Hydrocarbon Groups and Their Relationships to Oil Properties and Behaviour

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ABSTRACT

This paper summarizes the results of hydrocarbon group analyses carried out primarily in the past year, by the Emergencies Science Division. Two new hydrocarbon group methods are described: 1) determination of saturates, aromatics, resins and asphaltenes (SARA) in crude oils, and 2) determination of wax content by GC/FID. Details are also given for a new method to measure the adhesion of oils. The relationships between the various hydrocarbon groups, and the effects on them of oil evaporation are shown graphically. Hydrocarbon groups are also correlated to physical properties (density, viscosity, and pour point) and to behavioural properties (adhesion, dispersibility, and emulsion formation).

INTRODUCTION

Oils can be fractionated into different hydrocarbon groups on the basis of solubility and adsorption characteristics. A common protocol consisting of a sequence of separations using dilute solutions in appropriate solvents and adsorption columns is known by the acronym SARA: saturates, aromatics, resins, asphaltenes. Many other fractionation methods exist, but it is beyond the scope of this paper to discuss them all. An excellent and detailed review of fractionation methods can be found in Speight (1991). In addition to the four groups mentioned above, two sub-groups are also of interest: waxes, a sub-group of the saturates, and BTEX+ (benzene, toluene, ethylbenzene, xylenes, plus C_3-substituted benzenes), a sub-group of the aromatics.

With the exception of BTEX+, all these group designations are indirect labels in terms of chemical composition. The saturates fraction is the most descriptive, because it contains only aliphatic compounds. The aromatics contain a variety of aromatic compounds with saturated groups attached. The resins are higher in heteroatom content and have a higher concentration of aromatic carbon. The asphaltenes are the highest molecular weight fraction and contain most of the polar compounds. The distinctions between aromatics and resins, and between resins and asphaltenes, are not clear. For all of these fractions, the definition of the separated material is a blend of chemistry and technique. Each group is defined mainly by the procedures followed in its isolation. For example, asphaltenes precipitated from n-pentane are not the same as asphaltenes precipitated from n-heptane. Waxes, may be defined either by the precipitation method used to obtain them, or as gas chromatography (with flame ionization detection)

(GC/FID) resolvable waxes. In spite of these vagaries, hydrocarbon group analysis can provide insight into the relationships between oil composition and physical properties, such as density, viscosity, and pour point, as well as behavioural properties, such as adhesion, chemical dispersibility, and emulsion formation.

METHODS

Saturates, Aromatics, Resins, and Asphaltenes

The determination of hydrocarbon groups in fresh crude oils is accomplished by using a combination of old and new methods. Asphaltenes are precipitated from n-pentane according to ASTM Standard Method D 2007. The deasphaltened oil, (maltenes), 0.4 gram to 0.5 gram, is placed on an open glass column (400 mm x 19 mm I.D. x 22 mm O.D., fritted, with stopcock) packed with 30 g silica and topped with 1.5 cm anhydrous sodium sulphate. The sample is eluted sequentially with 100 mL hexane, 100 mL hexane/benzene (1:1), 100 mL methanol, and 100 mL methylene chloride. The saturates are collected from the hexane, the aromatics from the hexane/benzene, and the resins are recovered from the combined methanol and methylene chloride fractions. Rotary evaporation is used to recover the bulk of the solvents, followed by nitrogen blow down. Each hydrocarbon group is weighed after solvent recovery is complete.

If the oil used has an initial boiling point (IBP) above 250 °C (determined by simulated distillation), a good mass balance can be obtained (>95%). However, most fresh crude oils will have an IBP well below 250 °C, and the loss of light ends during solvent recovery results in a poor mass balance. Fortunately, by making the reasonable assumptions that a) resin and asphaltene contents are not affected by evaporative losses, and b) the aromatic portion of the lost light ends can be equated to the BTEX+ content, it is possible to calculate the correct distribution of hydrocarbon groups.

BTEX+

A detailed description of the BTEX+ analysis can be found in Wang, Fingas, et al. (1995).

Waxes

Waxes were determined by two different methods. GC-resolvable waxes were calculated from GC/FID chromatograms obtained during simulated distillation (SIMDIS) analysis.

The SIMDIS analysis is performed with an AC Analytical Controls SIMDIS analyzer, comprised of a Hewlett Packard 5290 Series II gas chromatograph with an Analytical Controls Programmable Temperature Vaporizer (PTV) injector. The system uses a special high-temperature column which is aluminum-clad, fused silica, five metres long, 0.53 mm diameter, and has 0.09 μm phase thickness. The carrier gas used is helium at a flow rate of 19 mL/min. Samples are made up as 2% solutions (by weight) of whole crude oil in carbon disulphide (CS_2). Injection volume is 0.5 mL. The injector temperature program runs from 40 °C to 430 °C at 70 °C per minute. The oven temperature program runs from -20 °C to 430 °C at 10 °C per minute, with a three minute hold at 430 °C. Sub-ambient cooling is provided by liquid nitrogen. The flame ionization detector operates at 430 °C. The resolved $C_{18}+$ portion of the SIMDIS chromatogram was integrated and divided by the total (resolved + unresolved) area

under the chromatogram. This was multiplied by the oil recovery percentage as determined by the SIMDIS software.

Traditionally, waxes have been determined gravimetricly by precipitation and filtration from a six-fold dilution of deasphaltened oil and a 1:1 volume mixture of methyl ethyl ketone and dichloromethane at -32 °C. Because SIMDIS analyses were available for both fresh and evaporated oils, while gravimetric wax values were available only for fresh oils, GC-resolvable waxes were used for all hydrocarbon group correlations.

Density

All densities were measured with an Anton Paar digital density meter according to ASTM Standard Method D 5002 - *Density and Relative Density of Crude Oils by Digital Density Analyzer* (ASTM, 1993).

Viscosity

All viscosities were measured with a HAAKE RV20 Rotovisco concentric cylinder viscometer with M5 measuring system, SV1 and NV sensors, and HAAKE RC20 Rheocontroller, according to the protocol described by Jokuty, Fingas, and Whiticar (1994).

Pour Point

All pour points were measured in accordance with the modified version of ASTM Standard Method D 97 - *Standard Test Method for Pour Point of Petroleum* as described by Jokuty, Fingas, and Whiticar (1994).

Adhesion

A new method has been developed to determine the property of oil adhesion. For the purpose of this test, oil adhesion is defined as the mass of oil per unit area which will remain on a standard test surface, after "dunking and draining" for 30 minutes, under prescribed conditions. The standard procedure was developed using both fresh and evaporated oils with a wide range of viscosities. Test parameters that were evaluated included temperature, oil viscosity, time, and test-surface area.

