

Size Exclusion Chromatography and Nuclear Magnetic Resonance Techniques for Predicting Asphalt Yields and Viscosities from Crude Oil Analyses

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Size exclusion chromatography (SEC) and nuclear magnetic resonance (NMR) techniques for predicting asphalt yield and viscosity as functions of crude oil type and manufacturing conditions are detailed in this paper. SEC conditions were varied to yield crude oil component distributions to the asphalt phase that agreed with the thermodynamic requirements for distillation processes. Silanized-silica column packing and ultraviolet detection yielded better results than polystyrene packing and refractive index detection. Relatively standard NMR conditions were used to determine the ratio of aromatic protons to paraffinic protons. This ratio was used as a measure of the relative polarity of crude oil and asphalt components.

Asphalt producers have historically relied on fixed domestic crude sources to yield consistent quality. Recently, some producers have been required to use variable crude slates; this makes asphalt quality control more difficult. In response to this situation, mathematical models were developed to predict asphalt yield and viscosity as functions of crude oil type and manufacturing conditions (1). Inputs to these models are analytical results that require only 2 to 4 hr to obtain. The purpose of this paper is to detail the size exclusion chromatography (SEC) and nuclear magnetic resonance (NMR) techniques developed for these models.

To predict asphalt yield, molecular weight or size distribution and polarity of the crude oil constituents need to be known. The larger the concentration of the higher molecular weight asphalt components, the greater the asphalt yield over other constituents. For a given molecular weight, more of the aromatic compounds than paraffinic compounds will preferentially fractionate to the asphalt product. The viscosity of an asphalt depends on its molecular size distribution and on its aromatic/paraffinic composition. A more aromatic asphalt with higher polarity or an asphalt with larger molecular sizes will exhibit higher viscosities.

To obtain data needed for yield and viscosity predictions, SEC was selected for size distribution and proton NMR was

chosen for component polarity. To achieve the most accuracy and flexibility in modeling, the size distribution and polarity parameters had to be measured as independently as possible.

A typical analytical approach for obtaining molecular weight or size distribution data on a crude or asphalt is to first fractionate the material. Then SEC and molecular weight data are obtained on the fractions. From these results, a SEC retention time-versus-molecular weight calibration curve is established for the entire material (2, 3). This approach is quite time consuming. Also, it is difficult to determine if all molecular association and adsorption forces have been eliminated.

The SEC approach used in this work was to analyze, in its entirety, a given crude oil and all of the various asphalts distilled from the crude oil. Then, the percentage of component distribution to the asphalt phase was calculated and plotted versus SEC retention time. These experimental distribution-versus-retention time data were compared with those expected from thermodynamic principles for distillation processes. The SEC procedures were varied until the actual component distribution-versus-retention time data agreed with the thermodynamic requirement of a monotonically decreasing function (Figure 1). In this manner, SEC conditions were developed that assured a true component molecular size distribution essentially free of association or adsorption problems.

The typical NMR approach for obtaining aromatic/paraffinic (polar/nonpolar) component results is analysis by both carbon-13 and proton NMR (4-6). Then various carbon/hydrogen ratios are calculated to obtain a measure of the aromatic/paraffinic composition. This approach is quite time consuming. Only proton NMR was used in this study because it was found that the polarity interactions that control asphalt yield and viscosity could be modeled with the aromatic/paraffinic proton ratio.

EXPERIMENTAL PROCEDURE

The following SEC and NMR techniques were used to obtain molecular size and aromatic/paraffinic breakdowns on 5 crude oils and 11 asphalts distilled from these crudes. Using the results, asphalt yields and viscosities were correlated to distillation conditions at average accuracy levels of 0.6 percent (1).

