GPC Characterization for Assessing Compatibility Problems with Heavy Fuel Oils

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ABSTRACT

Precipitation of solids is one of the major problems associated with the shipping and handling of heavy residual oils especially No. 6 heating oil. ASTM specifications which currently include viscosity, flash point and pouring point are not adequate to predict the handling problems. The residual oils are becoming more complex in composition due to modern refinery techniques for cracking the heavier residues into distillable fractions. In this study, several heating oil samples, including a sample which partially solidified during transport, were analyzed using various techniques including separation by gel permeation chromatography (GPC), vacuum distillation, separation of petroleum asphaltenes by ASTM method, elemental analysis and proton and 13C NMR spectroscopy. The distillable species in the fraction separated by GPC were characterized by high resolution gas chromatography-mass spectroscopy (GC-MS). The study showed that the GPC can be used as a reliable technique for the analysis of heavy residual oils. The GPC separation of No. 6 heating oil gave three fractions enriched with chemically distinct asphaltenes. The second fraction was mostly straight chain paraffins. The third fraction was composed of low molecular weight aromatics. Although occasional verification of GPC data by GC-MS and by NMR spectroscopy is desirable, the GPC alone is an efficient analytical tool for evaluating the composition as well as predicting the handling problems associated with shipping and storage of various residual oils.

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INTRODUCTION

Modern refineries use new technologies to crack heavy bottoms to produce more light components from crude oil. These processes produce complex mixtures that are called residual oils. These heavy residual oils are valuable as chemical feed stocks as well as heating and fuel oils. Since the composition of these oils is very complex, their characterization is generally limited to obtaining certain ASTM specifications such as API gravity, viscosity, distillation temperature, and flash point. A number of studies [1 – 5] have been reported regarding certain chemical and physical characteristics of these oils. The compositions of the oils vary depending upon the origin of the crude as well as the refining techniques. Handling of the heavy oils is difficult and sometimes oils mixed during storage or transportation may undergo precipitation as well as solidification of a significant fraction of the oil. The ASTM specifications are not adequate for predicting these problems and are not indicative of the oil composition. Thus, other analytical tools to characterize heavy oils are badly needed.

Gel permeation chromatography (GPC) has been extensively used for molecular size determinations of large molecular weight species such as polymers, [6] coal liquids, [7 – 11] and petroleum asphaltenes [11 – 20]. GPC separates molecules on the basis of linear molecular size, and the samples elute in decreasing order of molecular length. The GPC has previously been used to separate a wide range of molecular sizes in coal derived liquids

[21]. Coal liquids are a complex mixture of hydrocarbons similar to heavy petroleum crude, One of the limitations of GPC is that the total number of peaks which can be resolved is limited compared with other modes of liquid chromatography. However, relatively larger samples can be analyzed without sacrificing much of the resolution in 20 to 40 minutes. Unlike adsorption chromatography, in most cases GPC columns do not retain any portion of the sample for all practical purposes. Regardless of the molecular size distribution, the analysis time is dependent on the solvent flow rate and the number of columns used, not on the sample size. This paper discusses the use of GPC and other methods for the characterization of heavy residual oils.

EXPERIMENTAL METHODS

Samples of ASTM grade No. 6 heating oil obtained from different sources were used in the study. The samples represented a wide spectrum of sources as well as aging. One heating oil sample had partially solidified during transport and the solid residue was selected for extensive study. All of the samples were analyzed for heptane solubles (oils) and insolubles (asphaltenes) by ASTM D3279. Several of the samples were also distilled under vacuum at 300^{o}C for the separation of distillates and residues.

The samples for GPC analysis were prepared by dissolving the heating oil sample in dry, additive-free tetrahydrofuran (THF) to obtain a 25% solution and the solution was filtered through micro-pore filters (Millipore, 0.5 pm size). The GPC separations were performed on a Waters Associate Model ALC/GPC 202 liquid chromatograph equipped with a refractometer (Model R401). A Valco valve injector was used to load about 250 μ l samples into the column. Styragel columns (each of 7.8 mm ID and 300 mm long) of three pore sizes; 1000 nm, 50 nm, and 10 nm, were used. Reagent grade THF, which was refluxed and distilled from sodium wire in a nitrogen atmosphere, was used as the GPC carrier solvent. A flow rate of 1 ml per minute was used. THF was stored under dry nitrogen, and all separations were conducted in a nitrogen atmosphere to prevent the formation of peroxides.

