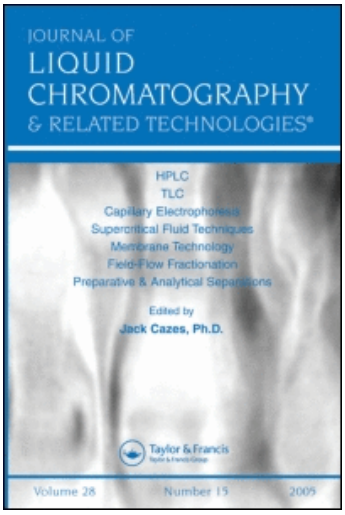

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Polyvinylacetate Gel Permeation Chromatography of H-Coal Liquids and Model Compounds. Comparison with Rigid Gel, Reversed Phase and Normal Phase Chromatography

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POLYVINYLACETATE GEL PERMEATION CHROMATOGRAPHY OF H-COAL LIQUIDS AND MODEL COMPOUNDS. COMPARISON WITH RIGID GEL, REVERSED PHASE AND NORMAL PHASE CHROMATOGRAPHY

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ABSTRACT

This paper reports the application of polyvinylacetate gel (Fractogel) for size fractionation of the H-Coal liquids and model aromatic hydrocarbons. The four H-Coal liquids were each divided into three classes according to solubility in hexane, benzene, and pyridine. A model mixture of eight compounds when applied to the Fractogel column yielded four fractions; a similar performance was given by a prepacked, Toyo Soda microparticulate column containing styrene-divinylbenzene copolymer. Regarding the twelve H-Coal solvent fractions, the chromatograms obtained from the Fractogel column were analogous to those from the Toyo Soda column. By making further use of model compounds, the Fractogel results are compared with those obtained from reversed phase chromatography on a Partisil ODS column and those from normal phase chromatography on a LiChrosorb silica column. These comparisons reveal the usefulness in separating certain aromatic hydrocarbons by the Fractogel column. Furthermore, judging from the chromatograms of a hexane-soluble H-Coal fraction obtained by the reversed phase and normal phase methods, the ODS column will complement the Fractogel column in fractionating the H-Coal liquids.

INTRODUCTION

The liquefaction of coal to produce conventional refinery products represents a better use of the solid fuel. The H-Coal process is a coal dissolution process carried out in an ebullated

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bed reactor in the presence of hydrogen and a desulfurization and hydrogenation catalyst. The crosslinks in the coal particles, whether they are methylene, oxygen, sulfur, or nitrogen bridges, undergo thermal homolysis. Upon transfer of hydrogen to the radical sites, depolymerized coal units are formed which are separated into four product streams: atmospheric still overhead (ASO), atmospheric still bottom (ASB), vacuum still overhead (VSO), and vacuum still bottom (VSB). We have been involved in the characterization of these products (1), and have reported a structural study of the H-Coal liquids by the FT-NMR method (2) as well as a combined use of gel permeation chromatography (GPC) and vapor pressure osmometry for fractionation and molecular weight information (3). Although Anbar et al. (4) have shown by field ionization mass spectra of the H-Coal liquids that their molecular weights range from about 100-600, the applicability of gas or liquid chromatography for their complete analysis is doubtful because of the residue problem. Some of these liquids contain polymeric compounds which tend to be retained on the column. In this regard, GPC comes close to being a total chromatographic method for the coal liquids. There are several reports on GPC separation of various coal-derived liquids (5,6,7). The column packing most commonly employed is a styrene-divinylbenzene cross-linked polymer. It is used more often in the form of a rigid gel as found in the microparticulate, prepacked columns such as the μStyragel of Waters Associates (5) and the Toyo Soda TSK column (6) from Japan and distributed by Varian Associates. A soft gel such as the Bio-Rad Bio-Beads is also used in homemade, slurry-packed columns (7). This polystyrene copolymer, either as the rigid or the soft gel, has its limitations for analyzing coal liquids. For example, the prepacked column is costly, has low sample loading capacity, and subject to clogging by sample precipitation. The Bio-Beads gel is more economical but has been found to exhibit a non-size exclusion mechanism of separation (7), making it difficult to interpret the chromatogram of a highly heterogeneous coal liquid. We have been studying vinyl acetate

copolymer, the Merck Fractogel PVA 500, as column packing material for the analysis of the H-Coal liquids. We have found it useful both analytically and preparatively and have compared its performance with that obtained on the Toyo Soda TSK G-2000H_{10} column. By means of model hydrocarbons, the Fractogel separation has been compared with data obtained from chromatography on a reversed-phase octadecylsilyl (ODS) column and a normal phase silica gel column. The latter two methods have also been applied to a H-Coal liquid. In these separations, the Fractogel and ODS columns are complementary to each other.

