Analysis of Athabasca maltene GPC fractions by means of ^{13}C NMR techniques

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Introduction

Athabasca maltene fractions have been separated by gel permeation chromatography (**GPC**) according to their relative importance in molecular weight (**MW**).

In order to elucidate the nature of the different **MW** Athabasca maltene fractions for resource evaluation and to obtain conversion of bitumen into synthetic crude oil and other products, the application of the **DEPT** (1) and quaternary-only (**QUAT**) (2)(3) **NMR** pulse sequences have been applied to these **GPC** fractions.

Experimental

The oil sands sample was obtained from the Suncor quarry in Fort McMurray, Alberta, Canada. Separation and analyses were performed using the Soxhlet extraction techniques (Dean-Stark method) (4). Bitumen separation into asphaltene and maltene was based on solubility in n-pentane (5). Preparative **GPC** separation of maltenes gave different molecular weight (**MW**) fractions. Number average molecular weights were determined by the vapor pressure osmometry method.

NMR experiments were performed on Bruker MSL 300 spectrometer (75,5 MHz) in a 10 mm probe in solution in $CDCl_3$ at room temperature.

Editing of the CH_n subspectra was accomplished by the appropriate combination of the **DEPT** and **QUAT** experiments according to the methodology described by Bendall and Pegg (2).

IGATED (Inverse gated heteronuclear decoupling) and **QUAT** experiments were run with chromium acetyl acetonate (~10 %) in order to reduce ^{13}C T_1 relaxation time. Complete quantitative carbon-type analysis (based on **IGATED**, **DEPT** and **QUAT** spectra) was obtained using methodology proposed by Netzel (6).

Results

The molecular weight distributions of the maltene **GPC** fractions are shown in Table 1.

GPC fraction	Yield, % of maltene	Number average **MW**
1	0.6	5831
2	1.5	5735
3	3.8	3696
4	7.5	2385
5	13.1	1402
6	18.5	800
7	23.7	568
8	19.7	365
9	8.9	315
10	2.7	289

Table 1 : *The yields and Molecular Weights (**MW**) for Maltene **GPC** Fractions.*

It can be seen that the **MWs** lie in a very broad range spanning from 289 to 5831 and that about 55 % of maltenes have **MW** lower than 600.

Maltene **GPC** fractions **4** through **9** were analysed using combination of **IGATED**, **DEPT** and **QUAT** pulse sequences.

Typical spectra obtained are shown on Figure 1.

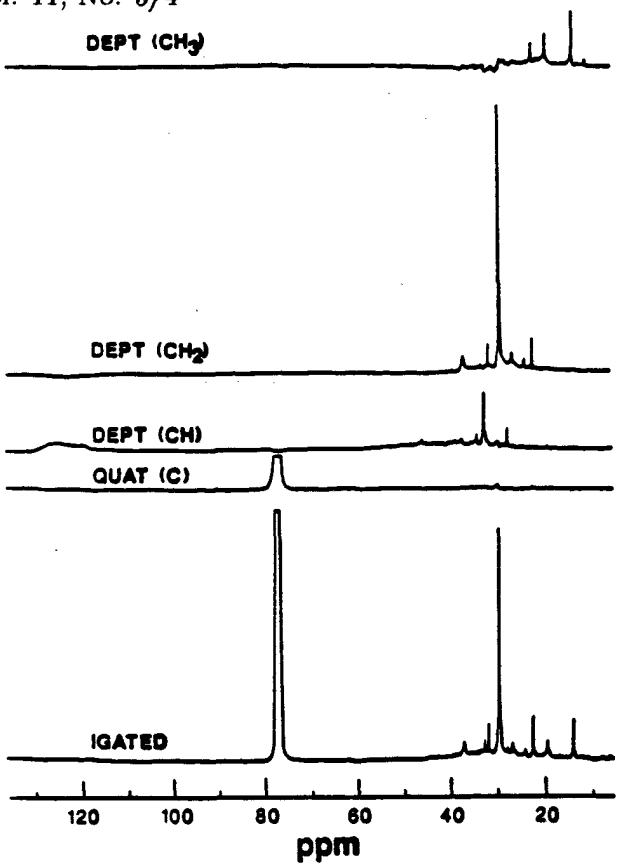

Figure 1 : *^{13}C NMR spectra of GPC fraction 4.*

Carbon type	C, % of total GPC fraction					
	4	5	6	7	8	9
CH_3						
α-methyl	3.3	3.4	4.9	6.0	7.3	6.8
≥ C_2 alkyls	4.0	4.8	5.0	7.9	8.0	8.3
CH_2						
long aliphatic chains	15.1	14.7	11.8	7.8	5.7	2.9
short chain alkyls	7.0	8.4	8.8	13.8	14.0	14.5
(CH+CH_2) cyclic	50.0	48.3	49.9	44.4	41.7	29.7
Aromatic carbon	18.0	16.7	14.1	18.0	20.0	35.5

Table 2 : *Average structural parameters*

From the table 2 it can be seen that :

- For the lowest **MW** fraction main substituents on aromatic and saturated rings are short chain alkyls and methyls.
- With increase in **MW** to 800 the concentration of carbon present in saturated rings increases while aromatic carbon content decreases.
- The concentration of carbon in long chain aliphatic substituents on the rings increases, whereas the content of short aliphatic chain carbons and methyls decreases.
- For fractions with **MW** above 800 changes in structural parameters are slight.

Figure 2 represents the carbon distribution versus the molecular weight.

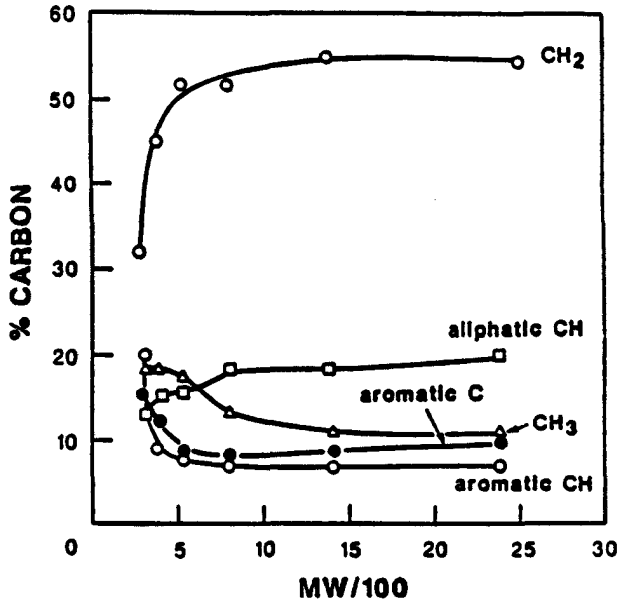

Figure 2 : *Carbon distribution vs molecular weight (MW)*

It can be seen from figure 2 that the aromatic carbon concentrations decrease with increase in **MW** from 315 to 800, and then changes are slight. At the same time proportion of aliphatic CH_2 and CH increase and CH_3 decrease with increase in **MW**.

Methylene carbon is the most abundant type of carbon for all fractions.

Conclusion

From the results obtained in this work it can be seen that there is a break in the properties of **GPC** fractions at a **MW** of around 800. These results are consistent with the results of **IR** and

light absorbance examination reported earlier (7)(8).

The separation of the maltenes into two classes at this **MW** would approximate the division of maltenes into "oils" and "resins" on activated Fullers earth by Montgomery and Boyd (9).

The division of the maltenes into two classes at **MW** of 800 would simulate the division that would occur if the maltenes were subjected to a deep vacuum distillation.

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