Straight chain alkanes from Applied Science and polystyrene standards from Waters Associate were used without purification for the molecular size calibration of the GPC. Since the solubility of the larger alkanes in THF is very low, approximately 0.5 – 2 mg of each standard was dissolved in 250 μ l of the THF for the linear molecular size calibrations. A solution containing both a calibration standard and the sample was used to determine the molecular size distribution of the sample. The heating oil sample was separated by GPC into three fractions based on linear molecular sizes. Fraction 1 was composed of species with linear molecular size greater than that of n-tetratetracontane (n-$C_{44}H_{90}$). Fraction 2 was composed of species with linear molecular sizes in the range of n-heptane to n-tetratetracontane (n-C_7H_{16} to n-$C_{44}H_{90}$). Fraction 3 was composed of species with molecular sizes less than that of n-heptane.

The fractions of heating oil samples separated by the GPC were evaporated using a slow nitrogen stream and the concentrates were used for further analysis. Fuel oil samples (as well as distillates, residues and GPC fractions) were also dissolved in deutero-chloroform ($CDCl_3$) and analyzed by proton and ^{13}C NMR spectrometry. The proton NMR spectra of the samples were obtained by using a Varian T-60 NMR spectrometer. A Varian FT-80A NMR spectrometer was used for the ^{13}C NMR spectra of the samples.

Detailed analysis of the GPC Fractions 2 and 3 were performed using high resolution gas chromatography-mass spectrometry (GC-MS). The instrumentation consisted of a Perkin-Elmer Sigma 1 gas chromatograph interfaced to a Fennigan mass spectrometer located at Agricultural Analytical Services of Texas A&M University. A 30m glass capillary column coated with OV 101 and manufactured by J&W, Inc. was used for the GC-MS studies. The elemental analysis was performed at the Center for Trace Characterization at Texas A&M.

RESULTS AND DISCUSSION

The separation of coal liquids by gel permeation chromatography using 10 nm Styragel and solvents like THF and toluene has been reported [7 – 9, 11 – 24]. Coal liquids and heavy residual oils are similar in their physical appearance as well as handling problems. The major difference between coal liquids and heavy residual oils is that the oils do not contain oxygenated compounds, such as alkylated phenols, in substantial quantity. As shown by Lynch and Thomas [13] and Long [14], the average molecular size of the asphaltene species in heavy residual oils is much larger than that of coal liquids. Hence, heavy residual oils require the use of Styragel columns with exclusion limits such as 1000 nm and 50 nm in addition to the 10 nm columns generally used for the coal liquids.

Figure 1 shows the GPC separation of solids which had precipitated from a fuel oil sample using different column combinations. Since the sample dissolved almost completely in THF, with the exception of a few solid particles (less than 1%), THF was selected as the mobile liquid phase in the GPC. A GPC column bank containing three 30-cm columns with pore sizes of 1000 nm, 50 nm, and 10 nm, respectively, could produce good separation of oil.

