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Rapid hydrocarbon type separation of vacuum residues

Veda Ramaswamy, Vimal Kothiyal, Indra D. Singh, and Rajamani Krishna

Indian Institute of Petroleum, Dehra Dun 248 005, India

Rasche Trennung der Kohlenwasserstofftypen von Vakuum-Rückständen

Summary. A simple and fast column chromatographic procedure for the separation of vacuum residues into saturates, mono-, di-, polyaromatics and polars has been standardized using silica-alumina-bauxite adsorbents and gradient elution with n-pentane, benzene, and methanol. The cut points have been monitored employing ultraviolet and infrared spectroscopy. The method is applicable for preparative separation of short residues from processed products.

Introduction

For efficient and successful utilization of petroleum residues, for example by thermal cracking, it is necessary to have detailed information on its compositional and structural aspects. For a detailed characterization of petroleum residues, it is essential to separate the residues into fractions, which in turn can be characterized by various available instrumental analytical techniques. The requirement in such hydrocarbon-type separation is for a faster, cheaper and accurate method. Conventional techniques of liquid chromatography have extensively been used for the separation of petroleum distillates [1–5] on preparative scale for quantification and further characterization by ultra violet (UV), infra red (IR), nuclear magnetic resonance (NMR) and mass spectrometric (MS) techniques. The development of high-pressure liquid chromatography (HPLC) has brought about a significant advancement in the separations of distillates and residues from crude oils. The extension of these methods to include short residues from crude oils and processed products yield results of limited accuracy. Mckay et al. [6] have used the USBM-API method [2] for separation of 675 °C+ petroleum residue, but this method is very time consuming and requires excessively large amount of solvents. Sawatzky et al. [7] have developed a faster column chromatography method with relatively more sophistication (e.g. heated column and pumps) for separating distillates as well as residues. A rapid HPLC method for the separation of vacuum distillates as well as atmospheric and vacuum residues into saturates, aromatics and polars have been reported by Bollet et al. [8]. Grizzle et al. [9] have reported a preparative HPLC method for the separation of different distillates and residues from a crude oil into acids, bases, saturates mono-, di- and polyaromatics. They have also separated compound-types into acids and bases.

Centrifugal liquid chromatography with refractive index and UV detectors has been used by Shiroto et al. [10] for separating deasphalted oil obtained from vacuum residues and heavy crudes into saturates, aromatics and polar compounds. Recently, an automated HPLC method has been developed for the determination of saturates, aromatics and resins in deasphalted crude oil residues (343 °C+) using an improved flame ionization detector [11]; this method is, however, not preparative. Conventional liquid chromatography, while affording separation on a sufficiently large scale, has the added advantage of simplicity, cost and a preparative scale to enable gross structural and spectroscopic characterization of the subfractions obtained. Yoshida et al. [12] have used silica-alumina dual column chromatography for separating atmospheric residues (343 °C+) and their corresponding visbroken residues into hydrocarbon types. This method, however, when applied to short residues, does not yield satisfactory results. They have not considered the material irreversibly adsorbed on the column, and in the case of short residues, such materials can be significant in amount.

In the present paper, a classical column chromatographic separation procedure for separation of maltenes obtained from short residues (feeds as well as visbroken products) into the hydrocarbon types is reported. The cutpoints for different types of compounds were monitored by ultraviolet and infrared spectroscopic techniques. Finally, a fast and simple method has been achieved for a fairly accurate separation of saturates, monoaromatics, diaromatics, polyaromatics and polars from the short residues.

Experimental

The separation scheme for the short residue 500 °C+ is illustrated in Fig. 1. A sample of short residue from Arab Mix crude obtained from a refinery was used for standardization of the procedure. Asphaltenes, which is defined as the 'n-pentane insolubles' were precipitated from 20 g of short residue with 1 l of n-pentane. The asphaltenes were filtered after shaking the sample in n-pentane for 1 h and the solution kept for 16 h. The maltenes obtained after evaporating n-pentane from the filtrate were used for adsorption chromatography. A column packed with silicagel-alumina gel-bauxite was used to separate the maltenes into saturates, monoaromatics, diaromatics, polyaromatics and polar compounds. The column is 2 cm i.d. and 150 cm long glass

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Offprint requests to: R. Krishna

