aromatic rings are not as protonated and are therefore more highly substituted than the rings in fraction 9. It may also be seen from Table 5 that the degree of naphthenic ring substitution (cyclic CH/(cyclic CH₂ + CH)) decreases substantially with increasing MW. The concentration of carbon in long chain aliphatic substituents on aromatic and naphthenic rings increases from 3% to 12% while going from fraction 9 to 6, whereas the content of short aliphatic chain carbons decreases from 15% to 9%. There is also a trend for methyl carbon to decrease with an increase in MW.

For fractions with MW > 800 (no. 4 and no. 5) the changes in structural parameters are not as significant as they are for lower MW fractions. Carbon aromaticities of these samples (Table 4) change only slightly (from 14 to 18%) with an increase in MW from 800 (no. 6) to 2385 (no. 4). The concentration of carbon in saturated rings is almost the same in fractions 6 and 4. The contents of α -CH₃ and short chain CH₂ slowly decrease, while that of long aliphatic hydrocarbon chains further increases.

Table 4 Carbon type distribution for the maltene g.p.c. fractions (combined use of IGATED, DEPT and QUAT sequences)

Carbon type	C (% of total) for various g.p.c. fractions					
	4	5	6	7	8	9
Aliphatic						
CH	20.0	18.3	18.5	15.5	17.2	14.8
CH ₂	53.6	55.0	53.3	52.1	44.7	32.3
CH ₃	9.3	10.7	13.0	16.8	17.8	17.7
Aromatic						
CH	7.1	6.8	7.1	7.0	8.8	19.4
C	10.0	9.2	8.1	8.6	11.4	15.8
(C + CH) (direct determination by IGATED sequence)	18.0	16.7	14.1	18.0	20.0	35.5

The estimated errors for carbon type distribution are no more than $\pm 7\%$

Table 5 Average structural parameters

Carbon type	Definition	C (% of total) for various g.p.c. fractions					
		4	5	6	7	8	9
CH ₃							
α -Methyl	C ₁ ^a -isoalkyls ^b	3.3	3.4	4.9	6.0	7.3	6.8
\geq C ₂ Alkyls	from integral of 10–17.5 ppm region	4.0	4.8	5.0	7.9	8.0	8.3
CH ₂							
Long aliphatic chain (A)	from intensities of the peaks at 31.9, 29.7 and 22.7 ppm	15.1	14.7	11.8	7.8	5.7	2.9
Alkyl α and β to aromatic or naphthenic ring (B)	\geq C ₂ (CH ₃) \times K ^c	7.0	8.4	8.8	13.8	14.0	14.5
Cyclic (includes Ar(CH ₂) _n Ar)	CH ₂ ^d -A-B	31.5	31.9	32.7	30.5	25.0	14.9
CH							
Cyclic	CH ^d -isoalkyl ^e	18.5	16.4	17.2	13.9	16.7	14.5
(CH + CH ₂) cyclic		50.0	48.3	49.9	44.4	41.7	29.4
CH cyclic/(CH + CH ₂ cyclic)		0.37	0.34	0.34	0.31	0.40	0.49
Percentage aromatic CH of total aromatic carbon	based on the results in Table 4	41.5	42.5	46.7	44.9	43.6	54.7

^a α -Methyl + isoalkyl, from integral of 17.5–23.0 ppm region in DEPT

^b From intensities of the peaks at 19.7 and 22.7 ppm

^c K = 1.6–1.9³³

^d CH₂; CH total (see Table 4)

^e From the peaks at 37.3 and 32.7 ppm

CONCLUSIONS

As can be seen from the results obtained in this work, there is a break in the properties of g.p.c. fractions at a MW of around 800. These results are consistent with the results of i.r. and light absorbance measurements reported earlier^{13,14}. The separation of the maltenes into two classes at this particular MW would approximate the division of the maltenes into 'oils' and 'resins' on activated Fullers earth observed by Boyd and Montgomery². The combined yield for fractions 7–10 of 55 wt% of the maltenes is of the same order as the 51.8% oil yield obtained by Selucky using chromatography on silica gel³⁴. Also, the division of the maltenes into two fractions at a molecular weight of 800 simulates the division that would occur if the maltenes were subjected to deep vacuum distillation.

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