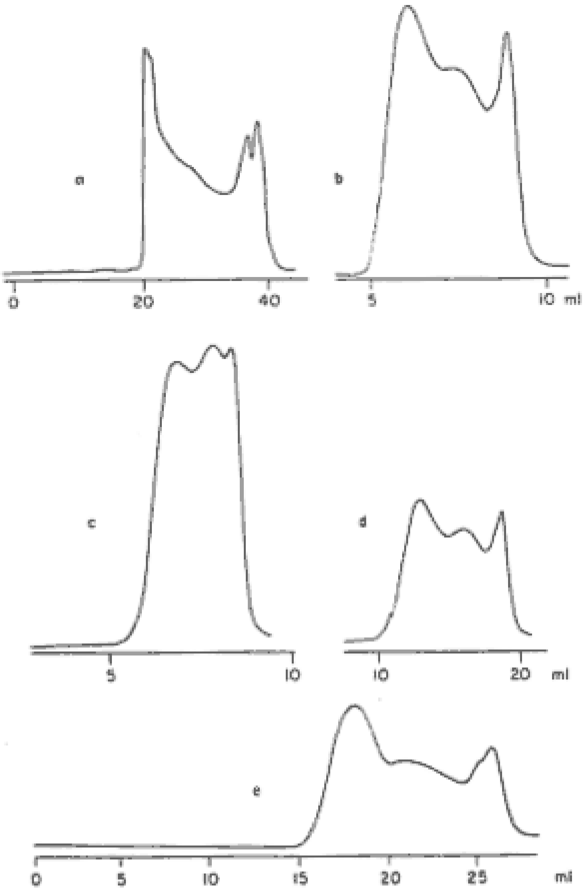


Figure 1. Separation of heating oil sample (from that portion solidified during shipping) by GPC using 30 cm X 7.5 mm ID S.S. columns packed with 10 nm styragel column(s): (a) four 10 nm columns, (b) one 50 nm column, (c) one 1000 nm column, (d) one 500 nm and one 1000 nm column, (e) bank of three column banks with 10, 50 and 1000 nm pore sizes.

After examining several column arrangements, the column combination from Fig. 1e was used in the remainder of this study. Using this combination, the precipitated solids from the fuel oil sample was separated into three fractions as illustrated in Fig. 2. The equivalent linear molecular size range for each fraction was given in the experimental methods section. The proton NMR spectra of the three fractions of the heating oil sample are shown in Fig. 3. The proton NMR spectra show the distribution of chemically bound hydrogen among the aromatic rings, aliphatic chains and other carbon atoms with varying chemical shifts due to different functional groups. The spectra give more or less quantitative data about the chemical nature of the components present in the heating oil fraction. An estimation of the aromatic and the aliphatic moieties in the sample was attempted using the area of the peak clusters. Both Fractions 1 and 3 have species with aromatic moieties and Fraction 2 has mostly alkanes. Fraction 1 was non-volatile and could not be analyzed by GC-MS. Fractions 2 and 3 were analyzed by GC-MS, and the major peaks were identified and listed in Tables 1 and 2. As expected, all the volatile species in Fraction 2 are straight chain alkanes while Fraction 3 is composed of aromatics. Fractions 2 and 3 may also contain species which are not shown in the GC-MS because they are nonvolatile or decompose under GC-MS conditions. The results of the elemental analysis of the partially solidified heating oil and its three GPC fractions after the removal of THF are listed in Table 3.

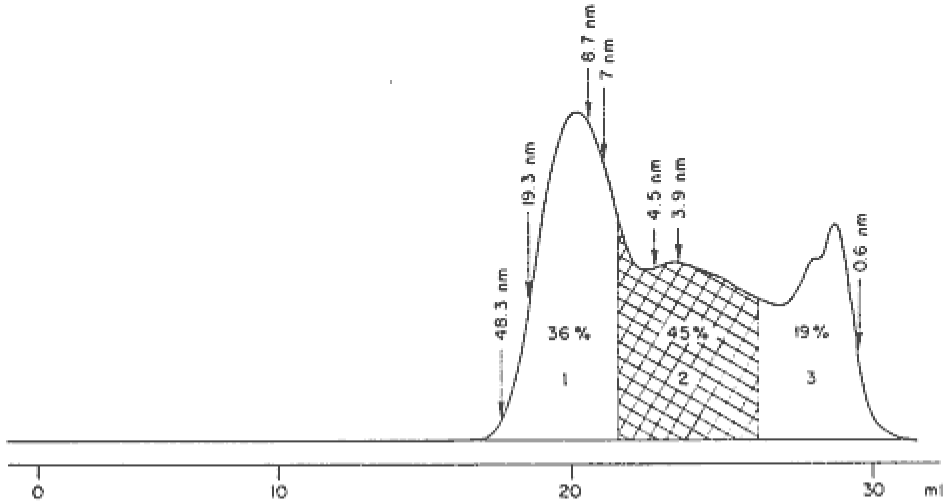


Figure 2. Separation of heating oil into three fractions. The GPC was calibrated using polystyrene standards and n-alkanes.

