latest version after Reviewers' comments
Aug 23/1985

HPLC SEPARATION AND GC CHARACTERIZATION OF POLYNUCLEAR AROMATIC FRACTIONS OF BITUMEN, HEAVY OILS AND THEIR SYNTHETIC CRUDE PRODUCTS

S. Coulombe and H. Sawatzky

OCTOBER 1984

ERP/ERL 84-71 (J)

ENERGY RESEARCH PROGRAM
ENERGY RESEARCH LABORATORIES
DIVISION REPORT ERP/ERL 84-71 (J)

HPLC SEPARATION AND GC CHARACTERIZATION OF POLYNUCLEAR AROMATIC FRACTIONS OF BITUMEN, HEAVY OILS AND THEIR SYNTHETIC CRUDE PRODUCTS

by

S. Coulombe* and H. Sawatzky*

ABSTRACT

Characterization of bitumen, heavy oils, crude oil distillation residues and their processed products involves separation of the mixtures into several compound classes according to their molecular structure. However, these fractions are still very complex and often need further separation in order to get a better insight into their composition as well as the processing reactions involved in their upgrading. In this paper, the polynuclear aromatic fraction is divided into three subfractions by high performance liquid chromatography. Gas chromatography is then used to quantify these fractions and to determine their average molecular weight by a new method derived from simulated distillation. Crude oil distillation residues and their hydrocracked products are used to demonstrate this method.

---

* Research Scientists, Hydrocarbon Processing Research Laboratory, Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada, K1A 0G1.

INTRODUCTION

Upgrading of bitumen, heavy oils and crude oil distillation residues to synthetic crudes involves reactions which are difficult to define in detail because of the complexity of the feeds and products. Our laboratory deals with the characterization of hydroprocessed products from Canadian bitumen and heavy oils as well as residuals from conventional oil. The characterization of these feedstocks and their products will lead to a better knowledge and a greater optimization of process reactions.

Many separation schemes known as hydrocarbon-type separations have been developed over the years to allow a better determination of the crude oil components. The well-known API-60 and SARA methods were developed to obtain an improved characterization of heavy samples[1,2]. The API-60 method has been modified in this laboratory[3] in order to reduce the analysis time, sample size and weight of adsorbents and for an improved separation of polyaromatic and polar fractions into polynuclear aromatic, polar and basic compounds. However, the polyaromatic fraction is still very complex and further separation into more detailed ring classes would be useful to acquire more information on this class of compounds as they are possible intermediates between asphaltenes and lighter material. For this reason Chmielowiec et al.[4,5] have developed an HPLC method in which the polyaromatics, tetraaromatics and compounds having five or more aromatic rings (penta+ aromatics) are separated.

However, the conventional HPLC detectors are not quantitative, i.e., they do not generate signals proportional to the mass of compounds introduced. Therefore, quantitation of the subfractions is not readily available from the HPLC run. Another drawback is that it would be tedious to collect HPLC effluents for weighing because the quantities involved are very small.For this reason we developed a method where the HPLC effluents are collected and then injected in a gas chromatograph. Quantitation is done using a FID detector. In order to get the maximum information from a single GC run we also developed a new average molecular weight determination method based on a calculation similar to gel permeation chromatography.

This paper focuses on the HPLC separation of polyaromatic fractions into subclasses followed by the GC quantitation and molecular weight determination. Limitations of the methods are discussed. These methods have been applied to polynuclear aromatic fractions from crude oil vacuum bottoms.

EXPERIMENTAL

The samples are two conventional oil distillation residues (+525°C) and hydrocracked products obtained at different severities. Properties of the feeds are described in Table 1. These feeds were hydrocracked under mild (products A1 and B1) and severe conditions (products A2 and B2) as indicated by the pitch conversion level and the conversion of asphaltenes and maltenes (Table 2). The hydrocracking process has been described elsewhere[6].

The separation and characterization schematic diagram is described in Figure 1. The hydrocracked products processed under mild and severe conditions were distilled to 200°C to remove the naphtha fraction and deasphaltened with pentane. A modified API separation described previously[3] was applied to the remaining fraction for its separation into saturates, monoaromatics, diaromatics, polyaromatics, polar materials and basic compounds.

The polyaromatic fraction is further separated in triaromatics, tetraaromatics and penta+ aromatic ring compounds by HPLC using a Waters-μ-Bondapak NH_2 column (30 cm x 3.9 mm) on a Varian 5000 LC chromatograph. The detector was a Schoeffel SF770 UV spectroflow monitor having an 8 μL cell. Separations were performed at 2 mL/min using solvent gradient as follows: 100% hexane for 10 min followed by a linear gradient to 10% methylene chloride in hexane from 10 to 12 min. The solvent composition remained as such until the sample was eluted completely.