In the early stages of development standard penetrometer cones were used to provide a standard surface. There were major problems with the initial procedure mainly caused by surface effects due to the size of the cone, and the long period of time required for most of the oil to drip off of the cone before a measurement was made. By changing to a standard penetrometer needle, which has a much smaller surface area, it was possible to increase reproducibility and show differences between oils with similar (ie. within a few hundred centipoise) viscosity values. Using a needle also greatly reduced the drip time required before a measurement could be made. As no major effects due to variations in temperature (±5 °C) were seen during the preliminary work, all subsequent testing using the needle was done at room temperature (18 to 26 °C).

Equipment
Eberbach reciprocating shaker
100 mL beaker (Pyrex #1000)

Standard penetrometer needle used for ASTM Standard Test Method D5, with eye-hook adaptor for hanging

Mettler AE260 analytical balance (using hook on bottom of balance)

Plexiglass draft shield with two sliding doors on side (32.5 cm high, 45 cm long, 22.5 cm wide)

Lab jack with a maximum height of 29 cm (15 cm x 15 cm)

Procedure

The oil sample is allowed to stand at room temperature for 1 hour. The sample bottle is then shaken for 30 minutes using the reciprocating shaker. The balance is prepared for measurement by hanging a penetrometer needle, for which the surface area of the stainless steel section has been calculated, from the balance hook and allowing the weight to stabilize. The weight of the clean needle is recorded. Approximately 80 mL of oil is poured into a 100 mL beaker. The beaker is elevated, using the lab jack, until the top of the stainless steel needle meets the top of the oil. Care must be taken to avoid having the oil creep up onto the brass section of the needle, as the surface area calculation is based only on the stainless steel portion. The needle is left in the oil for 30 seconds, and then the beaker is lowered, allowing the needle to hang undisturbed. After 30 minutes the weight of the needle plus oil is recorded. The needle is cleaned with dichloromethane and allowed to dry before the measurement is repeated. A minimum of four measurements are made for each oil. The same beaker of oil can be used for all measurements. The oil adhesion is then calculated as the average weight of oil remaining on the needle divided by the needle's surface area.

Chemical Dispersibility

Chemical dispersibility with Corexit 9527 or 9500 was determined using the swirling flask test. Either of two different solvent extraction procedures was used, followed by spectrophotometric analysis (Fingas, Kyle, *et al.*, 1995).

Emulsion Formation

Emulsions were formed using either a rotary agitator from Associated Design (Fingas, Fieldhouse *et al.*, 1995), or a "Mackay apparatus" (Mackay and Zagorski, 1982).

RESULTS

Table 1 summarizes all the data used in this study. The oils are listed alphabetically and the following information is included: evaporative loss, saturates, aromatics, resins, asphaltenes, GC-resolvable waxes, and gravimetric waxes (weight %), BTEX+ (μg/g), viscosity (mPa·s) and density (g/mL) at 15 °C, pour point (°C), adhesion (g/m^2), dispersibility (volume %) with Corexit 9527 or 9500, and emulsion formation (yes or no).

Hydrocarbon Groups

Saturates

From Table 1 it can be seen that oils vary a great deal in their distribution of hydrocarbon groups. In general, saturates are the largest component, accounting for more than 50% of the mass of fresh oils in 68% of the oils studied. Figure 1 shows a frequency distribution of fresh oil saturate contents by decades. As oils evaporate, saturate contents almost always decrease. While many oils show a moderate decrease, a few drop spectacularly. Figure 2 shows the dramatic effect of evaporation on the saturate content of Arabian Medium crude oil.
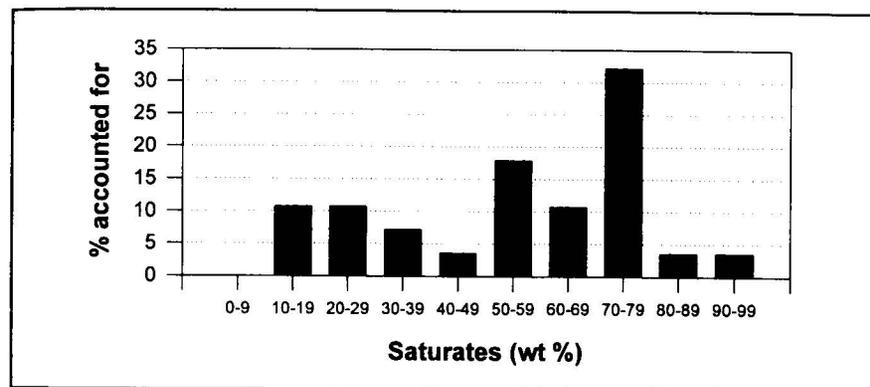

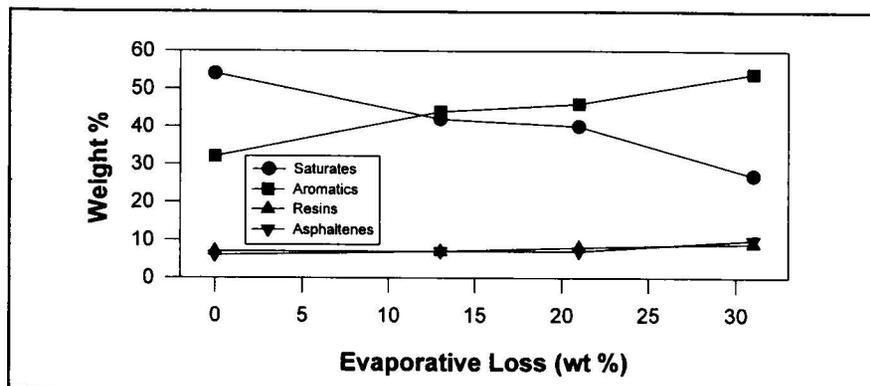**Figure 1** Frequency distribution of saturates in fresh oils

