SEPARATION AND DETERMINATION OF POLYNUCLEAR AROMATIC COMPOUNDS IN BITUMEN, HEAVY OILS AND THEIR SYNTHETIC CRUDE PRODUCTS.

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INTRODUCTION

Characterization of bitumen, heavy oils, crude oil distillation residues and processed products has always been a problem because of the complexity of the material involved. In our laboratory we are particularly concerned with the characterization of hydroprocessed products from the western Canadian bitumen/heavy oils, as well as residuals from conventional oil during conversion to synthetic crudes. The characterization of products obtained under different conditions and severities will lead to a better insight of the processing conditions. The polynuclear aromatic components are of special interest because of their conversion and formation in hydrogenation and dehydrogenation reactions. In order to follow the fate of the various aromatic components all characterization must be done on a molar basis so that changes in the number of different structures with severity of processing can be determined. Decreases of molecular weight due to cleavage of side chains can obscure changes if characterizations are on weight bases only.

Many separation processes such as the well known API-60 and SARA methods (1,2) have been developed to allow a better determination of the components of crude oils. The API-60 separation has been modified in this laboratory (3) to reduce analysis time, sample size and weight of adsorbents and for separation of the polyaromatic and polar fraction into polyaromatics, polars and bases. However the polyaromatic fraction is still very complex and further separation by ring classes would give a better knowledge of the composition of this fraction and of the changes that occured during upgrading of the synthetic crudes.

High performance liquid chromatography (HPLC) is a technique that is more and more widely used to complement or replace the conventional hydrocarbon-type separation (4,5). On the other hand, HPLC has been used to perform the separa-

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tion of polynuclear aromatic hydrocarbons according to the number of rings using amino- or diamino-bonded phase (6,7). In our work the separation of polynuclear aromatic hydrocarbons by HPLC has been applied to hydrocarbon type separation to complement the existing techniques (8,9). Fractions obtained from this separation can further be characterizeed for average molecular weight and quantitation and could be monitored by GC/MS for further identification.

In this study we have used HPLC on amino-bonded phase for the separation of the polyaromatic fraction obtained from an hydrocarbon-type separation into three, four and five-or-more aromatic rings molecules. Fractions corresponding to those classes are collected and the quantity and average molecular weight are determined for each of the fractions.

Average molecular weight is calculated using a gas chromatography technique similar to simulated distillation. In the latter, boiling point range is estimated relying on the fact that hydrocarbons are generally eluted from a non-polar column in order of their boiling points (10). Using a calibration curve showing the correlation between boiling points and retention times, it is then possible to find the boiling range of a given oil sample. The same kind of assumption is made here between the logarithm of the molecular weight and retention time since boiling point generally goes up with molecular weight for each class of compounds.

Average molecular weights are calculated by evaluating areas of slices in which the GC peak is divided. Each slice is associated with a retention time period from which a molecular weight is calculated by means of a calibration curve. Final calculation is completed using a method similar to the determination of molecular weight by Gel Permeation Chromatography. Thus the number average molecular weight is defined by:

$$\overline{Mn} = \frac{\sum N_i M_i}{\sum N_i} = \frac{\sum Area_i}{\sum (Area_i/M_i)}$$

where N_i is the number of molecules having the molecular weight M_i and $Area_i$ is the area of a slice i and is equivalent to $N_i M_i$.

Quantitation of the sample peak is possible by adding an internal standard. So a single GC run will give a quantitation of a sample and an evaluation of its average molecular weight.

MATERIALS AND METHODS

The samples were a conventional oil distillation resi-
due (525°C plus) and two hydrocracked products obtained at
different severities of hydrocracking. The hydrocracking
process has been described elsewhere (11). The separation
and characterization schematic diagram is shown in Figure 1.
The hydrocracking products processed under mild and severe
conditions have been distilled to 200°C to remove the naphtha
fraction and deasphaltened with pentane. A modified API
separation which was described elsewhere (3) has been applied
to the sample for its fractionation into saturates, monoaro-
matics, diaromatics, polyaromatics, polar materials and basic
compounds.