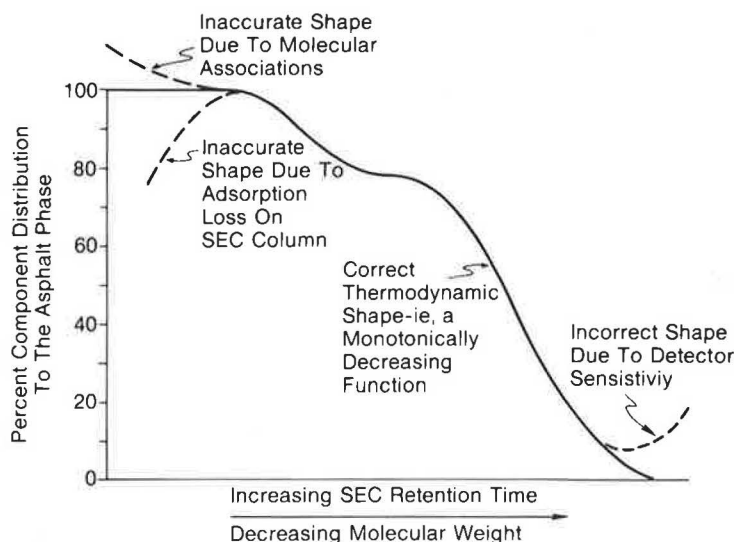


FIGURE 1 Thermodynamic requirement for component distributions to asphalt phase versus SEC retention time.

SEC

The liquid chromatograph consisted of a Spectra-Physics Model SP8700 pump, a Spectra-Physics Model SP8400 UV/VIS variable wavelength detector, a Spectra-Physics Model 748C column oven, a Bascom-Turner Model 4120 data acquisition system, a Valco Model HH-60 injection valve, and a Phase Separation LTD flow meter. The chromatograph was controlled with an in-house-designed microprocessor system based on a Motorola 6800 CPU and a Pro-Log STD BUS. A silanized 60-Å silica-based (6.2-mm inside diameter \times 25 cm) DuPont Zorbax® PSM 60S SEC column was used with a Brownlee (4.6-mm inside diameter \times 3 cm) RP-18 guard column.

The column was eluted with helium-purged tetrahydrofuran (THF, Burdick and Jackson) at a flow rate of 1 ± 0.01 mL/min. Best results were obtained with the column heated to 90°C and the detector set at a wavelength of 220 nm. The detector was not thermostated. During each 10-min run, the data system acquired 1,000 absorbance measurements. Solutions (25 μ L) of 0.05 percent by weight of crude or asphalt in THF were injected. Both valve and column were thermostated in the column oven. Samples were prepared with helium-purged THF and stored in nitrogen in septum vials.

NMR

A Varian EM-390 90-MHz spectrometer was used in this study. Asphalt and crude oil samples were dissolved in carbon tetrachloride (spectrophotometric grade) to obtain low-viscosity solutions. Tetramethylsilane was used as the reference standard. Other NMR operating parameters are as follows:

RF power: 0.30 mG
Filter time constant: 0.05 sec

Sweep time

Spectrum: 5 min
Integrals: 1 min
Sweep width: 10 ppm
End of sweep: 0 ppm
Sample spin rate: 40–60 rps
Sample temperature: 34°C

To obtain relative polarity values, two regions of the NMR spectrum were integrated. Paraffinic protons were assigned to the 0 to 5.33 ppm region and aromatic protons to the 5.33 to 9.00 ppm region.

DISCUSSION OF RESULTS

As previously mentioned, the models need independent measurements of polarity and molecular size distribution. Development of NMR techniques for determining the polarity input was relatively straightforward. However, considerable difficulty, which has also been noted by others (7, 8), was encountered with the molecular size distribution analysis. Gel permeation chromatography or, to use the modern term, size exclusion chromatography (SEC) was the technique of choice. The first attempts used Waters μ -Styragel® columns, THF solvent, and refractive index (RI) detection. The data obtained from this system could not be used. The apparent molecular size distribution of various distillation fractions did not agree with the distributions predicted from thermodynamic principles. The moderately high polarity of the Waters polystyrene column packing gave separations based on polarity and absorption in addition to molecular size. Also, the RI detector emphasized the polarity separation mechanism. For example, the chromatograph of a typical crude oil obtained under these conditions clearly shows the effects of absorption and RI detector re-