Figure 2 Hydrocarbon groups in Arabian Medium Crude Oil

Table 1

Oil Name	Evaporative Loss wt %	Saturates wt %	Aromatics wt %	Resins wt %	Asphaltenes wt %	Waxes (gc) wt %	Waxes (grav) wt %	BTEX+ µg/g	Density (at 15 °C) g/mL	Viscosity (at 15 °C) mPa·s	Pour Point °C	Adhesion g/m2	Dispersibility vol %	Emulsion Formation yes/no
Alaska North Slope	0	53	37	6	4	3		22080	0.8814	21			22	
Alaska North Slope	15	52	38	7	3	3		20320	0.8976	38			19	
Alaska North Slope	22	46	41	9	5	3		9510	0.9216	140			32	
Arabian Light	0				3		6	15420	0.8658	14	-28		25	yes
Arabian Medium	0	54	32	7	6	3		11350	0.8783	29	-11		10	yes
Arabian Medium	13	42	44	7	7	3		9350	0.9102	91	-4			
Arabian Medium	21	40	46	8	7	3		2600	0.9263	275	-2			
Arabian Medium	31	27	54	9	10	4		100	0.9495	2160	7			yes
Atkinson	0				2		1	2360	0.911	65	-38		45	
Brent	0	72	23	4	1	5	6	24380	0.8351	6	-6		2	no
California API 15	0	15	50	16	19	4	3	5280	0.977	6550	-9		18	no
Eugene Island Block 43	0	81	16	3	1	6	2	5430	0.8404	13	0			no
Eugene Island Block 43	7	78	17	4	1	6		4040	0.8518	21	7			no
Eugene Island Block 43	16	77	15	7	1	6		480	0.8594	36	7			no
Eugene Island Block 43	24	78	16	5	1	7		100	0.8665	65	11			
FCC Light Cycle Oil	0	17	58	4	20	2	0	880	1.062	7418	1		60	no
FCC Medium Cycle Oil	0	25	73	2	0	7	2	590	0.9835	32	-6	2		
Federated (1994)	0	74	21	3	1	5		27250	0.8293	4		11		
Federated (1994)	18	68	26	4	3	5		24800	0.8584	12		13		
Federated (1994)	27	69	27	3	1	5	2	23350	0.8293	16	-36	23	5	no
Green Canyon Block 109	0	51	39	9	1	1		6160	0.8921	39	-27			no
Green Canyon Block 109	8	46	43	10	1	1		5210	0.9101	98	-21			no
Green Canyon Block 109	14	44	44	11	1	1		1230	0.9218	225	-16			no
Green Canyon Block 109	22	42	43	14	1	1	2	40	0.9341	690	-32		26	no
Gullfaks	0	59	35	5	1	2		19860	0.8701	15	-32			no
Gullfaks	10	58	35	6	1	2	8	17480	0.8891	31			10	
Hibernia	0	62	31	6	2	5		27730	0.8457	11			26*	yes
Hibernia	18	59	33	6	2	5		20340	0.875	4003			34*	
Hibernia	26	58	34	6	2	6		9960	0.8849	5864				

Table 1

Oil Name	Evaporative Loss wt %	Saturates wt %	Aromatics wt %	Resins wt %	Asphaltenes wt %	Waxes (gc) wt %	Waxes (grav) wt %	BTEX+ µg/g	Density (at 15 °C) g/mL	Viscosity (at 15 °C) mPa·s	Pour Point °C	Adhesion g/m2	Dispersibility vol %	Emulsion Formation yes/no
High Viscosity Fuel Oil	0	18	43	13	26	2		2550	1.014	13460	2			no
Hondo	0	32	38	14	16	3	6	10960	0.9356	786	-15		3	yes
IFO 180	0	29	51	11	10	2		2700	0.9670	2324		49		
IFO 180	2	32	45	12	11	2		2000	0.9685	3232		63		
IFO 300	0	26	52	12	10	2		1920	0.9859	14470		91		
IFO 300	6	27	47	12	14	2		1370	0.9871	22135		126		
Iranian Heavy	0				3		4	17330	0.8756	20	-22		10	yes
Louisiana	0	73	21	4	1	2	2	14780	0.8518	8	-28		33	no
Louisiana	10	69	25	5	0	2		11370	0.8696	16	-23			
Louisiana	21	66	27	6	0	2		1490	0.8837	36	-12			
Louisiana	32	64	29	7	0	2		40	0.8953	80	-8			
Main Pass Block 306	0	65	29	5	1	1	1	18940	0.8606	9	-53	11	36	no
Malongo	0				2		14	6870	0.8701	86	21		5	yes
Maya	0	38	39	8	16	2	7	9590	0.9255	280	-15		2	yes
Maya	9	33	41	8	18	2		6700	0.9515	1980	-9			
Maya	15	31	41	10	17	2		2020	0.9657	8670	-2			
Maya	22	28	39	11	22	2		50	0.9868	405000	17			
Mississippi Canyon Block 194	0	71	25	4	0	2	1	14440	0.8483	7	-40	11	31	no
Oseberg	0	57	34	7	2	3	5	18130	0.8522	12	-9		16	yes
Oseberg	28				3			1810	0.906	70	3			yes
Point Arguello Light	0				5		10	11790	0.8739	22	-22			yes
Rangely	0	71	21	5	4	7	14	10650	0.8567	33	-9		7	no
Rangely	11	68	24	5	3	7		6960	0.8765	61	17			
Rangely	21	65	24	6	4	7		1170	0.892	173	18			
Rangely	30	61	27	6	6	8		80	0.9059	6320[b]	21			
Ship Shoal Block 269	0	79	15	6	0	2	1	19050	0.8309	5	-42	7	33	no
Sockeye	0				5		5	15470	0.8965	45			5	yes
South Pass Block 60	0	71	20	8	1	4	1	16000	0.8453	9	-9	10	44	no
South Pass Block 60	17	67	26	7	1	4		10000	0.8709	22	-3			no

Table 1 Oil Name	Evaporative Loss wt %	Saturates wt %	Aromatics wt %	Resins wt %	Asphaltenes wt %	Waxes (gc) wt %	Waxes (grav) wt %	BTEX+ µg/g	Density (at 15 °C) g/mL	Viscosity (at 15 °C) mPa·s	Pour Point °C	Adhesion g/m2	Dispersibility vol %	Emulsion Formation yes/no
South Pass Block 60	25	64	27	8	1	4		2260	0.8809	41	9			no
South Pass Block 60	38	61	28	9	2	5		40	0.8979	161	12			yes
South Timbalier Block 130	0	78	16	5	0	2	1	19400	0.8487	7	-27	11		no
Statfjord	0	68	26	5	1	4	4	25690	0.8354	7	-2		24	
Sumatran Heavy	0	46	30	13	10	2	16	1370	0.9312	13302^b	18			no
Sumatran Light	0				6	17	28	3160	0.860	41475^b	38			no
Taching	0	72	13	8	6	10	32	2100	0.870	5138000^c	38			no
West Delta Block 97	0	92	7	1	0	2		31960	0.7783	1	-27	1		no
West Delta Block 97	23	81	18	1	0	2		32350	0.8020	1	-18			no
West Delta Block 97	48	87	10	3	0	3		5650	0.8118	3	-15			no
West Delta Block 97	74	85	14	2	0	6		130	0.8320	7	-5			no

^{a} shear rate = 100/s; ^{b} shear rate = 10/s; ^{c} shear rate = 0.1/s (not used in correlations)