The polyaromatic fraction is further separated in tri-
aromatics, tetraromatics and 5 or more aromatic ring com-
pounds by HPLC using a Waters µ-Bondapak-column (300 mm x 3.9
mm). The HPLC system consisted of a Varian 5000 Liquid Chro-
matograph with a Schoeffel SF770 UV spectroflow monitor toge-
ther with a 8 µL cell (λ = 254 nm). Separations were per-
formed at a flow rate of 2 mL/min with solvent programming as
following: from 0 to 10 minutes, solvent was 100% hexane
then solvent was gradually changed between 10 and 12 minutes
to 10% methylene chloride in hexane in order to elute the
aromatic compounds with more rings.

The gas chromatographic system consisted of a Perkin
Elmer gas chromatograph in conjunction with a Varian 401 Data
Station via a Varian Control Station. The Data Station was
connected to an Apple computer (Vista-Plus arrangement)
through one of the control channels in order to perform the
average molecular weight calculation. Temperature program-
ming runs were performed on the separated polyaromatic frac-
tions from hydrocarbon-type separation and on HPLC separated
fractions. Initial temperature of 60°C was held for 2
minutes. Then a 10 degrees per minute gradient increased the
temperature to 350°C at which the oven was held for 4
minutes. The column was a 1/8 inch x 1 m stainless steel
tubing packed with 5% Dexsil 400 on Chromosorb W-HP as the
stationery phase. The flow rate was 50 mL/min. Injection
and FID detector temperature were 250 and 375°C respectively.

HPLC grade hexane and methylene chloride were pur-
chased from Fisher. Polyaromatic standards were purchased
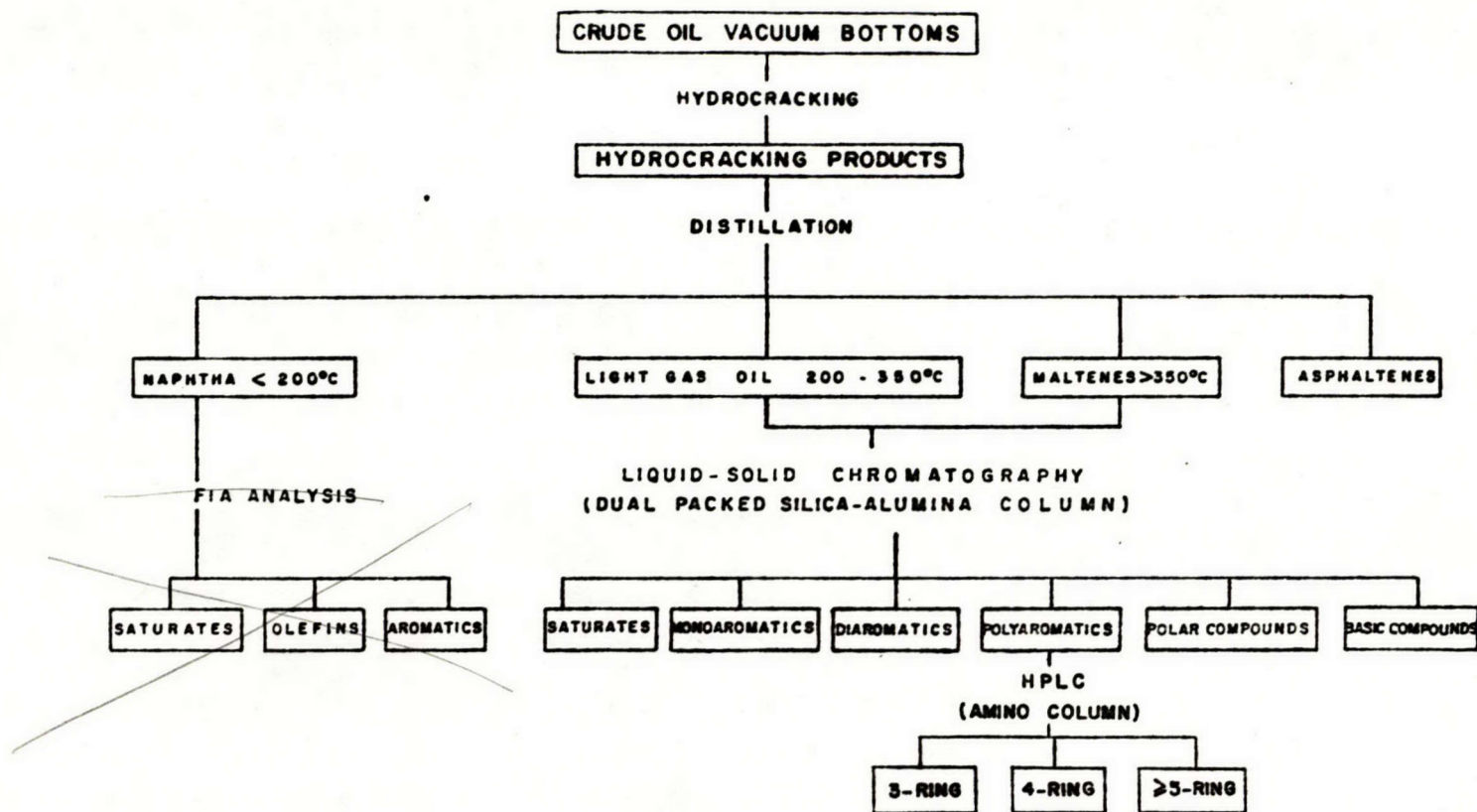from different companies and used without further purifica-
tion.