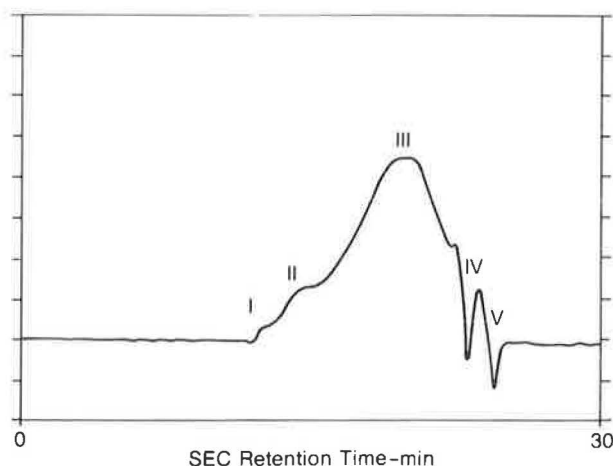


FIGURE 2 Chromatogram of crude oil. Obtained with a set of two Waters 500-Å μ -Styragel® columns at 50°C eluted with THF at 1 mL/min; Waters RI detector at X8 sensitivity; and 100- μ L sample of 2 percent by weight.

sponse (Figure 2). In particular, it is believed that the separated Fractions I and II are not collections of material with similar molecular size but rather represent material with similar polarity. The large negative peaks, IV and V, rendered the chromatogram useless for this analysis because meaningful component distributions to the asphalt phase could not be calculated. In an effort to improve this situation, an ultraviolet (UV) detector was substituted for the RI detector. Using the new detector, the chromatograms of the same crude and of an asphalt derived from it were significantly improved by the elimination of the negative peaks (Figure 3). Meaningful component distributions could then be calculated from this plot, but the result would not accurately correspond to molecular size because multiple peaks were still observed.

Then silanized-silica Zorbax® PSM 60S columns were used. The Zorbax columns gave smooth chromatograms with no separated peaks or shoulders (Figure 4). These chromatograms

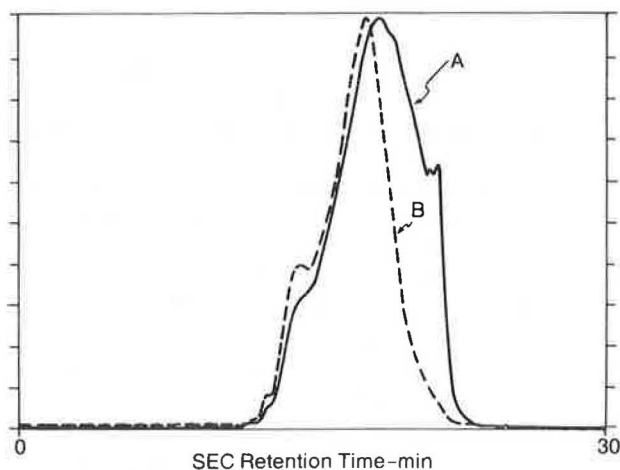


FIGURE 3 Chromatogram of (A) whole crude oil and (B) asphalt distilled from this crude. Obtained with two 500-Å μ -Styragel® columns at 50°C eluted with THF at 2 mL/min; UV detection at 254 nm; and 100- μ L samples of 2 percent by weight in THF.