Aromatics

Aromatics make up the second largest hydrocarbon group for most oils. However, they exceeded 50% of fresh oil mass in only 4% of the oils studied. A frequency distribution for aromatics is shown in Figure 3. While aromatics usually increase with oil evaporation, as in Figure 2 above, sometimes they change very little, as in Figure 4.
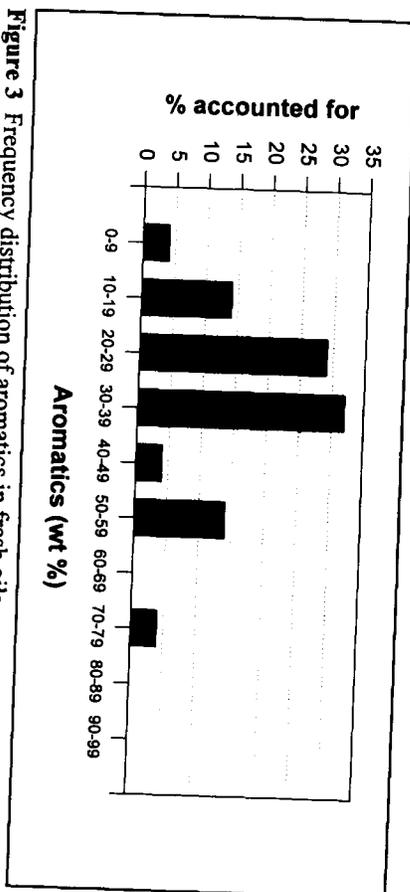

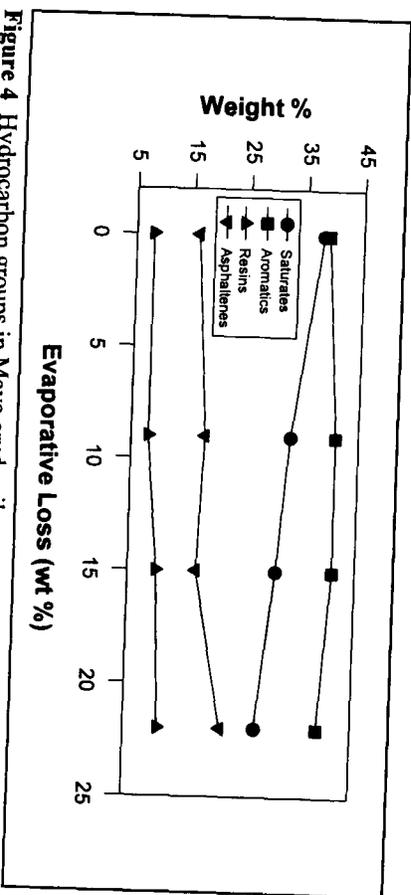Figure 3 Frequency distribution of aromatics in fresh oils

Resins

Resins typically make up less than 10% of fresh oil mass. A frequency distribution for resins is shown in Figure 5. As oils evaporate resin contents usually increase slightly, as in Figure 2, but can sometimes show a more pronounced increase as in Figure 4.
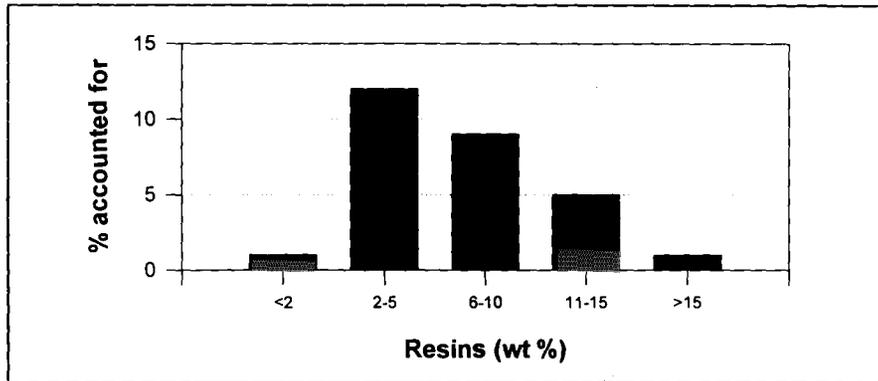

Figure 4 Hydrocarbon groups in Maya crude oil

Figure 5 Frequency distribution of resins in fresh oils

Asphaltenes

Asphaltenes account for an even smaller percentage of fresh oil mass than do resins in 82% of the oils studied. Figure 6 shows a frequency distribution for asphaltenes. As with resins, asphaltenes tend to increase slightly during the evaporation of most oils, but as seen in Figure 4 above there are oils for which asphaltene content is greater than resin content, and increases substantially with evaporation.
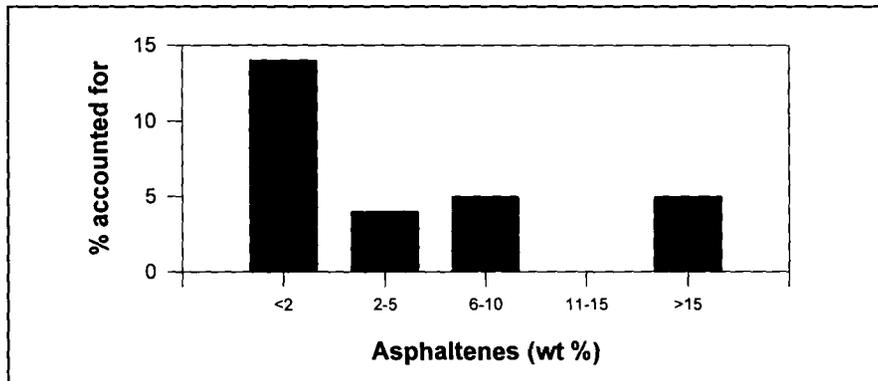

Figure 6 Frequency distribution of asphaltenes in fresh oils

Waxes

As can be seen from Table 1, GC-resolvable waxes make up a small percentage of the mass of most oils. Almost 80% of the oils in Table 1 have GC-resolvable wax contents of 5% or less, and only one wax value exceeds 10%. GC-resolvable wax contents do not, in general, agree with gravimetricly determined wax contents. Possible reasons for this disagreement are put forward later in this paper.