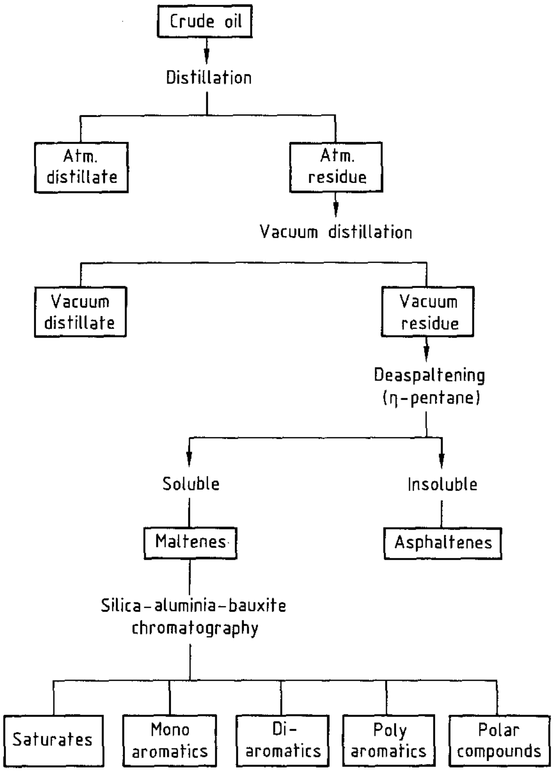

Fig. 1. Separation scheme

Table 1. Elution scheme for the separation of maltenes into hydrocarbon types

Solvent	Volume (ml)
1 n-Pentane	200
2 5%-Benzene in n-pentane	300
3 20% Benzene in n-pentane	300
4 Benzene	300
5 Methanol	200
Total	1300

tubing fitted with a 500 ml eluant reservoir at the top and a stop cock (4 mm bore) at the bottom to regulate the flow rate. The bottom 60 cm of the column was packed with fully activated (4 h at 180° ± 10 °C) 28 – 200 mesh silica gel (Fisher grade 12). Above the silica-gel layer the column was packed with a 65 cm layer of fully activated (16 h at 400 °C) 80 – 200 mesh Alcoa-F 20 alumina gel. Above the alumina column was packed a 6 cm layer of fully activated bauxite (16 h at 500 °C). A flow rate of 3 – 5 ml/min was regulated using nitrogen. The method employs a sample to gel ratio of 1:100. 40 ml of n-pentane is used for prewetting the column. 3 ± 0.2 g of sample is diluted with 10 ml of n-pentane and charged to the column reservoir and the container is rinsed three times with 10 ml n-pentane. Table 1 gives the volume and polarity of solvents used for the gradient elution of different types of compounds.

Results and discussion

The asphaltenes separated by n-pentane is found to be 19.3 wt% and the repeatability of the deasphaltening procedure was found to be satisfactory (5% of the amount present for triplicate data). The maltenes, which are further subdivided into saturates, monoaromatics, diaromatics, polyaromatics and polar compounds are quantitative with very small cross-contamination and the separations can be achieved in the absence of any spectroscopic monitoring as it is based on the mass yields of fractions corresponding to elution volume range 0 – 225, 225 – 500, 500 – 775, 775 – 1075 ml and the soxhlet extract of the adsorbed material, respectively.

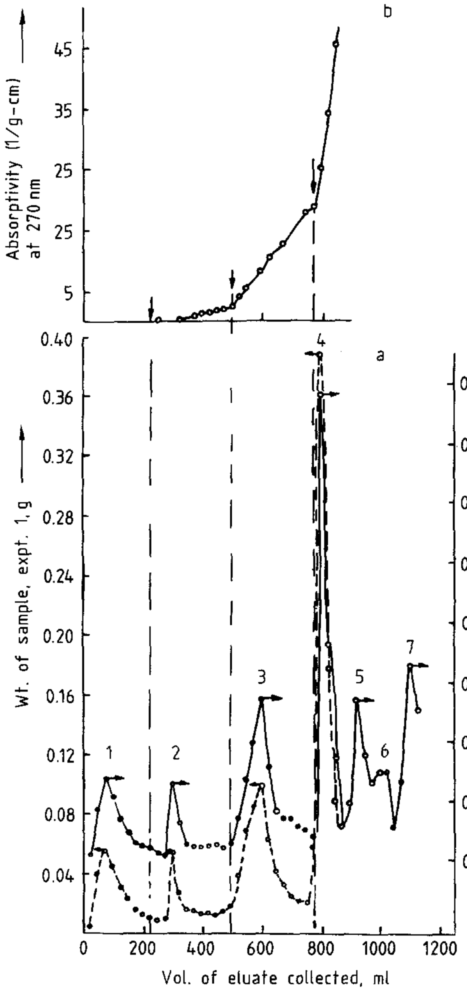

Fig. 2. a, b. Silica alumina bauxite chromatographic separation of maltenes from a 500 °C + vacuum residue: **a** adsorptogram showing the degree of repeatibility obtainable; **b** ultraviolet spectral study of subfractions to decipher the cutpoints