MATERIALS AND METHODS

The H-Coal liquids were received from the University of Kentucky Institute for Mining and Minerals Research. The coal liquefaction was performed by the H-Coal process in the syncrude mode with reactor temperature at 450°C, exit reactor partial pressure of hydrogen at 2245 psig. The nominal boiling ranges of the liquids are: ASO C_4-200°C, ASB 200-350°C, VSO 350-520°C, and VSB is a chunky tar.

The instrument for chromatography consists of a M6000A pump, U6K injector and model 440 absorbance detector operating at 254 nm for analytical and 313 nm for preparative run. These components are products of Waters Associates, Milford, Mass. The Fractogel PVA 500, 32-63 μ, was purchased from MCB, Inc., Ohio. This gel was slurry-packed to 800 psig into a 610 mm x 7.8 mm stainless steel column; two columns were joined in series. It was eluted at 1 mL/min with chloroform-methanol 3:1. The rigid gel column, TSK G-2000H_{10}, 610 mm x 8 mm containing 10 μ particles, was purchased prepacked from Toyo Soda of Japan. The mobile phase for the TSK was straight chloroform at a flow rate of 1 mL/min. The theoretical plate count of the Fractogel column set was about 1500, while that of the TSK column was about ten times greater, as determined by injecting a 2% acetone solution. The samples for injection were prepared in the same solvent as the mobile phase used. The concentrations for the model hydrocarbons were 1 -10 x

10^{-3} M. For the H-Coal liquids, solutions of about 15 mg/mL were prepared for analytical runs, and about 20 times that for preparative separation.

For the reversed-phase column, Whatman Partisil ODS was packed into a 250 mm x 4.6 mm stainless steel column. It was eluted with acetonitrile-water 1:1 at 3 mL/min. The same kind of column was packed with Merck LiChrosorb Si60 for normal phase chromatography. It was eluted with n-hexane at 0.4 mL/min. Both columns contained 10 μ particles and showed a plate count of about 5000.

RESULTS AND DISCUSSION

Since application of the Fractogel polyvinylacetate column in coal liquid analysis was rather new, an attempt was made to understand the way by which the coal liquid components can be fractionated. For this purpose, eight model aromatic hydrocarbons were injected into the Fractogel column individually and also as mixtures. Their retention volumes are shown in Table 1 which are also compared with those obtained from the Toyo Soda column. As the Fractogel column is twice the length of the Toyo Soda column, the retention volumes from the Fractogel are about two times as large as those from the Toyo Soda. For the mixture of eight compounds, the Fractogel chromatogram as shown in Figure 1 reveals four bands: band 1 contains phenyltridecane, band 2 1,2-diphenylethane and triptycene, band 3 biphenyl and 1,5-dimethylnaphthalene, and band 4 contains benzene, naphthalene, and phenanthrene. The separation of this mixture on the Toyo Soda column is similar (see Figure 2), the main difference being that the second band in the Fractogel chromatogram is herein resolved into two peaks, with triptycene eluting first followed by 1,2-diphenylethane. The clean-cut resolution of phenyltridecane (MW 260) from trypticene (MW 254), a polycyclic, suggests that the separation is based on the length of the molecules. Likewise, 1,2-diphenylethane (MW 182) and phenanthrene (MW 178) are well separated based on a difference in the molecular length.

TABLE 1

Retention Volumes of Eight Model Aromatic Hydrocarbons from the Fractogel and Toyo Soda Column

Model Compounds	Molecular Weight	Retention Volume, mL	
		Fractogel	Toyo Soda
Phenyltridecane	260	21.3	13.0
Triptycene	254	26.7	14.2
1,2-Diphenylethane	182	27.7	14.6
1,5-Dimethylnaphthalene	156	31.0	15.8
Biphenyl	154	32.2	16.0
Phenanthrene	178	35.6	16.8
Naphthalene	128	35.8	17.0
Benzene	78	36.5	17.1

Hence, the lack of separation between 1,5-dimethylnaphthalene (MW 156) and biphenyl (MW 154) which are similar in length is not surprising. However, it is unexpected that the parent aromatic compounds of one, two and three rings can neither be resolved on the Fractogel nor on the Toyo Soda, the latter having about 10 times the theoretical plates of the former. The useful molecular weight range for the Fractogel column is about 100-600, while that of the Toyo Soda is about 100-2000. Phananthrene (MW 178) is not approaching the total permeation limit of either column and should be resolvable from benzene. Nevertheless, this does not detract from applying the Fractogel column in the fractionation of the H-Coal liquids. The pattern of separation is established in that the aromatic compound with long side chains will elute first while the unsubstituted will lump together and elute last.