BTEX+

BTEX and C_3-substituted benzenes are the most volatile aromatic compounds found in oil. They are of concern for health and safety reasons *vis a vis* response personnel, and also because of their relatively high solubility and aquatic toxicity. BTEX+ can make up as much as 3% of fresh oil mass. However, the high volatility of these compounds means that they decrease rapidly as oil evaporates. Figure 7 illustrates this for two light crudes.
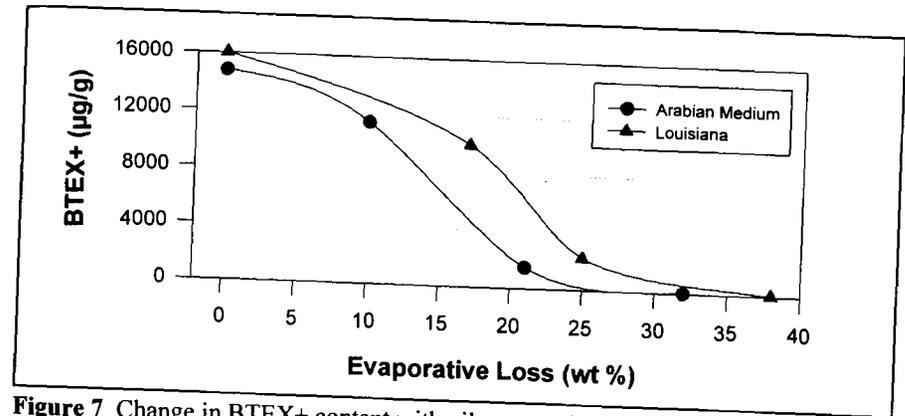

Figure 7 Change in BTEX+ content with oil evaporation

Relationships to Physical Properties

Density

The density of fresh and evaporated crude oils can be correlated closely to saturates content, as shown in Figure 8.
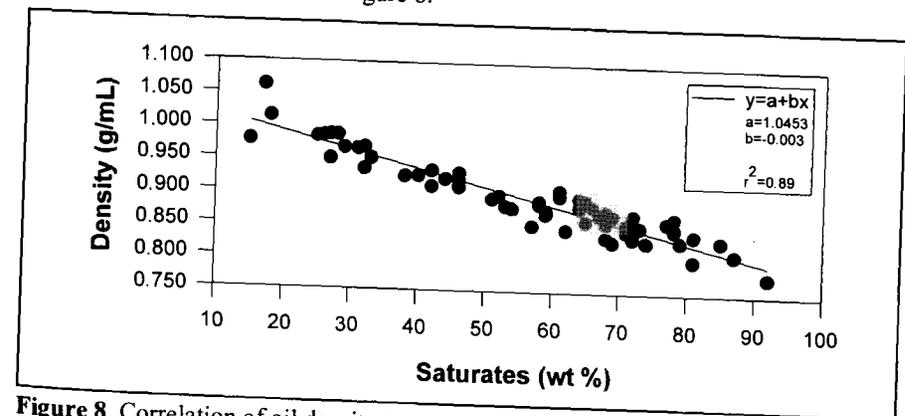

Figure 8 Correlation of oil density to saturates content

Viscosity

Viscosity does not correlate simply with hydrocarbon groups. A reasonably good ($r^2=0.79$) correlation can be obtained between the common logarithm of viscosity and the sum of asphaltenes, resins, and waxes (GC). This is shown in Figure 9.
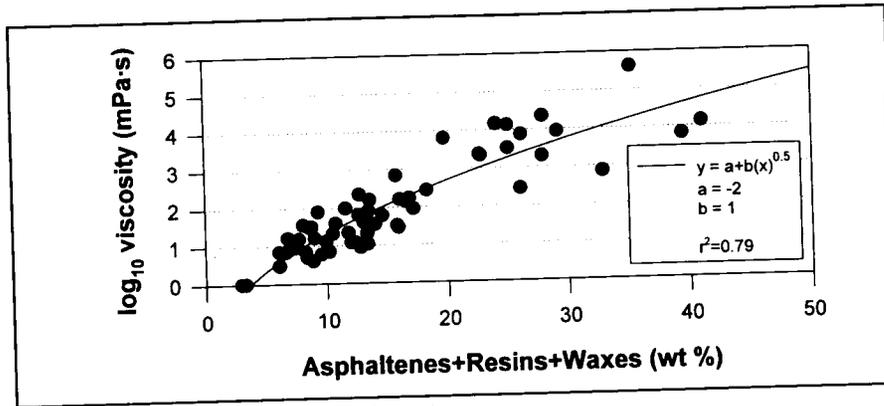

$$y = a+b(x)^{0.5}$$
$$a = -2$$
$$b = 1$$
$$r^2=0.79$$

Figure 9 Relating viscosity to hydrocarbon groups

Pour Point

For fresh oils, pour point correlates fairly well to wax content, as shown in Figure 10. No correlation was attempted for both fresh and evaporated oils because the GC wax contents vary so little with evaporation.
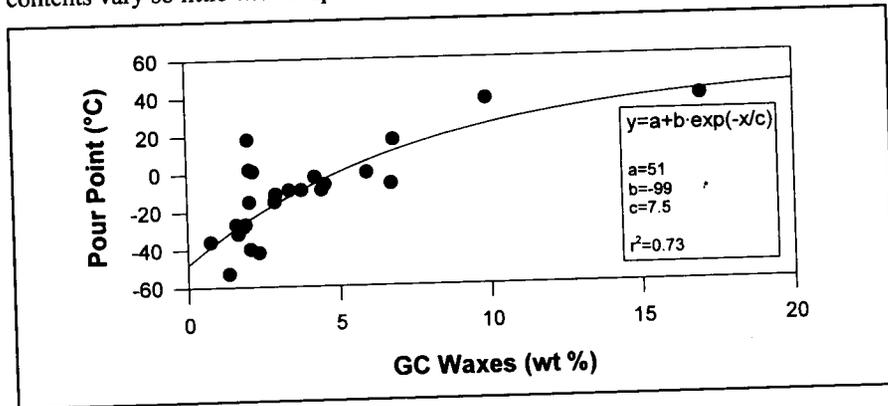

$$y=a+b \cdot exp(-x/c)$$
$$a=51$$
$$b=-99$$
$$c=7.5$$
$$r^2=0.73$$

Figure 10 Correlation of pour point to wax content

Relationships to Behaviour

Adhesion

Adhesion correlates well with hydrocarbon groups. Figure 11 shows a high correlation between adhesion and saturates content, and Figure 12 displays an even greater correlation between adhesion and asphaltene content. Further improvement to

the correlation can be obtained by combining asphaltene, resin, and saturate contents into a single variable, as shown in Figure 13.
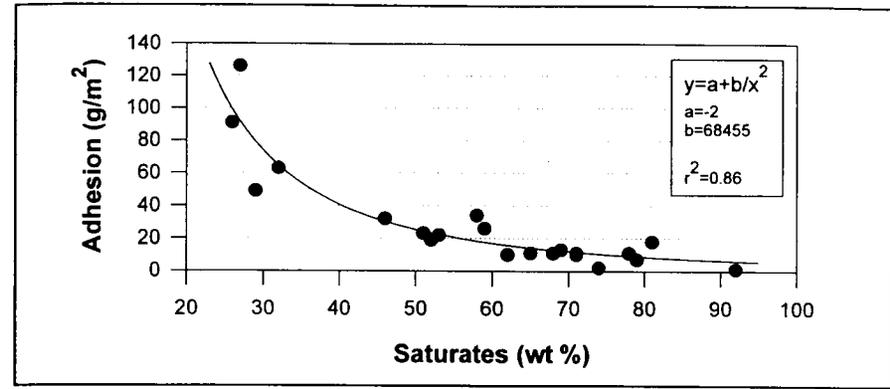