The HPLC effluents were concentrated until adequate signal was obtained from the FID detector when injected in a gas chromatograph. At that point an internal standard (usually acenaphthylene) was added to the solution. The gas chromatographic system consisted of a Perkin Elmer Sigma 1B gas chromatograph controlled by a Sigma 10 console unit. Data collection was performed by a Vista 401 Data Station via a Varian control station. The data station was connected to an Apple computer (Vista-Plus arrangement) in order to perform the quantitation and the molecular weight calculation. Typical runs consisted of temperature programming as follows: initial temperature of 60°C for 2 min, then 10°C/min gradient to a final temperature of 350°C which was held for 4 min or more. The column consisted of a 1/8 inch x 1 m stainless steel tubing packed with 5% Dexsil

300 on Chromosorb W-HP as the stationary phase. The flowrate was 50 mL/min. Injector and FID detector temperatures were 300 and 375°C respectively.

HPLC grade hexane and methylene chloride were purchased from Fisher. Polyaromatic standards were purchased from various suppliers and used without further purification.

RESULTS AND DISCUSSION

HPLC of polynuclear aromatic standards

Retention data of a series of thirty-one polynuclear aromatic standards were obtained to determine the cutpoints between triaromatics, tetraaromatics and penta+ aromatics. As shown in Table 3, the compounds generally are separated according to their number of aromatic rings. However, retention can be influenced by several factors. Substitution is one as demonstrated by pyrene and 1-methylpyrene and by 1,2-benzanthracene and the dimenthylbenz a anthracenes. Addition of saturated rings is also expected to modify the retention times. Condensation of the molecules also affects the retention time. For example retention time increases from pyrene to 9,10-benzophenanthrene to 2,3-benzanthracene as the condensation is less pronounced. Thus, it is obvious that a combination of these factors will cause some overlap between the different fractions. However, in fossil hydrocarbons, polycyclic molecules having a low level of ring condensation such as quarterphenyl are not likely present. Table 3 shows retention data reported as capacity factors which are defined by:

$$k = \frac{t_R - t_o}{t_o}$$

where t_R is the retention time of the compound of interest and t_o is the retention time of a compound that is not retained by the column. These data show that heavy molecules such as coronene have a very strong retention under isocratic conditions. In order to elute the entire sample within a reasonable time a solvent gradient starting after the last cutpoint was used. The gradient was chosen to ensure complete elution of heavy polyaromatic molecules. PAH standards of molecular weight ranging from 202 to 510 g/mol were recovered from the column using this gradient.

Gas chromatographic determination of average molecular weights

Simulated distillation is well known and widely used to estimate the boiling range of an oil sample. This method assumes that hydrocarbons are eluted from a non-polar GC column in order of increasing boiling points. Since the molecular weight generally increases with the boiling point a relation should exist between the molecular weight and the retention time. In this case the relation is logarithmic as shown by a typical calibration curve for aromatic compounds in Figure 2.

Since we can determine the molecular weight associated with a given retention time the calculation of average molecular weight can be done by a method similar to the determination of molecular weight by gel permeation chromatography where the area under a peak is divided into slices, each associated to a narrow molecular weight range. Thus the number average molecular weight is defined by:

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

where N_i is the number of molecules having the molecular weight M_i and

$Area_i$ is the area of a slice i. When using a FID detector the area under a peak is proportional to the quantity of a sample (weight of carbon). Thus, N_iM_i is proportional to the area.

We also considered the influence of structure on retention time. Figure 2 shows that all aromatic compounds tend to fall on the same calibration curve. However, as shown in Figure 3 the retention times can be very different for aliphatic chain compounds, naphthene ring compounds and aromatics. This means that a different calibration curve would be necessary to determine the molecular weights of other classes of compounds. Therefore, it is not possible to determine the molecular weight of the saturates since this fraction includes paraffinic and naphthenic molecules.

GC quantitation

The main purpose of the gas chromatographic run was to quantitate the polyaromatic fractions. HPLC effluents were concentrated to a level where an adequate signal was generated in the FID detector. Quantitation also involves the use of proper standards. A standard solution was prepared from a known amount of similar sample. Then an internal standard is added to both standard and sample (after concentration of HPLC effluents). This internal standard method will allow correction for different injection volumes, for the dilution factor that could be different for each sample and for integration problems resulting from very different peak shapes. A test was done with two known amounts of polyaromatic fractions (one standard and one "sample"). The relative standard deviation for three replicates was 3.5% and the real and experimental values were within the standard deviation range.