Figure 1. Scheme of the separation and characterization.

RESULTS AND DISCUSSION

In this work we analyzed the polyaromatic fraction of a crude oil vacuum distillation bottom and its two hydrocracking products. Properties of the feed are given in Table I. This feed was hydrocracked under two sets of conditions. Table II shows the gross composition of the feed and the products obtained under mild conditions (product 1) and severe conditions (product 2). One can observe that asphaltenes and maltenes over 350°C are converted to a larger extent under severe conditions. Table III shows type separations.

Retention data of thirty-one polynuclear aromatic standards has been obtained to determine the cutpoints between these three fractions: triaromatics, tetraaromatics and molecules with 5 or more aromatic rings. As can be seen in Table IV, there is a general trend of the compounds to be separated according to the number of their aromatic rings, although complete resolution is not achieved. Results also show that substitution and addition of naphthene rings can cause some spreading in the retention times. Condensation of the molecules can also affect the retention time. For example retention times are increasing with pyrene, 9,10 benzophenanthrene and 2,3 benzanthracene as the condensation is less pronounced. It becomes clear that those two combined effects can cause some overlap between the different fractions. However in vacuum bottoms and moreover in hydrocracking products molecules with not highly condensed structures are not likely to be present in the samples.

Figure 2 shows HPLC chromatograms using a ultraviolet detector of polyaromatic fractions of the feed and the two hydrocracking products from that feed. The two time limits are indicating the cutpoints as determined by the retention time of the standard compounds (the order of elution being triaromatics, tetraaromatics and finally compounds with five or more aromatic rings). Thus it is possible to observe the shift in polyaromatic fraction upon hydrocracking, although the ultraviolet detector response is not quantitative. For instance the feed shows a lower concentration in tri-and tetraaromatics than the two products respectively to the penta + fraction. Moreover it is obvious that upon severe treatment more trinuclear aromatic compounds are formed.

TABLE I

PROPERTIES OF THE HYDROCRACKING FEED

Sample	Crude oil vacuum bottom
Specific gravity	1,023
Sulphur, wt%	4,05
Ash, wt%	0,035
Asphaltenes (n-pentane insolubles), wt%	17,80
Benzene insolubles, wt%	4,6
Carbon, wt%	84,91
Hydrogen, wt%	9,87
Nitrogen, wt%	0,21
Vanadium, ppm	144
Nickel, ppm	30
Iron, ppm	38

TABLE II

GROSS COMPOSITION OF CRUDE OIL VACUUM BOTTOM AND
HYDROCRACKING PRODUCTS (WT% OF LIQUID PRODUCT)

Sample	Pitch Convers. wt%	Naphtha IBP-200°C	200-350°C	Maltenes above 350°C	Asphaltenes
Feed	–	nil	nil	82.6	17.4
1	34.3	3.8	9.3	69.6	15.7
2	85.2	14.3	33.9	40.5	8.8