Evaluation of the method

A fixed volume of the eluant (25 ml) was collected directly from the bottom of the column and individually analyzed after solvent removal in nitrogen atmosphere. The weight recovered is plotted against the total volume of the eluted solvent. The plot so obtained (Fig. 2a) shows seven different peaks corresponding to elution volume range 0 – 225 ml (peak 1), 225 – 500 ml (peak 2), 500 – 775 ml (peak 3), 775 – 875 ml (peak 4), 875 – 975 ml (peak 5), 975 – 1050 ml (peak 6) and 1050 – rest (peak 7). The first three peaks correspond to saturates, monoaromatics, diaromatics, respectively, and the next four peaks correspond to polyaromatics and polar compounds. Some maltenes (polar hydrocarbons) which were irreversibly adsorbed on the gel were extracted by soxhlet extraction with benzene (fraction 8). Saturated hydrocarbons (peak 1/fraction 1) show a relatively long tailing which is likely due to the higher concentration of cycloparaffinic molecules in the sample. The peak for mononuclear aromatics shows a sharp elution of the species with 5% benzene in n-pentane. Again the band for dinuclear aromatics is relatively broad which is due to the presence of different types of two-ring aromatic structures. However, the polarity of eluant used for the elution of diaromatics (20% benzene in n-pentane) seems to be quite suitable for satisfactory elution of the diaromatic structures.

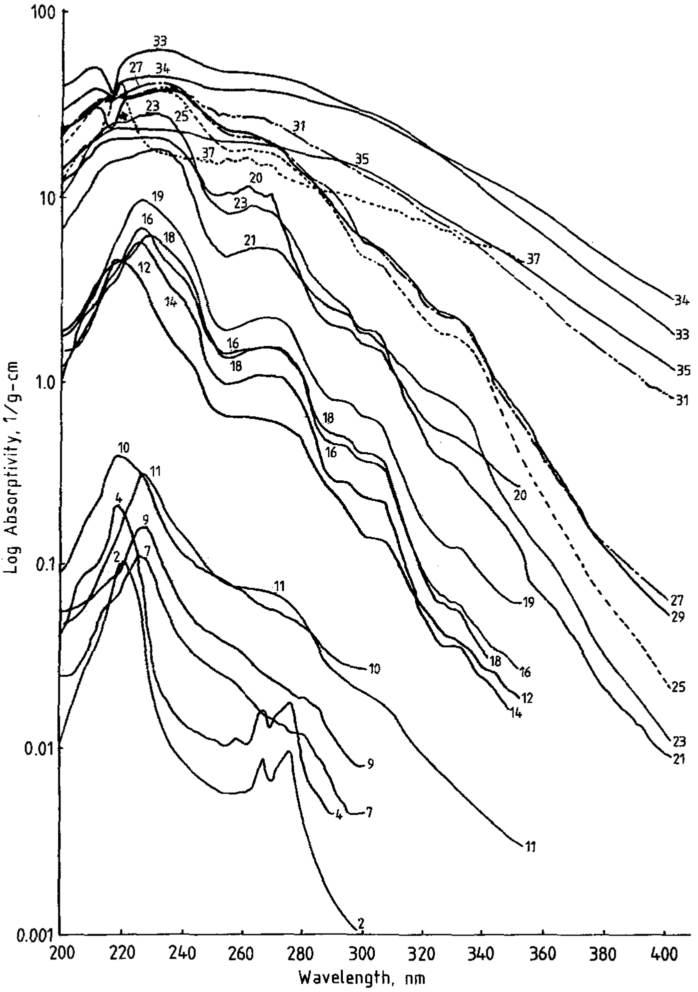

Fig. 3. Ultraviolet spectra of the subfractions from the column chromatographic separation

The peak for polyaromatics (peak 4/fraction 4) is relatively very sharp and the concentration of these structures is also very high. The last three peaks are characterized by both ultraviolet and infrared spectroscopic analysis. Figure 2a also shows the adsorptogram from two individual separations on the same non boiling short residue reflecting the good repeatability obtainable in separations by this method.