Characterization of heavy samples

Table 4 shows the compound-type distribution of the samples before HPLC fractionation[7]. This already shows a general pattern for cracking reactions. It can be seen that under mild conditions only a small portion of asphaltenes is cracked to lighter material. However, the content of saturates increased by a factor of 1.5. This correlates with the fact that all the aromatic fractions decrease thus contributing to the higher saturate and naphtha contents. For the monoaromatic fraction of feed A, if any of these compounds are produced from higher fractions they are not in sufficient quantities (wt %) to compensate for their cracking into saturates (including olefins). Upon severe treatment larger quantities of asphaltenes are converted together with polyaromatics and concentrations of the saturated hydrocarbons increase while the concentration of monoaromatic components still remains at about the same level.

Figure 4 shows a typical HPLC chromatogram showing the distribution of a feed and two hydrocracked products over the three polyaromatic subclasses. The cutpoints between the fractions as determined by the standards are indicated. One must note that the sharp peak towards the end is due to the elution of the components whose retention time is shortened by the solvent gradient. Although the ultraviolet detector response is not quantitative, it is obvious that upon hydrocracking the number of aromatic rings decreases with severity.

The HPLC fractionation allows a more detailed study of the fate of the polyaromatics. Gas chromatography is performed on the HPLC effluents for the determination of average molecular weights as well as the quantitation of the subfractions. It should be noted that solvent evaporation is necessary at this point in order to get a sample which will

be sufficiently concentrated to generate an adequate signal on the detector. In our experiment we concentrated the HPLC effluents to about 0.1-0.2%. This might seem a very high concentration for a FID detector, but since the sample is distributed over a large boiling range (or molecular weight range) the concentration of individual compounds is very low.

Figure 5 shows a typical chromatogram of a polyaromatic sample and the three generated HPLC subfractions. Molecular weight changes can be followed by the retention time variations. In this sample (product A2) it can be seen that the molecular weight is similar for the tri- and tetranuclear aromatics while the penta+ material is heavier. Table 5 shows the quantitation and molecular weight results as determined by GC. The molecular weights corresponding to feed A are in parenthesis because this heavy sample is strongly retained on the column even at high temperatures (see discussion below). This means that the molecular weight calculation is not accurate in this case. For this reason molecular weights were not determined by GC for feed B. The mild hydrocracked products (A1 and B1) were not entirely chromatographed either. However, in this case about 90% of the material eluted from the column and calculated molecular weights can be assumed close to the real values. In any case, one can see how the average molecular weight is reduced as the severity of treatment is increased. Another interesting fact is the difference between the fractions for one sample. For example, A2 and B2 mono- and dinuclear aromatics are significantly different from the higher aromatic molecules. This is expected since upon severe conditions we expect more side chains and naphthene rings to be cleaved from the main structure leaving the aromatic structure with only short substitution and few saturated rings.

However, for mild hydrocracking (A1 and B1) the average molecular weights of mono- and diaromatics are closer to those of the other fractions. This probably means that mild conditions are not sufficient to cleave side chains and naphthene rings after cracking of large molecules.

Table 5 also shows the quantitation results on a weight and mole basis respectively. The mono-, di- and polyaromatic values are taken from Table 4. The total polyaromatic fraction is the total fraction prior to HPLC separation and the amount indicated in this column was determined by solvent evaporation techniques. This quantity should be the sum of the three HPLC subfractions. It can be seen that for the feeds the individual amounts do not add up to the total amount. This is explained by the fact that the feed consists of heavy material which cannot be entirely chromatographed on the GC column because of its high boiling point (or low vapour pressure). This experiment could only account for about 50% of the material. Although we could not obtain the quantitative values for the feeds, the results indicate the molecular weight distribution of the material in the polyaromatic subfractions. However, for the mild hydrocracked products (A1 and B1), about 90% of the material was eluted from the column while 100% of the severe hydrocracked samples was eluted.

In any case one can see the general trend in the proportions of the different fractions upon treatment. In the polyaromatic subfractions if it is assumed that the material in the feed is mostly penta+ aromatics, we see that upon mild treatment this subfraction is reduced while the trinuclear and mainly the tetranuclear components increase. When considering all fractions it can be seen that the total polyaromatic subfractions decrease while the amount of the mono- and diaromatic fractions remains at the same

level. This is where the calculation on a mol/100 g basis could be important. Most of the trends observed from mild to severe conditions with the quantitation on a weight basis are similar to the calculation on a mol/100 g basis. However, on a weight basis, the amount of diaromatic fraction decreases or remains at the same level. But when looking at the results on a molar basis we see that the number of molecules increases (see B1 and B2), i.e., a larger number of molecules of lower molecular weight is produced upon severe treatment. These molecules come from the higher aromatic fractions that have been extensively cracked with possibly some hydrogenation. Thus, the two methods of calculating the quantitites of each fraction may be important in a detailed comparison of samples.