TABLE III

COMPOUND-TYPE DISTRIBUTION (% BY WT) OF CRUDE OIL VACUUM BOTTOM AND HYDROCRACKING PRODUCTS
(WT% OF LIQUID PRODUCT)

Sample	Saturates	Mononuclear Aromatics	Dinuclear Aromatics	Polynuclear Aromatics	Polar Compounds	Basic Compounds	Asphaltenes
Feed	14.3	11.8	13.1	22.9	12.0	7.4	17.4
1	23.23	11.43	12.00	16.85	12.44	2.82	15.7
2	47.92	12.80	9.00	9.97	5.13	0.97	8.8

TABLE IV

RETENTION BEHAVIOR OF POLYNUCLEAR AROMATIC STANDARDS BY
HPLC ON AMINO-BONDED COLUMN UNDER ISOCRATIC CONDITIONS

| Compound	k
Acenaphthene	0.4
Terphenyl	0.55
Fluorene	0.75
2-Methylfluorene	0.8
Acenaphthylene	0.8
1,2,3,4-Tetrahydrofluoranthene	0.8
3-Methylphenanthrene	0.9
Phenanthrene	0.95
2-Methylphenanthrene	1.1
4,5-Methylenephenanthrene	1.1
3,6-Dimethylphenanthrene	1.2
Pyrene	1.3
1-Methylpyrene	1.35
tetraphenylethylene	1.45
2,3-Benzofluorene	2.05
9-Phenylanthracene	2.35
9,10-Benzophenanthrene	2.4
7,12-Dimethylbenz [a] anthracene	2.5
9,10-Dimethylbenz [a] anthracene	2.65
2,3-Benzanthracene	2.75
1,2-Benzanthracene	2.8
3-Methylcholanthrene	3.35
3,4-Benzofluoranthene	3.45
9,10-Dibenzylanthracene	3.8
3,4-Benzofluoranthene	4.05
11,12-Benzofluoranthene	4.1
Perylene	4.2
Dibenzo [a,h] anthracene	6.7
1,2,3,4-Dibenzanthracene	6.9
1,2,5,6-Dibenzanthracene	7.0
Coronene	11.7
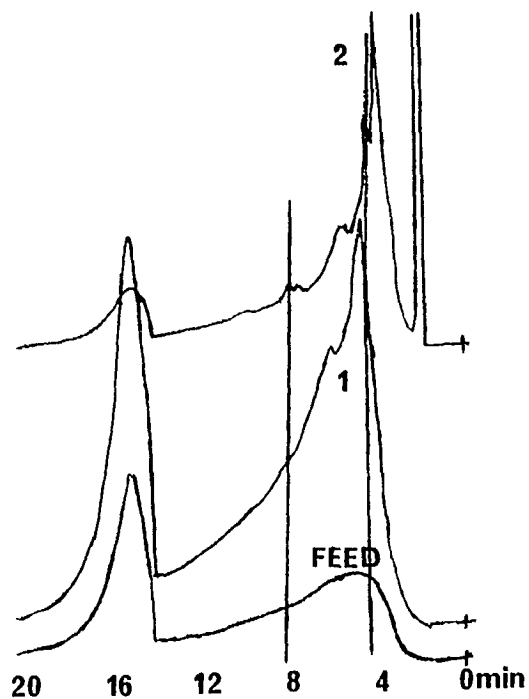
Figure 2.   HPLC chromatograms of the vacuum bottom feed and
            the two hydrocracking products obtained under
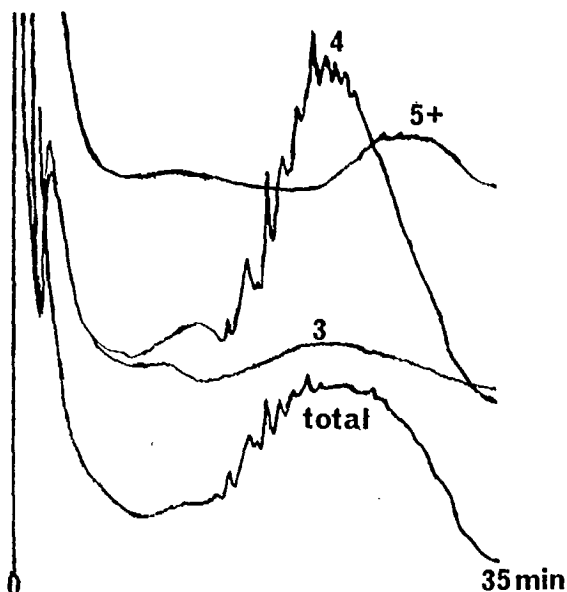   mild (1) and severe (2) conditions.