Evaluation using UV and IR spectral techniques

The UV absorptivity of all the individual fractions were determined at 270 nm employing a Shimadzu UV-VIS spectrophotometer (Model-UV 240). From the plot of elution volume vs. the absorptivity values (Fig. 2b) the cut points for saturates, monoaromatics, diaromatics and polyaromatics were taken on the basis of the criteria used in literature [1]. For saturates, the absorptivity is taken as < 0.05, for monoaromatics: $0.05 < a < 5.4$, for diaromatics: $5.4 < a < 37.2$ and for polyaromatics: $a > 37.2$. It can be seen from Fig. 2 that the cutpoints on the basis of absorptivity values at 270 nm confirm that the validity of the elution of different peaks in the adsorptogram is very good. Figure 3 shows the UV absorption in the region 200–400 nm (log absorptivity) of various 25 ml fractions collected. The absorptivity values for fractions after an elution volume of 875–900 ml (after peak 4 in Fig. 2) do not show any regular trend which is likely due to the contamination of polar compounds of different polarity as well as different condensed aromatics. Hence, qualitative infrared analysis of these individual 25 ml fractions (from elution volume range 875–1150 ml, experiment number 2) and the bulk fraction constituting peak 5, 6 and 7 (experiment number 1) of Fig. 2 and the Soxhlet extract, were performed to monitor the cutpoints for polyaromatics and polar compounds. Table 2 gives the absorbances of various bands due to polar compounds per unit concentrations per mm path length and Fig. 4 shows the infrared spectra of the fractions 4–7 (corresponding to peaks 4–7 in Fig. 2a) and the Soxhlet extract in the region 4000–3000 cm^{-1} and 2000–1500 cm^{-1}. The presence of phenols (3500 and 3540 cm^{-1}), pyrroles (3480 cm^{-1}) and carboxylic acids (1700 – 1705 cm^{-1}) are indicated in all the four fractions corresponding to peaks 5, 6, 7 and Soxhlet extract. While fractions 5 and 6 contain relatively less concentration of phenols and pyrroles and relatively high concentration of weaker acids, fraction 7 which is eluted with methanol shows a higher concentration of polar materials. The Soxhlet extract (fraction 8) showed relatively higher concentration of polar compounds by IR (Table 2) and this extract together with fraction 7 eluted with methanol can be designated as polar compounds (Table 3).

Table 2. Quantitative IR analysis of the separated polyaromatic and polar fractions for heteroatomic moieties

Peak no	Elution volume range, ml	Absorptivity, l/g cm at			
		3500 cm^{-1}	3540 cm^{-1}	3480 cm	1700 cm^{-1}
5	876 – 975	0.0072	0.0113	0.0222	0.7121
6	975 – 1075	0.0119	0.0127	0.0275	0.7484
7	1075 – rest	0.0173	0.0206	0.1295	0.0957
8	Soxhlet extract	0.0366	0.0252	0.096	0.6461

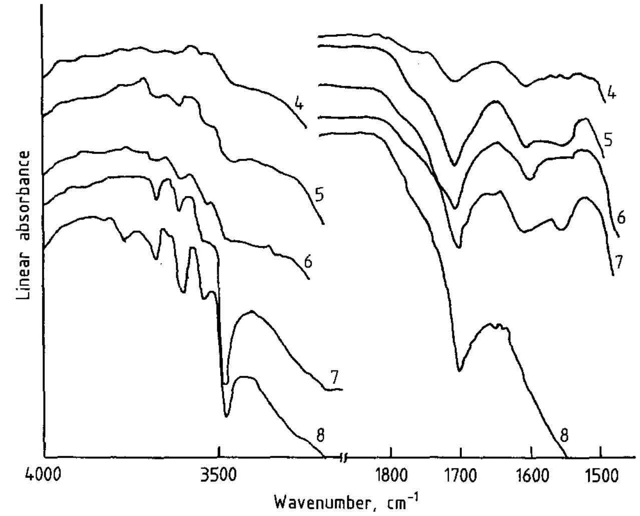

Fig. 4. Infrared spectra of some typical fractions from the column chromatographic separation

Table 3. Compositional data of the short residue (500 °C+) by the standardised separation method

Fraction number	Compound types	Concentration (wt%)	
		Present method	Silica bauxite chrom. after pretreatment of maltenes
1	Saturates	6.47	6.36
2	Monoaromatics	5.11	49.10
3	Diaromatics	14.76	
4	Polyaromatics	24.94	
5	Polar compounds	29.39	25.21

The compositional data thus obtained by the present method agree very well with the separation by silica-bauxite chromatography of maltenes after pretreatment with resins thus showing the advantages of shorter time of separation as well as detailed information on aromatics, (Table 3). The polar compounds (25.2 wt%) obtained are the sum of acids and bases separated by ion-exchange chromatography and the polar material separated on silica bauxite chromatography. The polar material obtained by the present method is more than that obtained by the other method (Table 3). The infrared spectra of total aromatics (49.1 wt%) shows the presence of polar material which explains the lower content of polar material by the method.

The agreement shows and justifies the cutpoint monitoring by UV, IR and the adsorptogram. The method is applicable to short residues boiling above 500 °C and is quantitative with a 95–96 wt% recovery of the sample and is fast. The mass yields of the elution volume ranges 0–225 ml, 225–500 ml, 500, 775 ml, 775–1075 ml correspond to saturates, mono-, di- and polyaromatics, respectively. The elution volume after 1075 ml together with the Soxhlet extract of the residual material in the column yielded the polar compounds in short residues.

Conclusions

A fast, accurate and cheap method for preparative separation of short residues from crude oils and processed products is standardized. A slight contamination of heteroatomic functionalities (weaker acids) in polyaromatics is observed. The time taken for one separation is nearly 8 h and 3–4 columns can be operated simultaneously by one operator.

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