CONCLUSIONS

This work shows how an HPLC separation added as a supplementary step to the usual hydrocarbon-type separation provides additional information on the fate of the polynuclear aromatic subfractions. The use of gas chromatography on the HPLC effluents allowed a fast quantitation as well as a rapid molecular weight determination especially when we consider the small amounts of material involved in an HPLC run. Combining results from both calculations has shown the differences in these fractions when quantitation on either a weight or a mole basis is used. However, there is a limitation to these methods because one must be sure that the material is entirely chromatographed to obtain accurate results.

REFERENCES

1. Hanes, W.E., Ward, C.C. and Sugihara, J.M. Proc. API Div. of Refining, 1971, 51, 375.
2. Jewell, D.M., Albaugh, E.W., Davis, B.E. and Ruberto, R.G. Ind. Eng. Chem. Fundam., 1974, 13, 278.
3. Sawatzky, H., George, A.E., Smiley, G.T. and Montgomery, D.S. Fuel, 1976, 55, 16.
4. Chmielowiec, J., Beshai, J.E. and George, A.E. ACS Preprints Div. Pet. Chem., 1980, 25, 532.
5. Chmielowiec, J., Beshai, J.E. and George, A.E. Fuel, 1980, 59, 838.
6. Lunin, G., Silva, A.E. and Denis, J.M. Chemistry in Canada, March 1981, p. 17.
7. Ahmed, S.M. and Sawatzky, H. Division Report 82-56(CF), 1982, Energy, Mines and Resources Canada, Ottawa.

TABLE 1

PROPERTIES OF THE HYDROCRACKING FEEDS

Properties	Crude oil vacuum bottom A	Crude oil vacuum bottom B
Specific gravity	1.023	1.019
Sulphur, wt%	4.05	4.34
Ash, wt%	0.035	0.030
Asphaltenes (n-pentane insolubles), wt%	17.4	13.8
Benzene insolubles	4.6	6.4
Carbon, wt%	84.91	85.02
Hydrogen, wt%	9.87	10.17
Nitrogen, wt%	0.21	0.26
Vanadium, ppm	144	102
Nickel, ppm	30	25
Iron, ppm	38	28

TABLE 2

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

Sample	Pitch Conversion wt%	Naphtha IBP-200°C	200-350°C	Maltenes above 350°C	Asphal-tenes
Feed A	-	nil	nil	82.6	17.4
A1	34.3	3.8	9.3	69.6	15.7
A2	85.2	14.3	33.9	40.5	8.8
Feed B	-	nil	nil	86.2	13.8
B1	38.6	4.7	11.3	67.9	14.8
B2	85.8	16.1	33.7	44.7	4.2

TABLE 3

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

Compound	k	Compound	k
Acenaphthene	0.4	9-Phenylantracene	2.35
Terphenyl	0.55	9,10-Benzophenanthrene	2.4
Fluorene	0.75	7,12-Dimethylbenz(a)anthracene	2.5
2-Methyl fluorene	0.8	9,10-Dimethylbenz(a)anthracene	2.65
Acenaphthylene	0.8	2,3-Benzanthracene	2.75
1,2,3,4-Tetrahydrofluoranthene	0.8	1,2-Benzanthracene	2.8
3-Methylphenanthrene	0.9	3-Methylcholanthrene	3.35
Phenanthrene	0.95	3,4-Benzopyrene	3.45
2-Methylphenanthrene	1.1	9,10-Dibenzylanthracene	3.8
4,5-Methylenephenanthrene	1.1	3,4-Benzofluoranthene	4.05
3,6-Dimethylphenanthrene	1.2	11,12-Benzofluoranthene	4.1
Pyrene	1.3	Perylene	4.2
1-Methylpyrene	1.35	Dibenzo(a,h)anthracene	6.7
Tetraphenylethylene	1.45	1,2,3,4-Dibenzanthracene	6.9
2,3-Benzofluorene	2.05	1,2,5,6-Dibenzanthracene	7.0
		Coronene	11.7

TABLE 4

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

Sample	Saturates	Mononuclear aromatics	Dinuclear aromatics	Polynuclear aromatics	Polar compounds	Basic compounds	Asphaltenes
Feed A	14.3	11.8	13.1	22.9	12.0	7.4	17.4
A1	23.23	11.43	12.00	16.85	12.44	2.82	15.7
A2	47.92	12.80	9.0	9.97	5.13	0.97	8.8
Feed B	19.2	11.7	14.0	24.5	11.6	5.0	13.8
B1	30.06	14.28	9.90	16.87	10.93	1.90	14.8
B2	52.81	13.78	9.89	9.64	6.19	0.30	4.21

