

ASPHALTENE CHARACTERIZATION BY A
NONSPECTROSCOPIC METHOD

Manuel A. Francisco
and
James G. Speight

Exxon Research and Engineering Co.
Clinton Township, Route 22 East
Annandale, New Jersey, U.S.A. 08801

INTRODUCTION

The emergence of the heavier crude oils as refinery feedstocks has become the accepted norm over the last decade (1). It is, however, a property of these feedstocks to be rich in asphaltenes (2,3,4) which are not very amenable to refinery processes and are usually responsible for coke lay-down and for catalyst deterioration (3,4).

The conventional definition of asphaltenes is based on the solution properties of petroleum residua in various solvents (5,6,7). This generalized concept has been extended to fractions derived from other carbonaceous sources, such as coal and oil shale. Thus, there are "petroleum asphaltenes", "coal liquid asphaltenes", "coal tar asphaltenes", "shale oil asphaltenes", "tar sand bitumen asphaltenes" and the like. With this extension, there has followed considerable scientific effort to further define asphaltenes in terms of molecular structures (9,10,11).

Nevertheless, it must always be recognized that asphaltenes (from whatever the source) are, in fact, a solubility class (Figure 1) and that the definition is, in fact, an operational one; that is, asphaltenes are soluble in benzene and insoluble in pentane. Usually, for virgin petroleum samples, the residuum is completely soluble in benzene. However, with heat-soaked samples or coal derived liquids, the benzene insolubles can be appreciable.

A more recent concept (14) extends the solubility classification of asphaltenes and involves, initially, a consideration of molecular weight vs. polarity for the molecular types found in petroleum residua and/or heavy oils (Figure 2). The polarity scale may be in definable arbitrary units, such as relative adsorptive strength on a solid, e.g. Attapulugus clay and/or silica gel (15), or by solubility in a variety of solvents of increasing polarity as practiced on separation of coal liquid fractions (13); this scale is thus a molecular weight-independent portion of the solubility parameter. For any particular

precipitating medium, say n-heptane, the precipitated asphaltenes will, therefore, consist of less polar materials of higher molecular weight and more polar materials of lower molecular weight; with n-pentane as the precipitating agent, both less polar and lower molecular weight materials are included in the precipitate and the total amount of precipitate increases (16,17). The concept also allows for a polarity range within the various asphaltenes where varying heteroatom (nitrogen, oxygen, and sulfur) contents of the petroleum asphaltenes or variations in the source (and method of preparation) that would be expected to influence polarity (18,19,20).

The present communication describes an extension to the concept of asphaltene polarity by the delineation of petroleum asphaltenes as a collage of functional types using ion-exchange chromatography.

EXPERIMENTAL

1. Feedstock

Arabian heavy crude oil vacuum (950°F+) residuum was used as the feedstock for all of these investigations.

2. Ion-exchange Fractionation

Separation of the feedstock by ion-exchange resins was carried out using a feedstock/solid ratio ~ 0.05* and the product fractions (Figure 3) were designated (a) bases; (b) acids; (c) neutral polars; and (d) neutral nonpolars.

3. Deasphalting

Separation into asphaltene and deasphalted oil fractions was achieved by mixing the fraction with n-heptane (1 gm. fraction:40 ml. n-heptane) at room temperature for 16 hr. with agitation. At the end of this time, the insoluble asphaltenes were separated by filtration and washed with fresh n-heptane (200 ml:1 gm. asphaltenes). The asphaltenes were "purified" from adsorbed material by dissolution in toluene (10 ml:1 gm. asphaltenes) and precipitated with n-heptane (80 ml:1 ml toluene); any soluble material was recovered and added to the deasphalted oil.

*The feedstock/resin ratio was computed on the basis of the number of active sites on the resin and is, therefore, subject to change and depends upon the nature of the resin.

4. General Techniques

Solvents were removed from the products by means of a Rotovap (60°C/40 mm Hg.) and final vestiges were removed by "drying" the products in vacuo (100°C/20 mm Hg).

RESULTS AND DISCUSSION

The application of chromatographic adsorption techniques to investigate functional and/or structural types in asphaltenes is not new (21,22) but problems of precise identification may be limited by the incomplete recovery of the asphaltene from the adsorbent, particularly when the functionalized ion-exchange adsorbents are employed. However, ion-exchange fractionation of whole feedstocks has been cited to result in an overall more complete recovery of the asphaltenes (23).

In the present work, it has been found preferable to fractionate the whole residuum by ion-exchange chromatography not only to build up a picture of the asphaltenes in terms of functional types but also to note the overall distribution of functional types in the whole feedstock as well as the nuances of the deasphalting technique.