Figure 3.   Example of distribution of components as obtained
            by GC for the polyaromatic fraction before HPLC
            separation (total), the triaromatics (3), the
            tetraaromatics (4) and the five-and-more aromatic
            cycle compounds (5+).

After HPLC separation gas chromatography is used for average molecular weight determination and quantitation using isopropylbenzene as an internal standard. Figure 3 is an example of a GC chromatogram obtained on the different fractions of the same sample. The peak on the tail of the solvent peak is the internal standard used for quantitation.

Table V shows the number average molecular weight calculated from GC runs for the feed and two products. The molecular weight is generally decreasing upon treatment which could be expected in hydrocracking as side chains are cleaved. However in the penta + fraction the average molecular weight does not change significantly. For those samples we also see that the molecular weight is generally increasing with the number of aromatic rings. However this could be different with other feeds since triaromatic compounds could have a higher molecular weight than pentacyclic material depending on the naphthene rings or the side chains that are present.

Table VI and Table VII show the results of the quantitation on weight bases and mole bases respectively. In the untreated vacuum bottoms the pentacyclic plus components are dominant with about half as much tetracyclic and relatively small amounts of tricyclic components.

During the mild hydrocracking, the pentacyclic plus components are drastically diminished while the tetra and tricyclic components increase to some extent. The tetracyclic components become dominant at this stage. Possibly some of the penta-cyclic + components were converted to smaller aromatic systems. While the mono and dinuclear components do not appear to change much on weight bases we know from other studies that their molecular weight decrease during processing and therefore the number of smaller aromatic structures does increase.

Also during the mild treatment there appeared to be little change in the asphaltene content so that conversion to polynuclear aromatic components does not appear to be the case.

After the more severe hydrocracking treatment there is little change in the pentacyclic plus components while the tri and tetracyclic components have diminished. The tetracyclic material remain the dominant polynuclear aromatics. At this stage the asphaltenes have also been drastically diminished but there appears to be no evidence that the conversion of asphaltenes involves the formation of polynuclear

TABLE V

NUMBER AVERAGE MOLECULAR WEIGHTS OF POLYAROMATIC FRACTIONS

Sample	Total Polyaromatic Fraction	Triaromatics	Tetraaromatics	Penta +
Feed	311	309	319	298
1	289	270	284	305
2	252	246	255	310

TABLE VI

DISTRIBUTION OF MATERIAL IN POLYAROMATIC FRACTIONS (WT%)

Sample	Total Polyaromatic Fraction	Triaromatics	Tetraaromatics	Penta +
Feed	22.9	1.8	7.3	13.7
1	16.85	3.7	10.4	2.7
2	9.97	1.3	5.7	3.0

TABLE VII

DISTRIBUTION OF MATERIAL IN POLYAROMATIC FRACTIONS
(MOLES/100g OF MATERIAL)

Sample	Total	Tri	Tetra	Penta +
Feed	7.3×10^{-2}	0.6×10^{-2}	2.3×10^{-2}	4.6×10^{-2}
1	5.8×10^{-2}	1.4×10^{-2}	3.7×10^{-2}	0.9×10^{-2}
2	4.0×10^{-2}	0.5×10^{-2}	2.2×10^{-2}	1.0×10^{-2}

aromatic compounds as might have been believed. However it is possible that the polynuclear aromatics might have been intermediates which underwent further conversion.

CONCLUSION

This work showed that the addition of an HPLC separation to the hydrocarbon-type separation allowed us to get a better insight of the polyaromatic fraction and of the trends in hydrocracking reactions involving tri and tetraaromatic components along with material having five and more aromatic rings. The use of gas chromatography provided a new and promising technique to evaluate the average molecular weight of bitumen, heavy oils and other related samples.

ACKNOWLEDGEMENTS

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