TABLE 5

COMPOUND-TYPE DISTRIBUTION IN AROMATIC FRACTIONS (WT%)

Samples		Mononulear aromatics	Dinuclear aromatics	Total polynuclear aromatics*	Trinuclear aromatics	Tetranuclear aromatics	Penta+ aromatics
Feed A	wt%	11.8	13.1	22.9	0.9	3.8	6.9
	MW	-	-	(311)	(309)	(319)	(298)
	moles**	-	-	(7.3)	(0.3)	(1.2)	(2.3)
A1	wt%	11.43	12.00	16.85	3.3	9.4	2.4
	MW	-	261	289	270	284	305
	moles**	-	4.6	5.8	1.2	3.3	0.8
A2	wt%	12.80	9.00	9.97	1.3	5.7	3.0
	MW	189	211	252	246	255	310
	moles**	6.4	4.3	4.0	0.5	2.2	1.0
Feed B	wt%	11.7	14.0	24.5	-	-	-
	MW	-	-	-	-	-	-
	moles**						
B1	wt%	14.28	9.90	16.87	1.7	8.6	5.2
	MW	242	264	292	285	269	295
	moles**	5.9	3.8	5.8	0.5	3.2	1.8
B2	wt%	13.78	9.89	9.64	2.4	5.9	1.3
	MW	-	205	248	233	273	270
	moles**	-	4.8	3.9	1.0	2.2	0.5

* Total polynuclear aromatics = total fraction before HPLC = tri + tetra + penta+

** Moles per 100g x 10^{-2}

FIGURE CAPTIONS

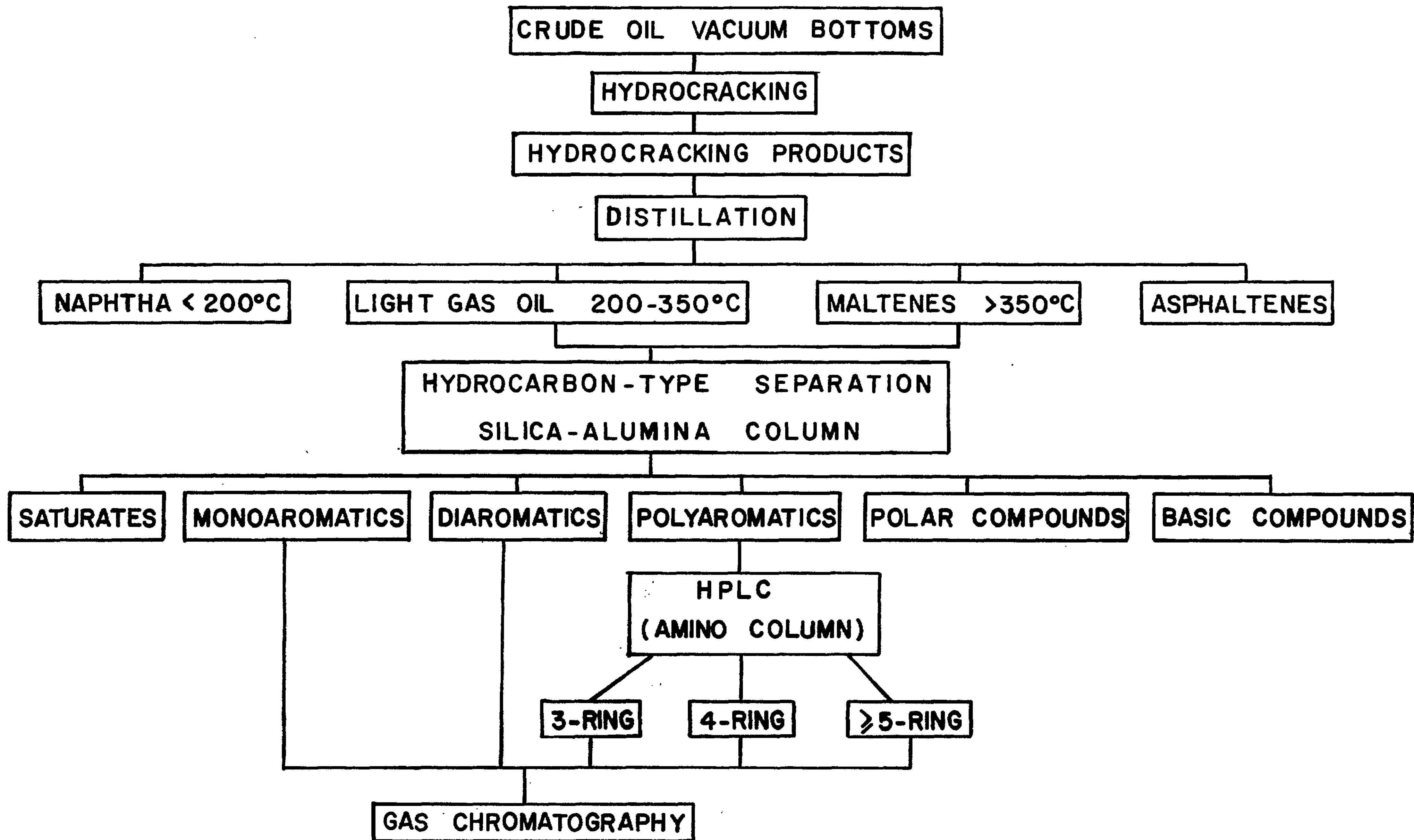
Figure 1 Separation and characterization schematics