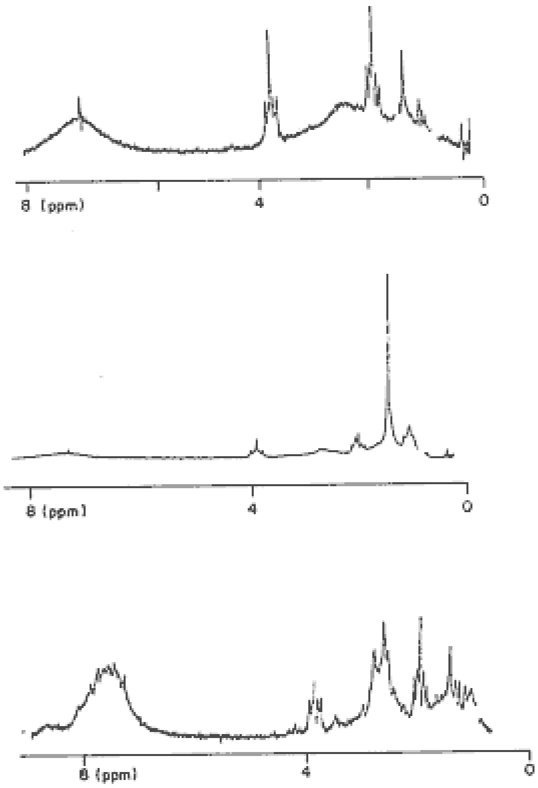


Figure 3. Proton NMR spectra of three heating oil fractions separated by GPC as shown in Fig. 2. Small amounts of THF were present in all three fractions; (a) GPC fraction 1, (b) GPC fraction 2, (c) GPC fraction 3.

Table 1. Hydrocarbon chains identified from GPC from fraction 2* (aliphatic fraction).

Retention time (min)	**Compound**
6.5	tetradecane
9.2	pentadecane
11.5	hexadecane
14.2	heptadecane
15.3	pristane
16.6	octadecane
18.0	phytane
19.4	nonadecane
21.3	eicosane
23.3	hendeicosane
25.3	docosane
27.2	tricosane
30.5	tetracosane
32.3	pentacosane
34.5	hexacosane
36.5	heptacosane
40.2	octacosane
44.3	nonacosane
49.4	triacontane

*n-Alkanes ranging from triacontane to tetratetracontane (n-$C_{30}H_{62}$ to n-$C_{44}H_{90}$) were identified by GC, although GC-MS could not detect them due to interface heating problems. Small peaks of branched alkanes were detected between straight alkane peaks.

Table 2. Components identified from GPC fraction 3 (aromatic fractions).

Retention time (min)	**Compound**
7.56	C_1-alkyl naphthalene
12.20	C_2-alkyl naphthalene

14.31	C_1-alkyl biphenyl
15.16	C_3-alkyl naphthalene
16.08	C_3-alkyl naphthalene
16.42	C_3-alkyl naphthalene
18.35	C_2-alkyl biphenyl
19.06	C_2-alkyl biphenyl
20.22	C_4-alkyl naphthalene
20.40	C_4-alkyl naphthalene
23.06	C_1-alkyl fluorene
25.44	phenanthrene
31.12	C_1-alkyl phenanthrene
35.18	C_2-alkyl phenanthrene, 2,5-dimethyl

Distillation under reduced pressure is widely used for the analysis of heavier residual oils. The heating oil sample was distilled under vacuum at 300°C. The GPC separation of the residue and the distillate are shown in Figs. 4a and 4b, respectively. The boundary between the volatiles and nonvolatiles is illustrated in the GPC curve of the original oil (Fig. 4d). The sample was also extracted with heptane and the GPC of the heptane insolubles is shown in Fig. 4c. By comparing the results for the distillation residue (Fig. 4a) and the heating oil sample prior to distillation (Fig. 2), one can observe that Fraction 2 does contain some nonvolatiles in addition to the alkanes identified by GC-MS (Table 2).