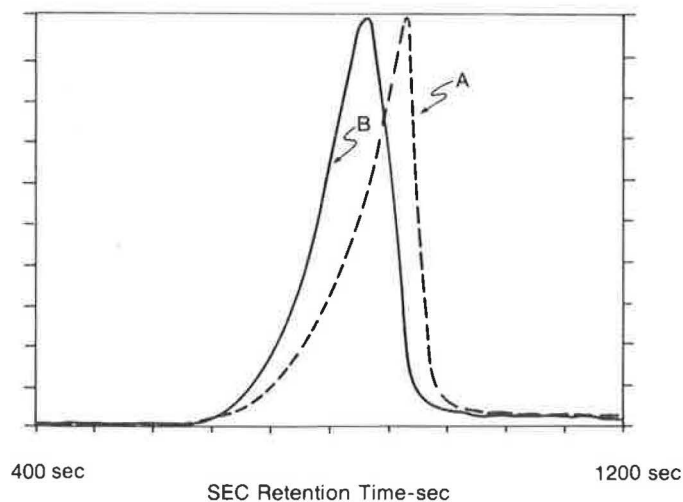


FIGURE 4 Chromatogram of (A) whole crude oil and (B) asphalt distilled from this crude. Obtained with three Zorbax® PSM 60S columns at 50°C eluted with THF at 1 mL/min; UV detection at 254 nm; and 10- μ L samples of 0.2 percent by weight in THF.

appeared to be reasonable for molecular size distributions of complex materials like crude oil and asphalts.

It was suspected that both the styrene- and the silica-based columns could absorb polar materials from crude oils or asphalts. Hence, chromatographic responses from both types of columns were compared. The same amount of sample was run on each column under the same chromatographic conditions. The chromatographic results show that recovery from the silanized-silica column was much greater than recovery from the polystyrene column (Table 1).

TABLE 1 RECOVERY DATA

Column	Total Area	
	Crude	Asphalt
Zorbax PSM 60S	1798	4556
μ -Styragel 10 ³ Å	920	3223

To test the resolution of the silanized-silica column, two asphalts distilled in a standard refinery process from a Wyoming crude were analyzed. The normalized chromatograms of these asphalts compared with that of the crude clearly reflect the expected different component distributions (Figure 5). Also, a crude and its overhead and residuum fractions obtained by the ASTM D 1160 distillation procedure were run (Figure 6). To see if the chromatographic resolution corresponded to the distillation, the normalized residuum curve, multiplied by its weight fraction from the whole crude, was subtracted from the normalized whole crude oil curve. The normalized difference curve was found to be equivalent to the actual overhead curve (Figure 7). Because these curves were essentially identical, it was thought that the SEC separation with the silanized-silica column corresponded to the distillation.

This initial work was performed using a detector setting of 254 nm, a column temperature of 50°C, and a sample concentration of 0.2 percent by weight in THF. These conditions

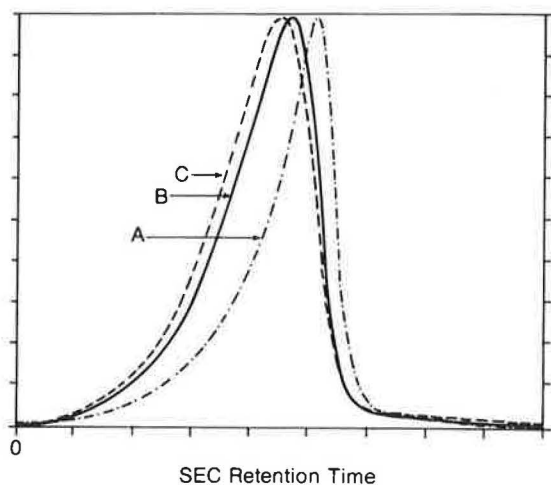


FIGURE 5 Chromatogram of (A) a Wyoming crude oil, (B) 200-250 pen, and (C) 85-100 pen asphalts distilled from this crude. Obtained with a Zorbax® PSM 60S column at 50°C eluted with THF at 1 mL/min; UV detection at 254 nm; and 10- μ L samples of 0.2 percent by weight.

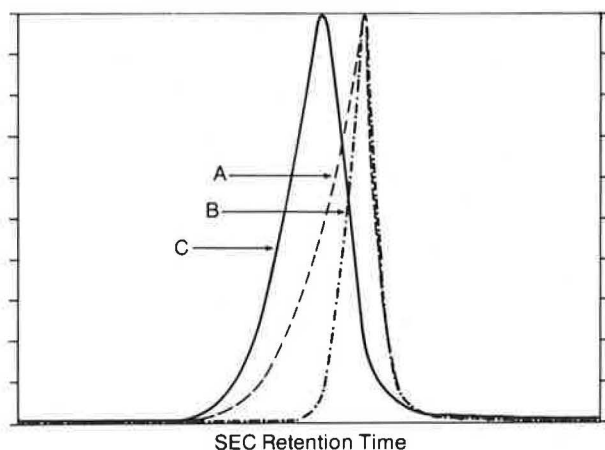


FIGURE 6 Chromatogram of (A) crude oil, (B) overhead fraction, and (C) residuum from ASTM D 1160 distillation. Obtained with a Zorbax® PSM 60S column at 50°C eluted with THF at 1 mL/min; UV detection at 254 nm; and 10- μ L samples of 0.2 percent by weight.