Figure 2 Molecular weight calibration curve with various aromatic structure.
(● 3 aromatic rings, ■ 4 aromatic rings and ▲ 5 or 6 aromatic rings)

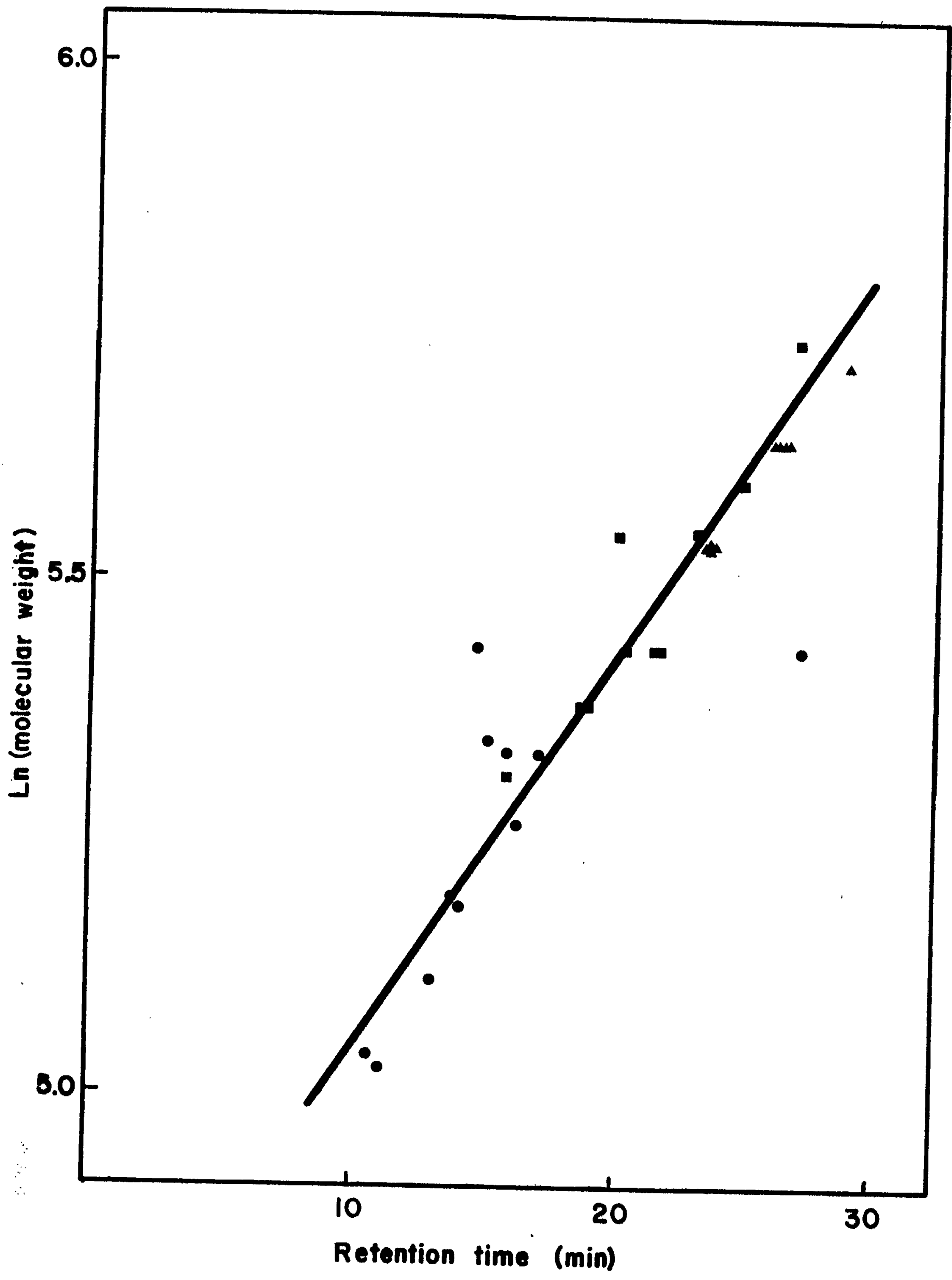
Figure 3 Relation between molecular weight and retention time for various compound types.
(● saturates, ▲ naphthenes, and ■ aromatics)