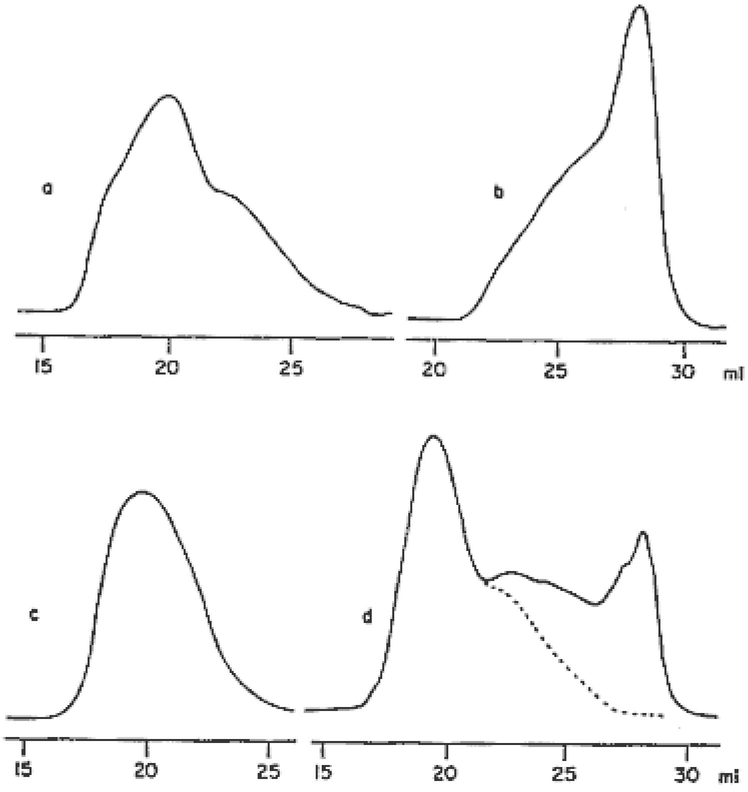


Figure 4. GPC curve of heating oil and its fractions; (a) residue obtained by vacuum distillation, (b) distillate, (c) heptane insolubles (as petroleum asphaltenes), (d) GPC curves of residue and distillate reconstructed to fit GPC curve of the heating oil sample.

Results from a ^{13}C NMR analysis of both residue and distillate are shown in Fig. 5. ^{13}C NMR spectroscopy is an important tool for the analysis of petroleum [25 – 27]. The proton NMR spectra of hydrocarbon mixtures such as heating oil and coal liquifaction products are also very useful. However, they give very broad absorption patterns and a relatively shorter range of proton chemical shifts. The increased range of ^{13}C NMR chemical shifts compared to proton NMR is mainly responsible for the unique power of ^{13}C NMR in structural identification. Upon comparing the spectra of known compounds shown in API Project 44 [28] with the spectra of the current

oils, the following observations were made. The peak at 14.19 ppm in Fig. 5a is due to terminal methyl groups of saturated long chain hydrocarbons. The intense absorption at 29.91 ppm is due to methylene groups in the middle regions of one or more long chain saturated hydrocarbon compounds. A relatively large peak area at 29.91 ppm (Fig. 5a) suggests that n-alkanes are the bulk species.