were accurate enough for selection of column and detector types. However, in terms of the thermodynamic model, the best SEC results were obtained at 220-nm wavelength, 90°C column temperature, and 0.05 percent by weight sample concentration in THF. In the thermodynamic analysis component distributions to the asphalt phase were determined as a function of SEC retention time or molecular size. A typical analysis showed that decreasing the UV wavelength from 260 to 220 nm yielded the correct component distributions at high retention times (Figure 8). At the higher wavelength, small molecular size components were overemphasized. Another study showed that increasing column temperature from 50°C to 90°C yielded the correct thermodynamic shape at low retention times (Figure 9). At 90°C, the adsorption of large molecular size

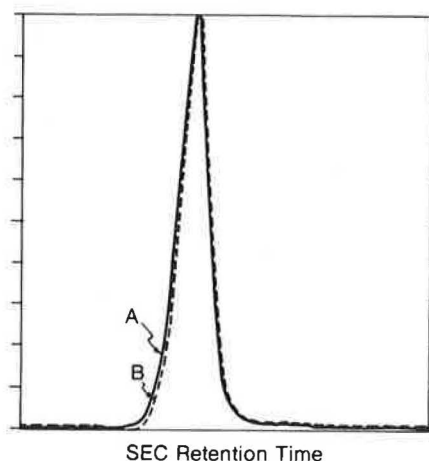


FIGURE 7 (A) Chromatogram of overhead from ASTM D 1160 distillation of crude. Obtained on a Zorbax® PSM 60S column at 50°C eluted with THF at 1 mL/min; UV detection at 254 nm; and 10- μ L sample of 0.2 percent by weight in THF. (B) Calculated chromatogram from whole crude chromatogram curve minus that of the residuum fraction.

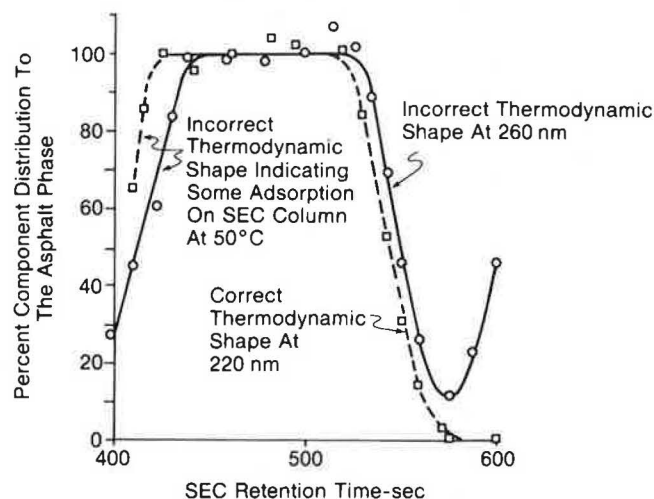


FIGURE 8 Distribution of components from a Wyoming crude to a 85-100 pen asphalt versus UV detector wavelength. Obtained on a Zorbax® PSM 60S column at 50°C eluted with THF at 1 mL/min and 25- μ L sample of 0.05 percent by weight.

components on the SEC column was essentially eliminated. Using the thermodynamic analysis, UV wavelengths of 210 to 280 nm, column temperatures of 25°C to 130°C, and sample concentrations in THF of 0.002 to 2.0 percent by weight were evaluated. In these evaluations, the asphalts used were manufactured by a standard refinery distillation process.