$$y=a+b/x^2$$
$$a=-2$$
$$b=68455$$
$$r^2=0.86$$

Figure 11 Correlation of oil adhesion to saturate content

$$y=a+b \cdot exp(x/c)$$
$$a=-6$$
$$b=16$$
$$c=7$$
$$r^2=0.90$$
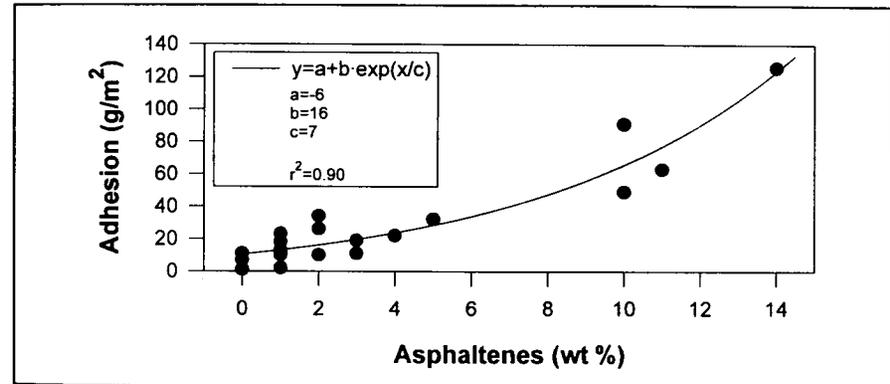
Figure 12 Correlation of oil adhesion to asphaltene content

$$y=a+b \cdot exp(x/c)$$
$$a=7$$
$$b=6$$
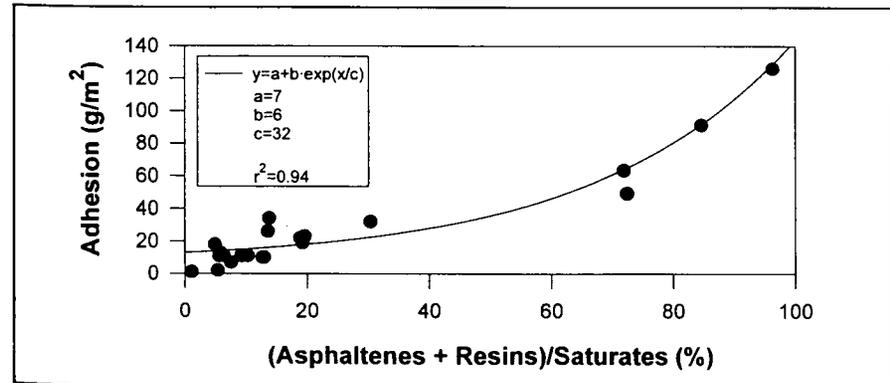$$c=32$$
$$r^2=0.94$$

Figure 13 Correlation of oil adhesion to asphaltene, resin, and saturate contents

Dispersibility

The relationship between chemical dispersibility and hydrocarbon groups is complex. Table 2 shows the small subset of data for which both hydrocarbon group and dispersibility data were available. An inspection of this data indicates that oils with high asphaltene contents do not disperse well. Also, oils with dispersibilities of greater than 30% have saturate contents greater than 65%. The two oils which have saturate contents greater than 65%, but dispersibilities less than 30% are also higher than average in either combined asphaltenes and resins, or waxes. In fact, if saturates, asphaltenes, and waxes are combined into a single variable by subtracting asphaltenes and waxes from saturates, a moderately good correlation to dispersibility can be obtained, as shown in Figure 14.

| Table 2 Oil Name	Saturates wt %	Aromatics wt %	Resins wt %	Asphaltenes wt %	Waxes (gc) wt %	Waxes (grav) wt %	BTEX+ µg/g	Dispersibility vol %
California API 15	15	50	16	19	4	3	5280	2a
Maya	38	39	8	16	2	7	9590	2a
Hondo	32	38	14	16	3	6	10960	3a
Green Canyon Block 109	51	39	9	1	1	2	6160	5a
Rangely	71	21	5	4	7	14	10650	7a
Arabian Medium	54	32	7	6	3	6	11350	10b
Oseberg	57	34	7	2	3	5	18130	16b
Statfjord	68	26	5	1	4	4	25690	24b
Gullfaks	59	35	5	1	2	2	19860	26b
Mississippi Canyon Block 194	71	25	4	0	2	1	14440	31b
Louisiana	73	21	4	1	2	2	14780	33b
Ship Shoal Block 269	79	15	6	0	2	1	19050	33b
Main Pass Block 306	65	29	5	1	1	1	18940	36b
South Pass Block 60	71	20	8	1	4	1	16000	44a
Brent	72	23	4	1	5	6	24380	45a

a Corexit 9527, b Corexit 9500
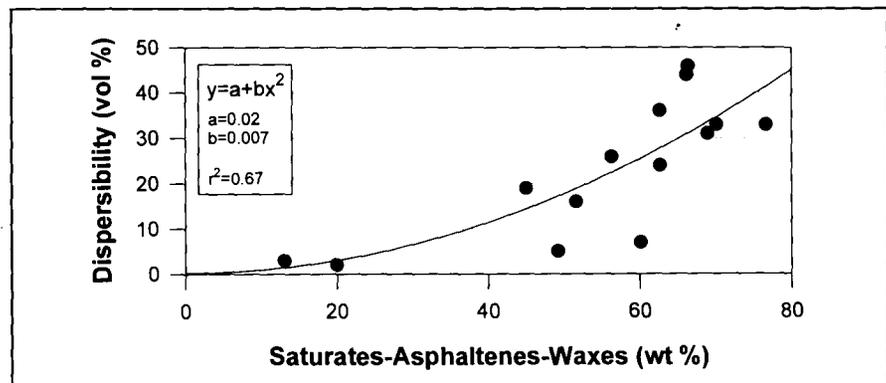
Figure 14 Correlation of dispersibility to saturate, asphaltene, and wax contents

$y = a + bx^2$
$a = 0.02$
$b = 0.007$
$r^2 = 0.67$

Emulsion Formation

Only 13 of the oils in Table 1 formed stable or meso-stable emulsions. Comparing those 13 with 28 which did not form emulsions, it is clear that oils with less than a 2% asphaltene content did not form emulsions. Also, on average, the saturate content was significantly lower in the oils which did form emulsions (50%), than in those which did not (70%).