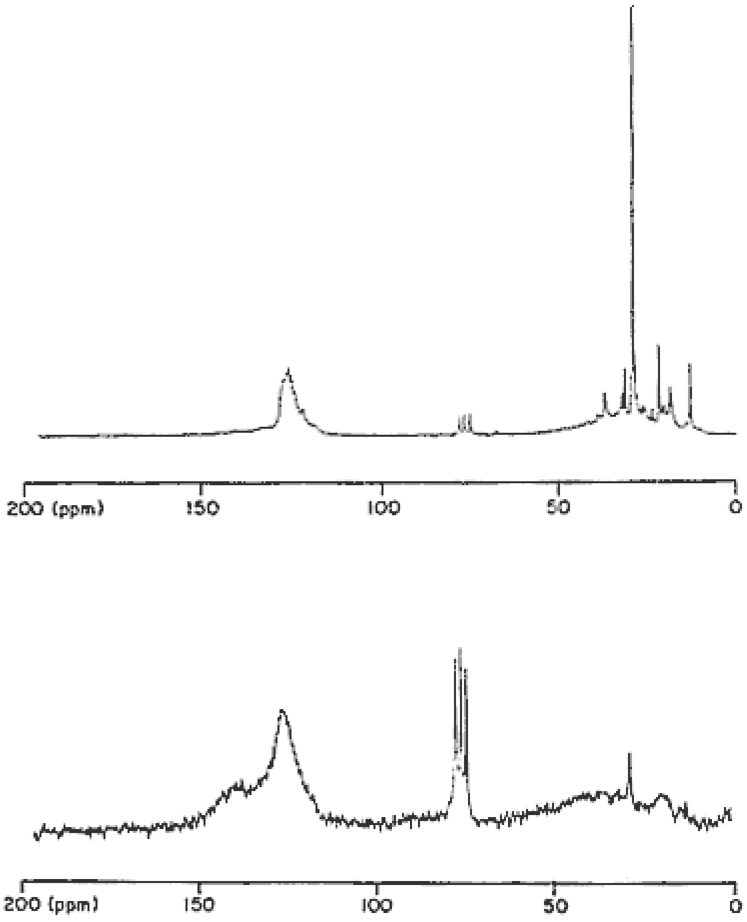


Figure 5. ^{13}C NMR spectra of (a) vacuum distillate, (b) residue of heating oil.

The ^{13}C NMR studies also confirmed that most of the peaks identified by GC-MS as alkanes were due to straight chain rather than branched hydrocarbons. GC-MS studies clearly showed that saturated hydrocarbons are the major constituents. The fragmentation pattern also showed that most of these hydrocarbons are straight chain alkanes. The ^{13}C NMR spectra of the distillate (Fig. 5a) showed that it was composed of straight chain alkanes as well as aromatics. The ^{13}C NMR spectra of the residue (Fig. 5b) indicates that it is composed mostly of aromatics and devoid of any straight chain alkanes.

The solidified oil sample was also separated into heptane solubles and heptane insolubles by ASTM Method D3279. The heptane insolubles which are soluble in benzene or toluene are called asphaltenes. The GPC curve for the heptane insolubles is shown in Fig. 4c. The amount of heptane insolubles is closely predictable from the GPC results from the sample alone (see Fraction 1 in Fig. 2). Unlike coal asphaltenes which have a molecular length distribution in the volatile alkane range ($C_{14}H_{30}$-$C_{40}H_{82}$) [24], the size distribution of petroleum asphaltenes lies outside of the volatile alkane range. The fact that petroleum asphaltenes are nonvolatile can be easily seen by comparing Figs. 4a and 4c. Hence, the GPC analysis of petroleum asphaltenes does not suffer interference from alkanes even if the alkanes are present as the major fraction.

The heavy residual oils which are marketed as No. 5 and No. 6 heating oil have varying composition depending upon the origins of the crudes as well as the refining or processing techniques. The GPC analysis of a few fuel oils are shown in Fig. 6. All these oils were marketed as No. 6 fuel oils, and they had met the ASTM specifications. These oils had no unusual handling problems during shipping or storing. The oils represented in Fig. 6 contained very little, if any, petroleum asphaltenes and were primarily paraffinic in nature. Other fuel oils can contain significant quantities of asphaltenes and light aromatics as shown in Fig. 7b. One fuel oil examined in this study contained about 15% asphaltenes, 40% paraffins and 45% light aromatics. The above GPC observations were supported by the asphaltene test according to ASTM D3279, and by the ^{13}C NMR and GC-MS analyses.