Thus, fractionation of Arabian heavy crude oil vacuum residuum by ion-exchange chromatography produced a series of fractions (Table 1) of varying functionality which could also be differentiated by infrared spectroscopy (Figure 4).

Subsequent heptane-deasphalting of these fractions not only allows cross-referencing of the two techniques but also allows the deasphalted oil and the asphaltenes to be represented on the basis of the different functionalities (Figures 5 and 6).

Obviously, the chemistry and structural features of petroleum asphaltenes will be dictated by the distribution of functional/structural types separated as an artifact of the deasphalting technique. This makes the representation of the structure/functionality of these carbonaceous constituents of petroleum by "average" structures very difficult to conceive (11,18).

Such carbonaceous materials are, therefore, best represented by a series of structural and/or functional types that are best fitted to describe their chemistry/reactivity.

LITERATURE CITED

1. "The Future of Heavy Crude Oil and Tar Sands", R. F. Meyer and C. T. Steele (editors), McGraw-Hill, New York, 1981.
2. J. G. Speight, "Asphaltenes as an Organic Natural Product and their Influence on Crude Oil Properties", presented at the Div. of Geochemistry, Am. Chem. Soc., New York, August 23-28, 1981.
3. J. G. Speight, "Th Desulfurization of Heavy Oils and Residua", Marcel Dekker Inc., New York, 1981.
4. M. L. Gorbaty and J. G. Speight, "The Characterization of Heavy Oils and Residua", paper presented at the 28th IUPAC Conference, Vancouver, B.C., Canada, August 16-21, 1981.
5. "Annual Book of ASTM Standards; American Society for Testing and Materials, Philadelphia, Part 24, Standard No. D-2006", 1975, withdrawn 1976.
6. "Annual Book of ASTM Standards; American Society for Testing and Materials, Part 15, Proposed Standard for Asphalt Composition".
7. "Standards for Petroleum and Its Products, Standard No. 1P 143/57", Institute of Petroleum, London.
8. J. G. Speight, R. B. Long and T. D. Trowbridge, Preprints, Am. Chem. Soc. Div. Fuel Chem., 1982, 27, (3/4), 268.
9. J. G. Speight, Applied Spectroscopy Reviews, 1972, 5, 211, and references cited therein.
10. T. F. Yen, PREPRINTS, American Chemical Society, Division of Petroleum Chemistry, 1972, 17(4), F102, and references cited therein.
11. J. G. Speight, Preprints, Am. Chem. Soc., Div. Petrol. Chem., 1979, 24(4), 910.
12. J. D. Brooks and G. H. Taylor, Chem. & Phys. of Carbon, Vol. 4, 243 (1968) Marcel Dekker, New York.
13. M. Farcasiu, T. O. Mitchell, D. D. Whitehurst, A.C.S. Div. Fuel Chemistry Preprints, Vol. 21, No. 7, 11, (1976).
14. R. B. Long, Preprints, Am. Chem. Soc., Div. Petrol. Chem., 1979, 24(4), 891.

15. L. W. Corbett, *Anal. Chem.* 41, 576 (1969).
16. D. L. Mitchell, J. G. Speight, *Fuel*, 1973, 52, 149.
17. L. W. Corbett, and U. Petrossi, *Ind. Eng. Chem. Prod. Res. Dev.* 17, 342 (1978).
18. J. G. Speight and R. B. Long in "Atomic and Nuclear Methods in Fossil Energy Research", R. H. Filby (editor), Plenum Press, New York, 1982, 295.
19. J. G. Speight and S. E. Moschopedis in "The Chemistry of Asphaltenes", J. W. Bunger and N. C. Li (editors), Am. Chem. Soc., Adv. in Chem. Series No. 195, Washington, DC, 1981, 1.
20. J. G. Speight, "The Structure of Petroleum Asphaltenes", Information Series No. 81, Alberta Research Council, 1978; and J. G. Speight, "Geochemical Influences on Petroleum Constitution and Asphaltene Structure" presented at the Div. of Geochem., American Chemical Society, Washington, DC, September, 1979.
21. M. L. Selucky, S. S. Kim, F. Skinner and O. P. Strausz in "The Chemistry of Asphaltenes", J. W. Bunger and N. C. Li (editors), Am. Chem. Soc., Adv. in Chem. Series No. 195, 1981, 83.
22. J. F. McKay, P. J. Amend, T. E. Cogswell, P. M. Harnsberg, R. B. Erickson and D. R. Latham in "Analytical Chemistry of Liquid Fuel Sources", Am. Chem. Soc., Adv. in Chem. Series No. 170, 1978, 128.
23. H. H. Oelert, *Z. Anal. Chem.*, 1969, 244, 91.