It has been customary to classify coal liquids according to solubility (8): hexane soluble fraction (HSF) contains the oils, hexane-insoluble, benzene soluble fraction (BSF) contains the asphaltenes and benzene-insoluble, pyridine soluble fraction (PSF) contains the asphaltols. The molecular weights increase in this

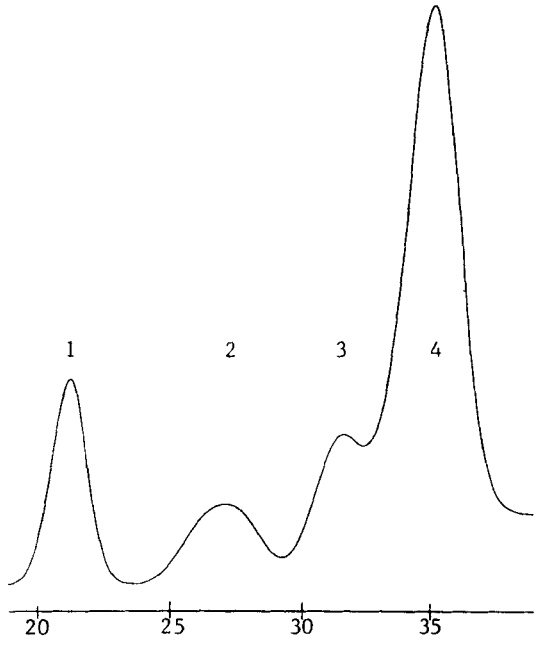

FIGURE 1. Separation of a mixture of eight model compounds as shown in Table 1 on a Fractogel column.

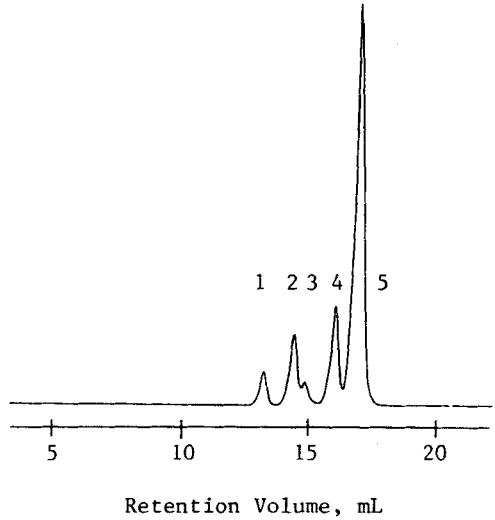

FIGURE 2. Separation of a mixture of eight model compounds as shown in Table 1 on a Toyo Soda Column.

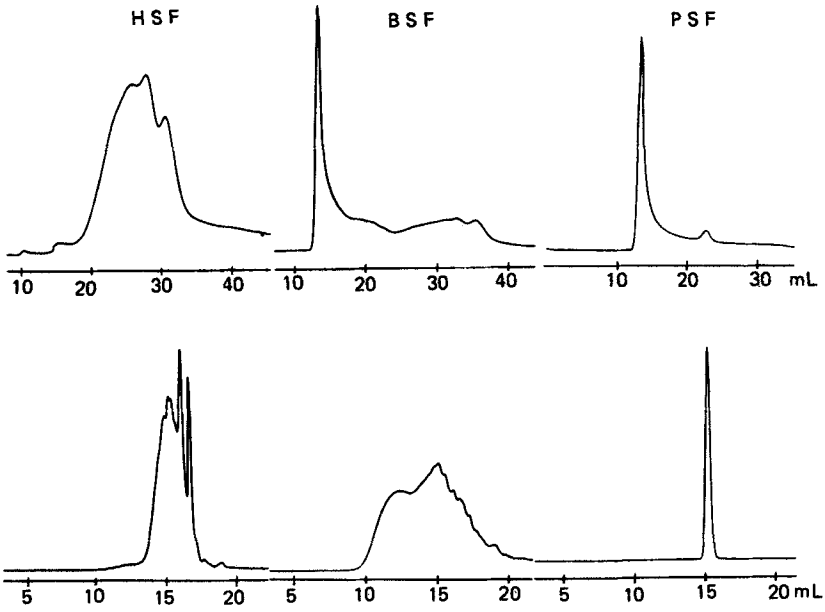

FIGURE 3. Gel Permeation chromatograms for the 3 ASO subfractions on Fractogel (top) and Toyo Soda column (bottom); retention volumes are shown.