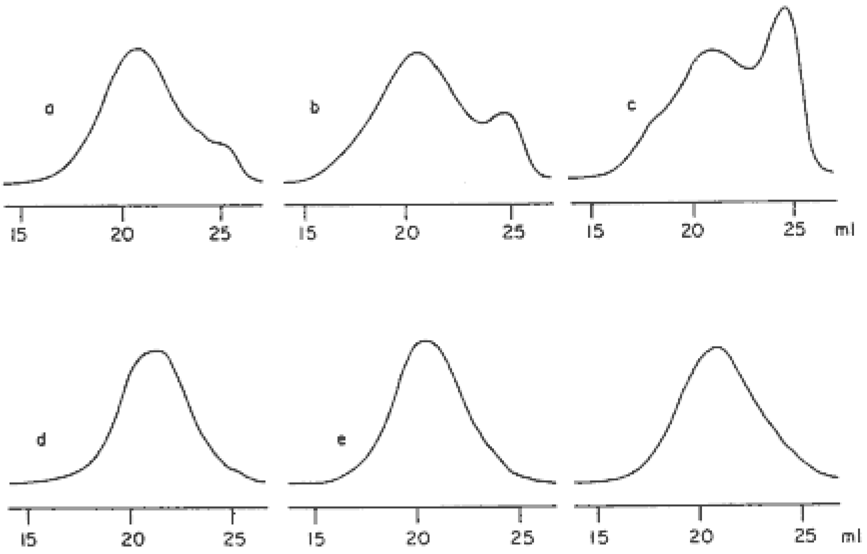
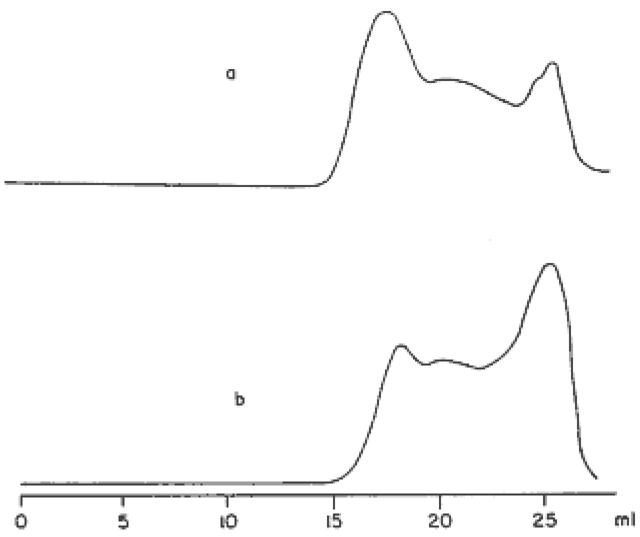


Figure 6. GPCs of various heating oil samples collected from commercial sources.

Due to the absence of high molecular weight asphaltenes, the oils represented in Fig. 6 could be handled without precipitation or solidification during shipping and storage. However, caution should be exercised when blending oils which contain more than 2 or 3% asphaltenes with oils which are primarily paraffinic. The GPC provides a convenient and relatively easy means to observe the asphaltene, paraffin and light aromatic content of heavy fuel oils and to anticipate potential blending and storage problems.

As discussed above, heavy residual oils may precipitate solids which settle to the bottom of tanks. These solids are very difficult and expensive to remove. Thus, a comparison of GPC analysis for the oil and separated solids is very revealing. An example is shown in Fig. 7. As the solids settle to the bottom, they entrap large amounts of liquids in the solid structure. This is reflected in the GPC curve in Fig. 7a. As expected, the solid sample has more of the larger molecules such as asphaltenes than does the original oil. Unlike the other oil samples shown in Fig. 6, this oil has more asphaltenes. It also has more light aromatics which dissolve the asphaltenes. The physical properties of this oil meet the ASTM specifications, but the GPC shows the presence of unusually large amounts of asphaltenes, which might solidify during shipping or storage.

Figure 7. GPC2 of (a) deposited oil solids and (b) oil before the separation of the residue.



CONCLUSION

The complexity of heavy residual oils will increase as the demand for fuels such as gasoline and jet fuel increases, and the refineries are forced to squeeze every drop from the "bottom of the barrel" using various hydrocracking technologies. Gel permeation chromatography (GPC) is a good analytical technique for monitoring these heavy oils. The GPC provides data on the linear molecular size distribution as well as the chemical nature of the oil (such as the asphaltene content, paraffinic content, and the light aromatic). Caution should be exercised when blending oils which contain asphaltenes with oils which are primarily paraffinic. Based on the GPC analysis of fuel oils, potential blending and storage problems may be anticipated.

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