Table 1: Fraction yields from the ion-exchange chromatography of Arabian heavy crude oil vacuum (950°F+) residuum

<u>Fraction</u>	<u>Yield</u>	<u>Functionality type</u>
Bases	29.6	Quinoline nitrogen
Acids	3.2	Carboxylic acids and phenols
Neutral polar	19.4	Carbazole nitrogen
Neutral nonpolar	46.5	Saturate and aromatic hydrocarbons

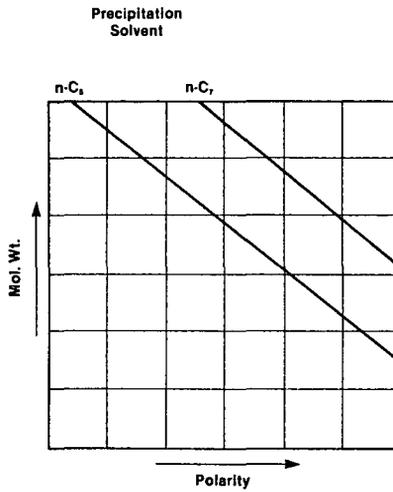


Figure 2: Schematic representation of asphaltene character

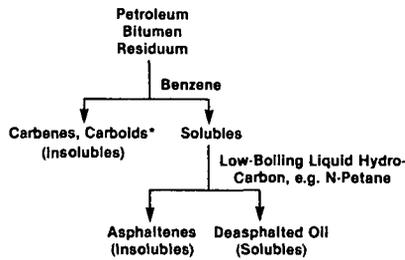


Figure 1: Schematic representation of asphaltene separation.

*In the case of coal liquids, these "insolubles" are often referred to as "preasphaltenes", "asphaltes", etc. based on solubility in solvents such as pyridine and/or quinoline (12,13).

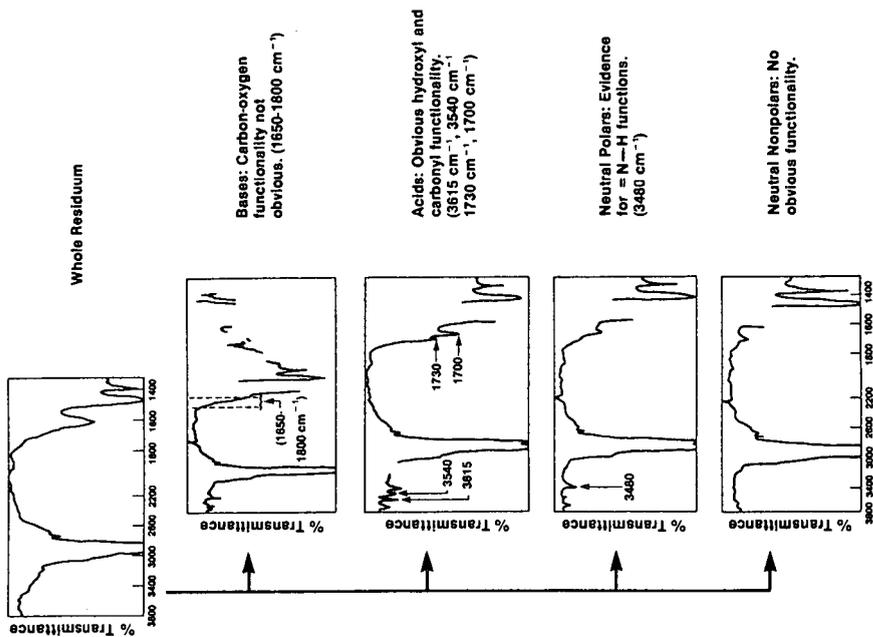


Figure 4: Infrared spectra of fractions separated by the ion-exchange technique

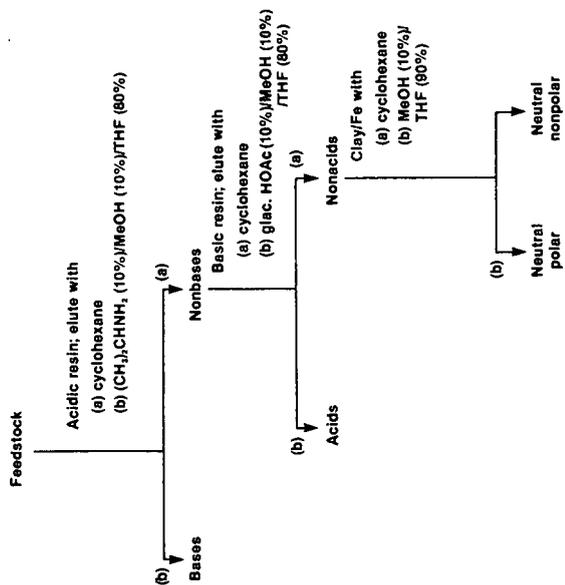


Figure 3: Schematic representation of the ion-exchange fractionation technique.