CONCLUSIONS

SEC and NMR conditions have been developed for use in predicting asphalt yield and viscosity as functions of crude oil type and manufacturing conditions. The SEC conditions were optimized by comparing experimental crude oil component

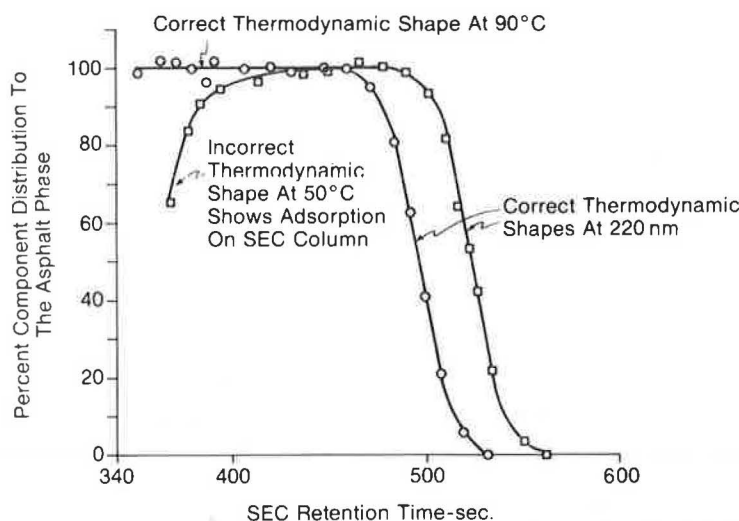


FIGURE 9 Distribution of components from a heavy Arabian crude to an AC-20 asphalt versus column temperature. Obtained on a Zorbax® PSM 60S column eluted with THF at 1 mL/min; UV detection at 220 nm; and 25- μ L samples of 0.05 percent by weight.

distributions to the asphalt phase with the thermodynamic requirement for distillation processes. Aromatic/paraffinic proton ratios from the NMR results were developed to measure the relative polarity of the crude oil and asphalt components.

REFERENCES

1. M. A. Plummer and C. C. Zimmerman. Asphalt Quality and Yield Predictions from Crude Oil Analyses. *Proc., Association of Asphalt Paving Technologists*, Vol. 53, 1984, pp. 138-159.
2. B. Brule. Calibration Curve for GPC Analysis of Asphalts. *Preprint Papers*, Division of Fuel Chemistry, American Chemical Society, Vol. 26, No. 2, 1981, pp. 28-37.
3. H. Reerink and J. Lijzenga. Gel-Permeation Chromatography Curve for Asphaltenes and Bituminous Resins. *Analytical Chemistry*, Vol. 47, No. 13, 1975, pp. 2160-2167.
4. S. Gillet, P. Rubini, J. J. Delpuech, J. C. Escalier, and P. Valentin. Quantitative Carbon-13 and Proton Nuclear Magnetic Resonance Spectroscopy of Crude Oil and Petroleum Products, Part 2: Average Structure Parameters of Representative Samples. *Fuel*, Vol. 60, March 1981, pp. 226-230.
5. J. M. Dereppe, C. Moreauz, and H. Castex. Analysis of Asphaltenes by Carbon and Proton Nuclear Magnetic Resonance Spectroscopy. *Fuel*, Vol. 57, July 1978, pp. 435-441.
6. Y. A. Al-Farkh, N. R. El-Rayyes, F. H. Al-Hajjar, and K. A. Al-Zaid. Studies on Kuwait Crudes. Structural Analysis of Asphalts and Their Fractions by Nuclear Magnetic Resonance. *Applied Spectroscopy*, Vol. 33, No. 4, 1979, pp. 406-409.
7. B. Brule. Characterization of Bituminous Compounds by Gel Permeation Chromatography (GPC). *Journal of Liquid Chromatography*, Vol. 2, No. 2, 1979, pp. 165-192.
8. C. Such, B. Bruel, and C. Baluja-Santos. Characterization of a Road Asphalt by Chromatographic Techniques. *Journal of Liquid Chromatography*, Vol. 2, No. 3, 1979, pp. 437-453.

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