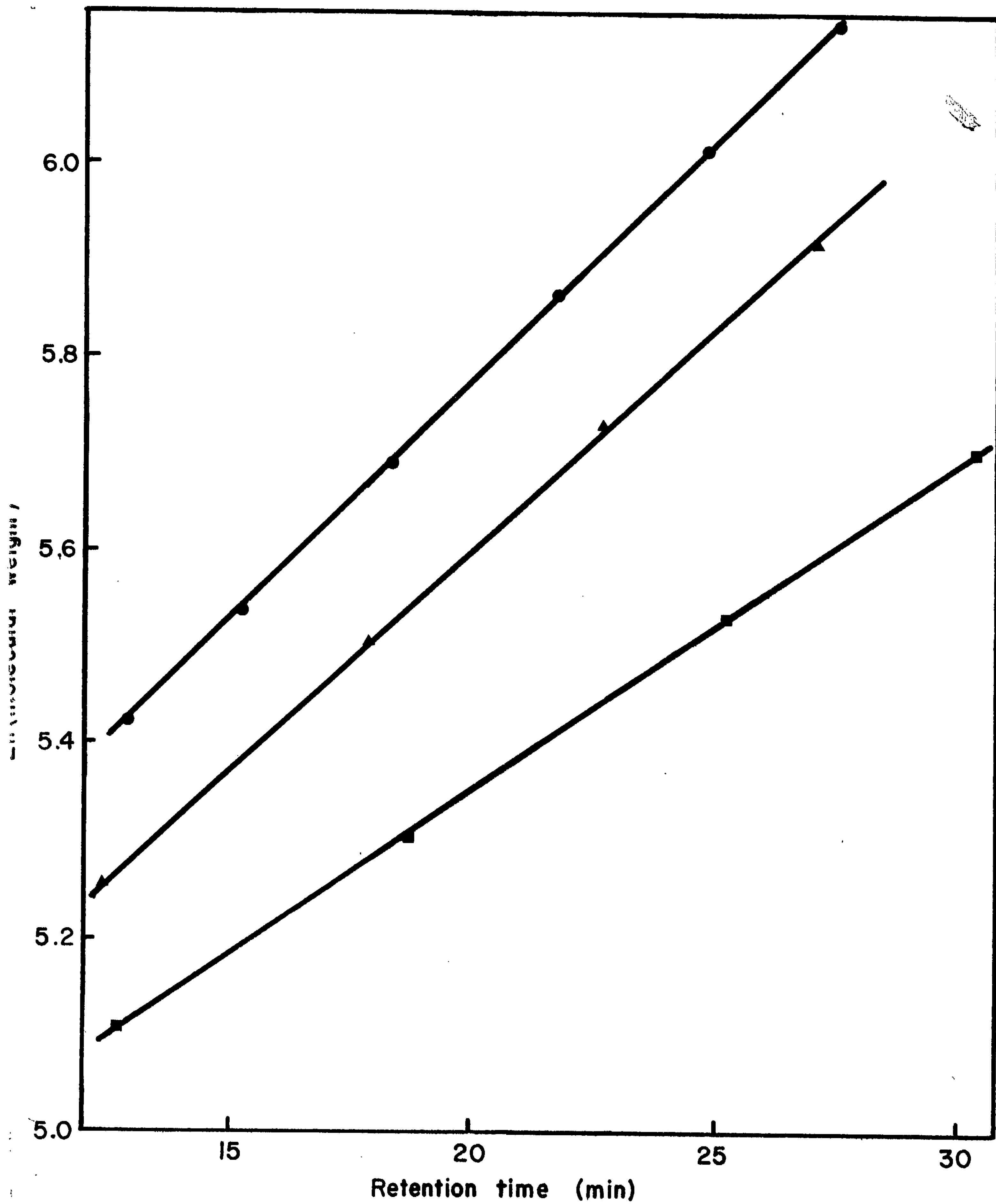
Figure 4 Example of HPLC chromatograms of one feed and its hydrocracked products obtained under mild (1) and severe (2) conditions.