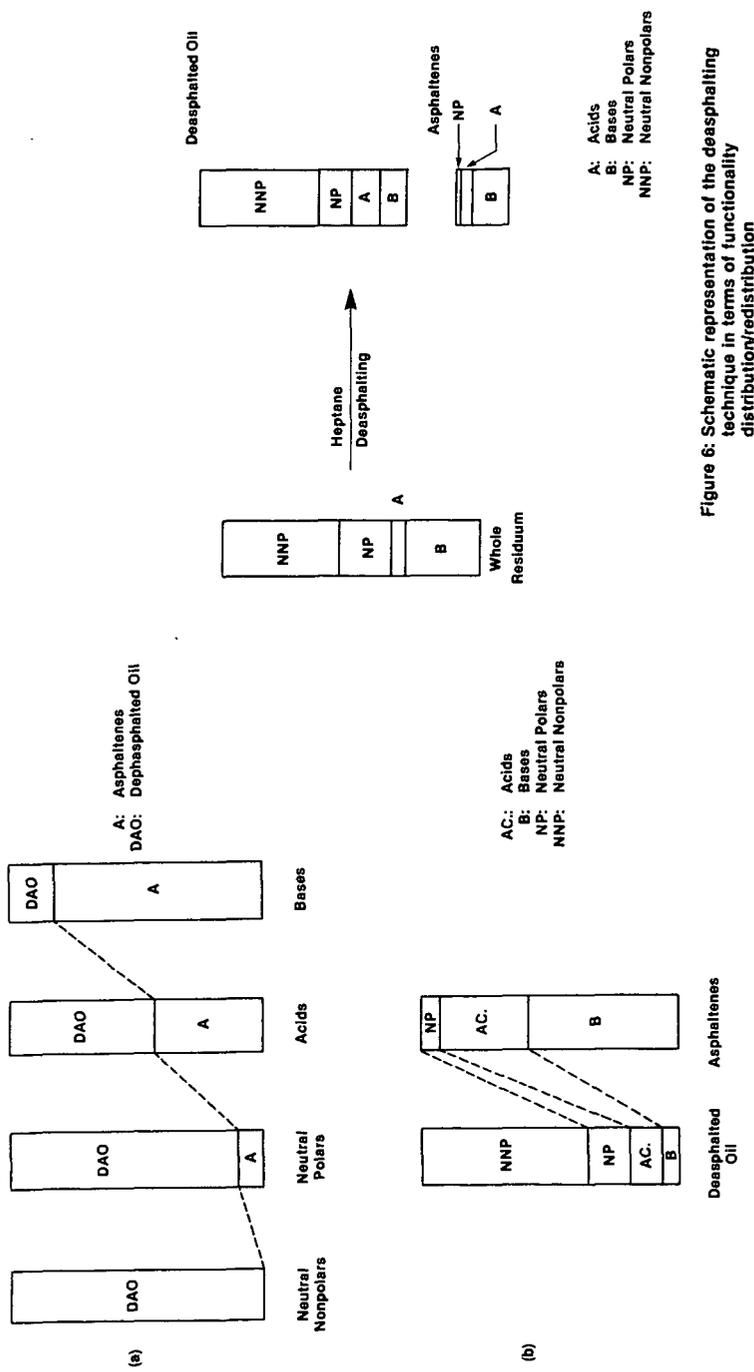


Figure 5: Schematic representation of (a) deasphalting the functionality fractions and (b) reconstruction of the deasphalted oil and asphaltene on the bases of functional types.

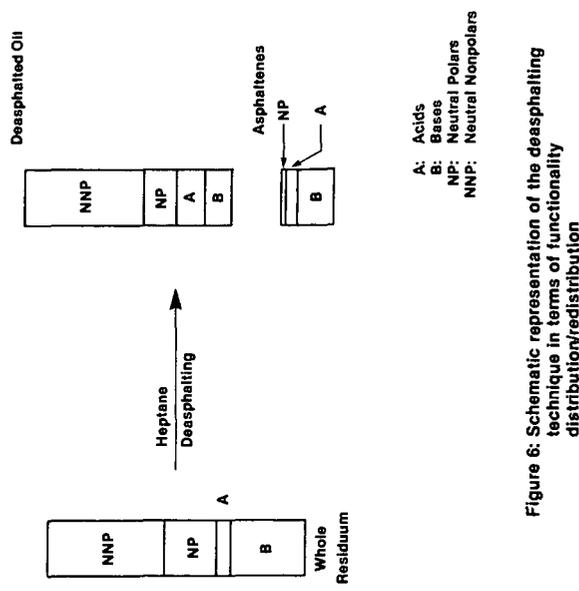


Figure 6: Schematic representation of the deasphalting technique in terms of functionality distribution/redistribution