order to about 1000 for most current liquefaction products. The four H-Coal liquids were solvent-fractionated accordingly, the HSF fractions of ASO, ASB, and VSO were more than 92 percent of the original mixture, while that of the VSB contained about 7 percent. The BSF ranged from 1 to 5 percent of the first three H-Coal liquids but amounted to about 50 percent of the VSB. The PSF was from 0.5 to 4 percent for the first three H-Coal liquids but was 42 percent of the VSB. These twelve solvent fractions were chromatographed on the Fractogel column set as well as on the Toyo Soda column for comparison. Figures 3, 4, 5, and 6 show the chromatograms for the three solvent fractions of ASO, ASB, VSO, and VSB, respectively, the top figures are the Fractogel chromatograms while the bottom are the Toyo Soda. Insofar as the HSF fractions are concerned, the Fractogel chromatograms show less well-resolved peaks than the Toyo Soda chromatograms. However,

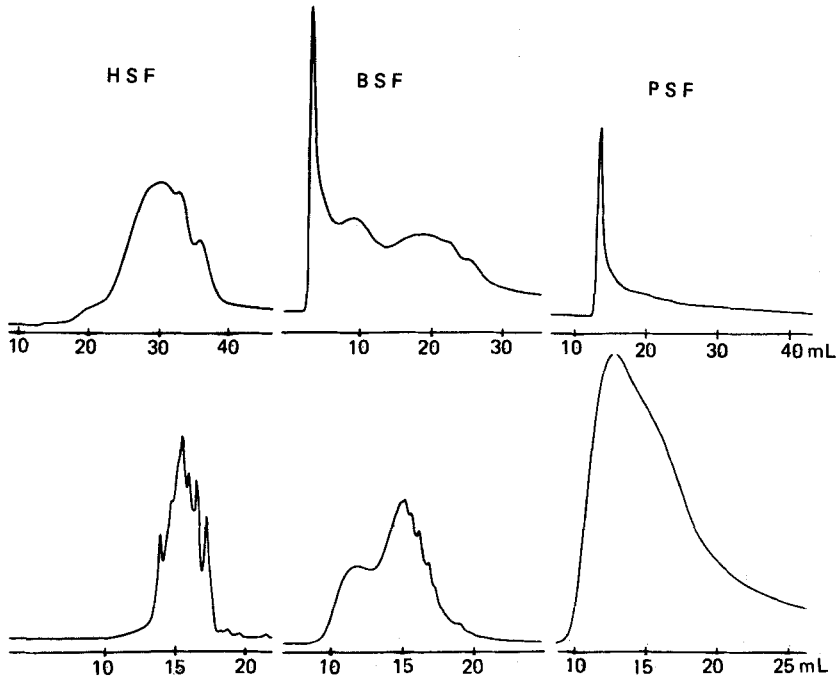

FIGURE 4. Gel permeation chromatograms for the 3 ASB subfractions on Fractogel (top) and Toyo Soda column (bottom); retention volumes are shown.

the bulk of their retention volumes are defined by the eight model compounds as shown in Table 1 for both the Fractogel and the Toyo Soda column. It appears that the phenyltridecane type is the largest size while benzene the smallest of the HSF components. In the case of the BSF and PSF fractions, the Fractogel chromatograms show a sharp peak at about 14 mL. Since the mobile phase contains 25 percent methanol in chloroform, the peak at 14 mL can be attributed to enlarged molecules resulting from solute-solvent interaction (5). It is plausible that the likes of phenolic groups and pyridine nitrogen in these fractions may form polymer-like molecules with methanol through hydrogen bonding. The absence of such a peak on the Toyo Soda chromatograms can be explained in terms of the exclusion limit of the Toyo Soda column