Figure 5 Example of GC chromatograms of a polyaromatic fraction and the three HPLC subfractions obtained.
(3 = triaromatics, 4 = tetraaromatics and 5+ = penta+ aromatics)

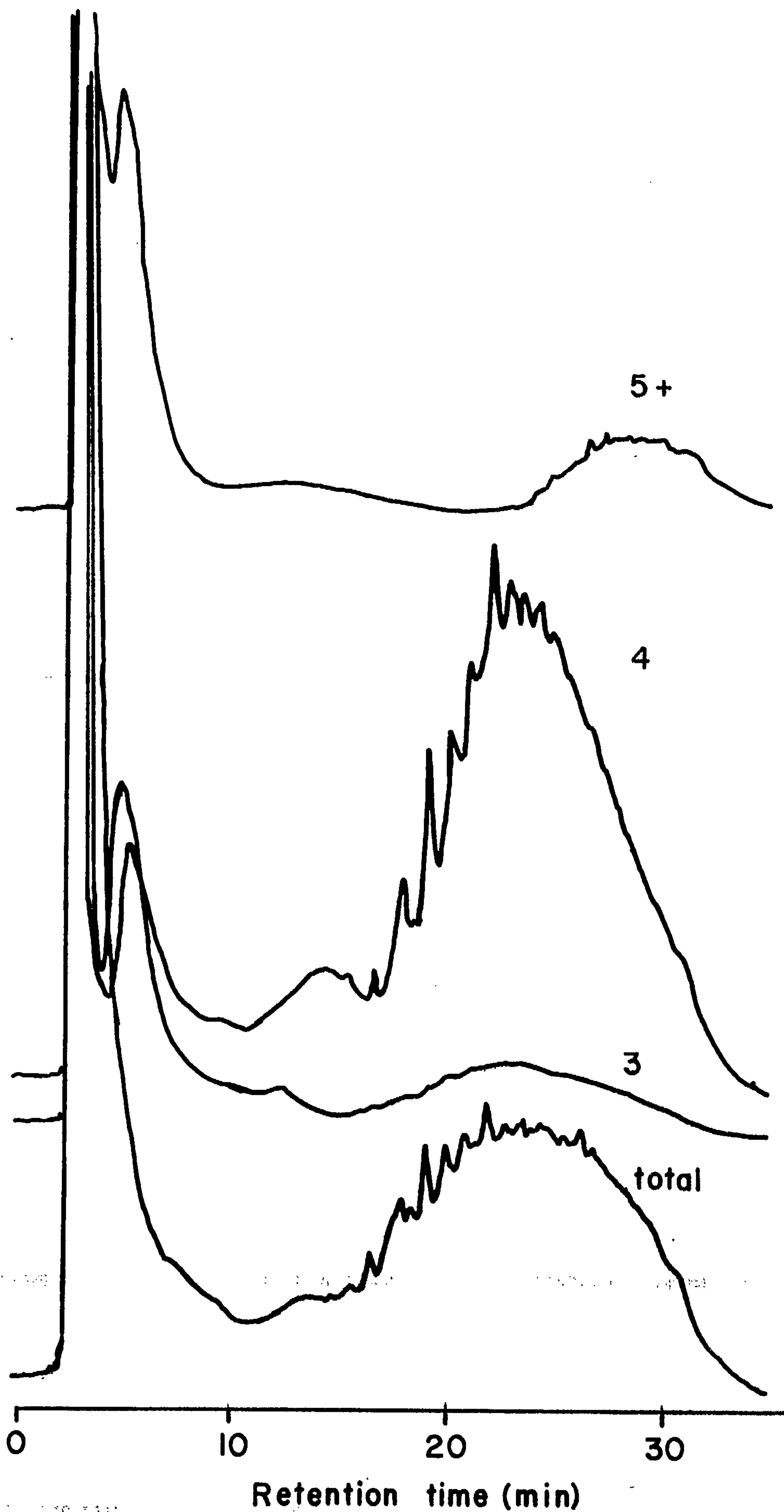


CRUDE OIL VACUUM BOTTOMS
HYDROCRACKING
HYDROCRACKING PRODUCTS
DISTILLATION
NAPHTHA < 200°C
LIGHT GAS OIL 200-350°C
MALTENES >350°C
ASPHALTENES
HYDROCARBON-TYPE SEPARATION
SILICA-ALUMINA COLUMN
SATURATES
MONOAROMATICS
DIAROMATICS
POLYAROMATICS
POLAR COMPOUNDS
BASIC COMPOUNDS
HPLC
(AMINO COLUMN)
3-RING
4-RING
≥5-RING
GAS CHROMATOGRAPHY


6.0
5.5
5.0
Ln (molecular weight)
10
20
30
Retention time (min)


6.0
5.8
5.6
5.4
5.2
5.0
15
20
25
30
Retention time (min)

2
1
feed
20
16
12
8
4
0
Retention time (min)


5 +
4
3
total
0
10
20
30
Retention time (min)