DISCUSSION

As demonstrated above, hydrocarbon groups can be related to oil physical and behavioural properties in a variety of ways. In some cases, hydrocarbon groups can be predictive of other properties. For instance, density can be predicted quite well from saturate content. However, as density can be quickly and easily measured, even in field situations, this particular relationship would be more useful applied in reverse. That is, one could use density to predict saturate content. This in turn could be useful in predicting adhesion, and to a lesser degree, dispersibility and emulsion formation.

However, it is not for their predictive capabilities that hydrocarbon groups are most valuable, rather it is for the insights they provide into the reasons for the variability of oil physical and behavioural properties. The findings of this paper are preliminary. In future work it should be possible to more exactly define the complex relationships of hydrocarbon groups to properties such as viscosity, dispersibility, and emulsion characteristics. For instance, if sufficient quantities of individual oil saturate, aromatic, resin, and asphaltene fractions were collected, viscosity measurements could be made on each fraction, allowing a more exact determination of the contribution of each fraction to the overall oil viscosity.

In the case of dispersibility, it is anticipated that improvements in the analytical methods used (GC versus spectrophotometry) and the use of Corexit 9500 in testing will yield a larger and much more consistent data set. Similar expectations will likely be realized in the case of emulsion characterization.

Most of the results discussed above are neither surprising nor controversial. However, there are two subjects which warrant further discussion: adhesion, and wax contents.

Adhesion

The very good correlations found between adhesion and hydrocarbon groups support the usefulness of the new adhesion test procedure. The adhesion test is simple, quick, and works on oils with a wide range of viscosities. Not only will it provide a direct measure of the relative degree to which oils will adhere to a surface, but where hydrocarbon group data is not available, both saturate and asphaltene contents could be inferred from adhesion data.

Waxes

Waxes determined by precipitation may be either higher or lower than those determined by GC. There could be several reasons for this. The precipitated waxes contain non-alkane components. In the cases of Hibernia and Maya, the resolvable component of the precipitated wax amounts to only 38% and 27%, respectively. Based on these figures it might be expected that Hibernia and Maya should have GC-resolvable

wax contents of 3% and 1%, respectively. In fact, using SIMDIS data obtained from these whole crude oils, (no deasphaltizing), they were found to have GC-resolvable wax contents of 6% and 3%, respectively. In general, gravimetricly determined waxes will be lower in GC-resolvable waxes than the whole oil because a)some waxes may be removed when the asphaltenes are precipitated, and b) not all the waxes will precipitate, even at -32 °C. Oils with a higher percentage of high molecular weight waxes will precipitate most completely. For example, Hibernia will be less affected than Maya. Figure 15 is a chromatogram of the calibration mixture, containing n-alkanes from C_5 to C_{120}. By comparing Figure 15 with the GC/FID chromatograms in Figures 16 and 17 it is apparent that Hibernia's wax distribution is shifted towards higher carbon numbers than is Maya's.
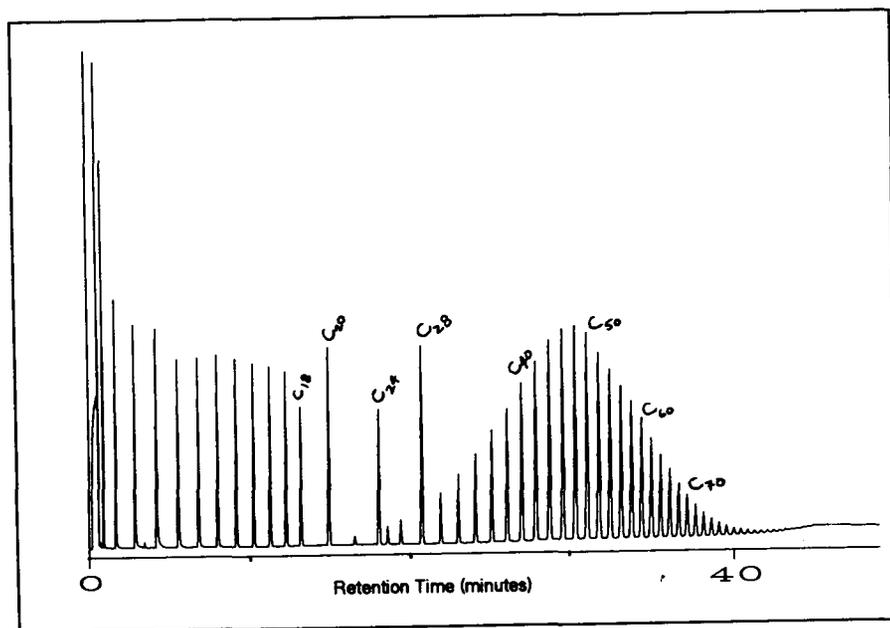

Figure 16 GC/FID chromatogram of waxes precipitated from Hibernia crude oil

Figure 15 GC/FID chromatogram of n-alkane calibration mixture

A second source of discrepancy between GC-resolvable and gravimetricly determined waxes is the very small resolvable component of some heavy oils. A comparison of Figures 18 and 19, chromatograms of Sumatran Light and Sumatran Heavy crudes, illustrates the problem, which primarily affects oils which are both heavy and very waxy, and do not always dissolve well in carbon disulphide.

A third problem, is the variability in calculated wax content which arises from inconsistencies in the method of integration, both for the C_{18}^+ portion of the chromatogram, and more importantly, for the manual integration of the total chromatogram area. Small shifts in baseline location can significantly affect the calculated wax content.
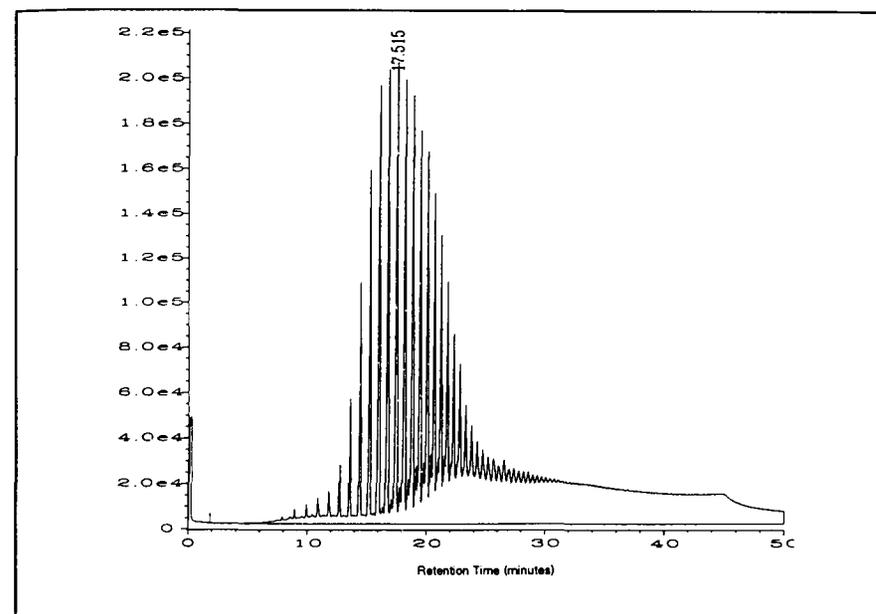

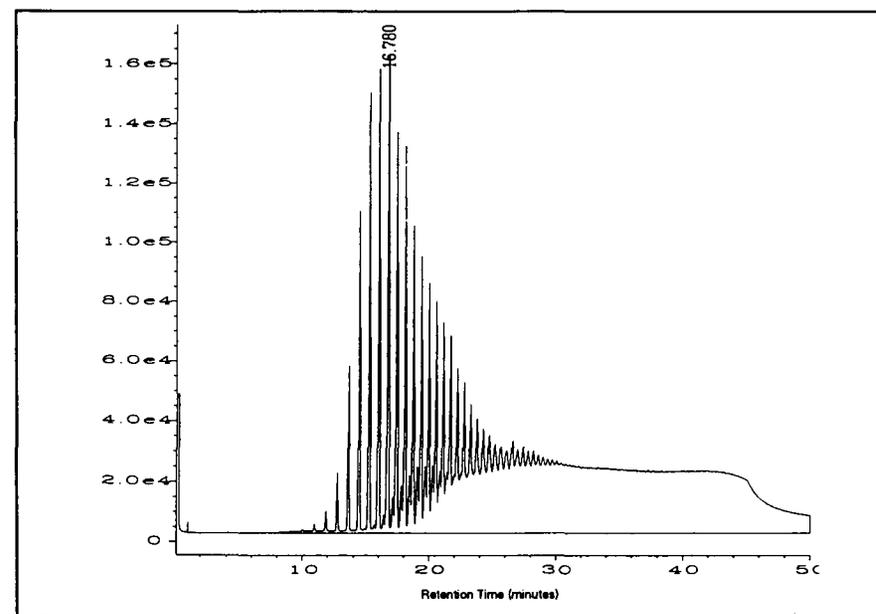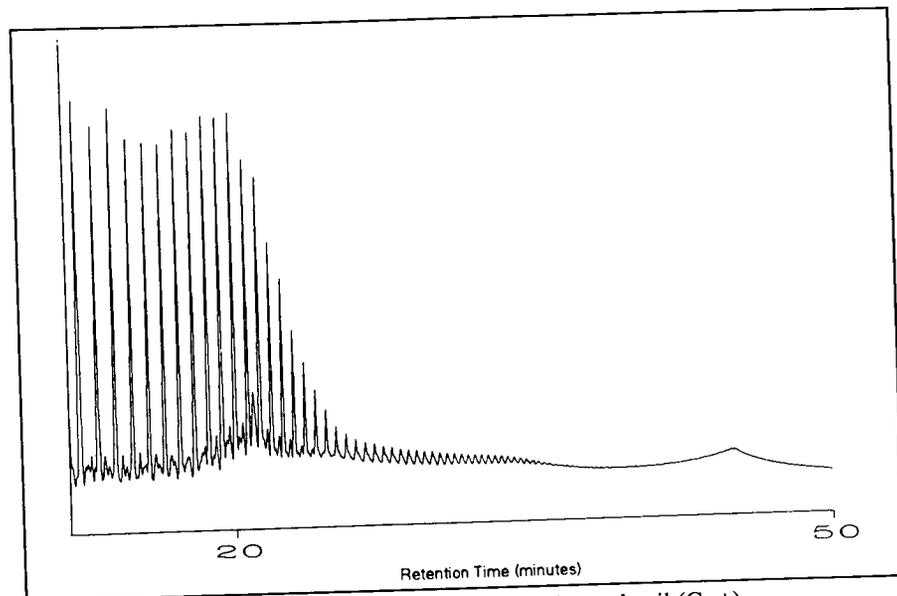**Figure 17** GC/FID chromatogram of waxes precipitated from Maya crude oil

Figure 18 GC/FID chromatogram of Sumatran Light crude oil ($C_{18}+$)
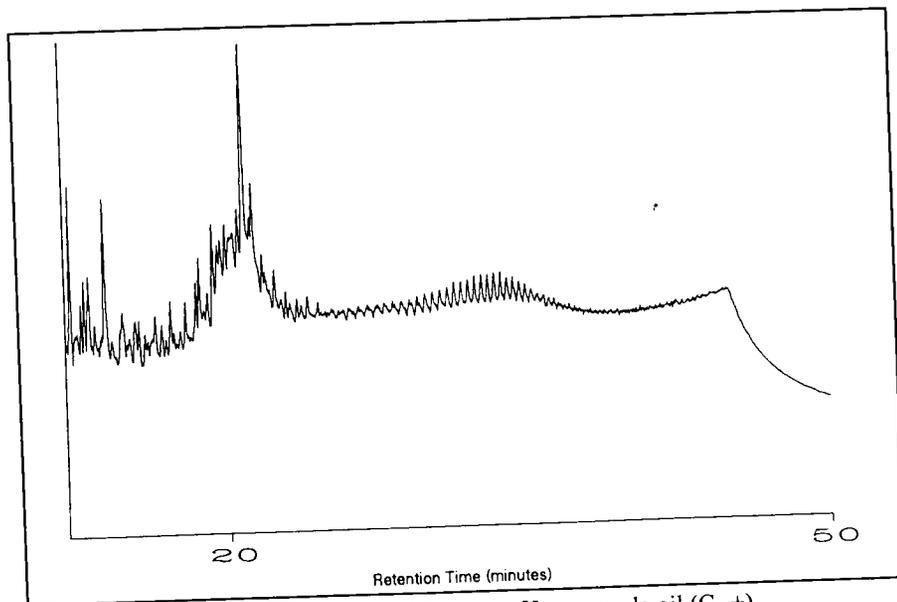

Figure 19 GC/FID chromatogram of Sumatran Heavy crude oil ($C_{18}+$)

CONCLUSIONS AND RECOMMENDATIONS

The determination of hydrocarbon groups in crude oils can contribute greatly to our understanding of both physical and behavioural oil properties. Many experiments remain to be carried out, both to fill in data gaps, and to confirm (or deny) untested hypotheses. Does asphaltene precipitation remove some waxes from the oil. Can better results be obtained with the GC determination of wax content by using a different solvent? Exactly how do the individual hydrocarbon groups contribute to oil viscosity? Theses are some of the questions that future research will attempt to answer.

ACKNOWLEDGEMENTS

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