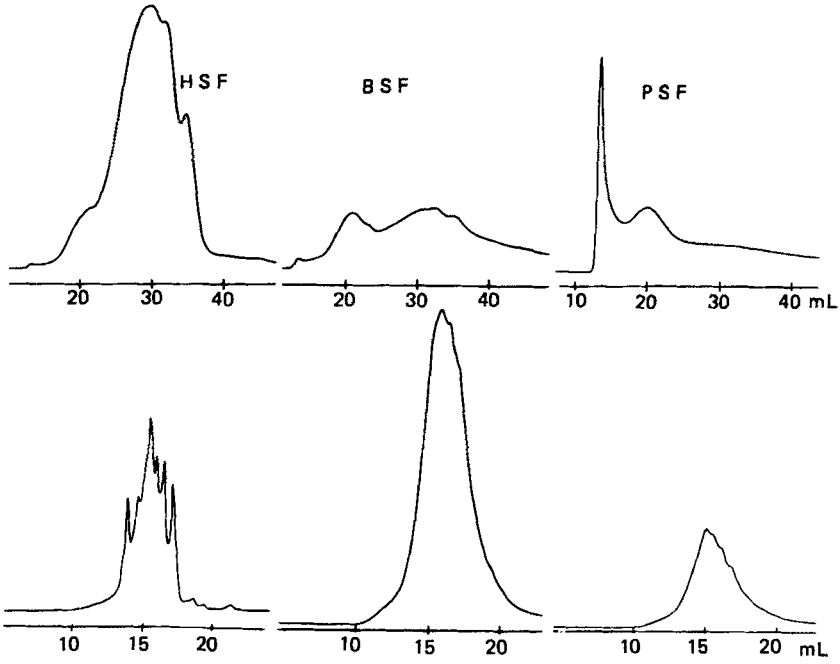

FIGURE 5. Gel permeation chromatograms for the 3 VSO subfractions on Fractogel (top) and Toyo Soda column (bottom); retention volumes are shown.

being three times as much as the Fractogel and that it was eluted with neat chloroform. Otherwise, the BSF and PSF chromatograms tend to show more distributions of larger molecules than the HSF, their separations being similar on both columns. The fine coal ash entrapped in the VSB fractions may account for the broad envelopes in all of the VSB chromatograms. Calibrations of these chromatograms to generate molecular weight information were carried out via preparative runs of the HSF on the Fractogel column. The fractions were subjected to vapor pressure osmometry for the determination of molecular weight. The latter, ranging from 627 for the exclusion fraction to 115 for the fraction at 32 mL, were plotted against the retention volumes of the collected fractions to generate the calibration curves. The molecular

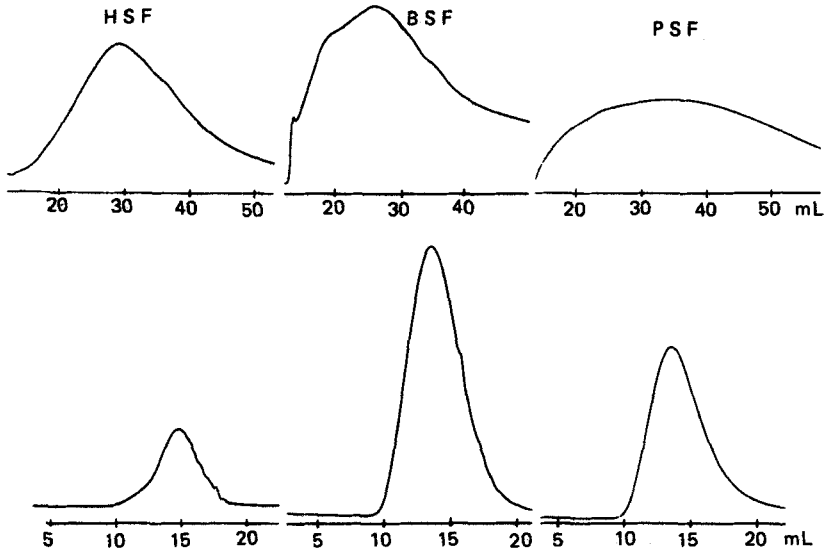

FIGURE 6. Gel permeation chromatograms for the 3 VSB subfractions on Fractogel (top) and Toyo Soda column (bottom); retention volumes are shown.

weight distributions of the H-Coal liquids have been reported (3), the number-average molecular weight distributions being in the range of 200-500 for the three solvent fractions. Since the Fractogel column can be loaded with about 20 mg of the coal liquid per injection to yield a chromatogram similar to that provided by the Toyo Soda column, and considering the low price and ease of packing of the gel, the Fractogel column has shown versatile use as both a preparative and an analytical column for the H-Coal liquids.

In order to determine the scope of separation on the Fractogel column, Table 2 shows the performance in separating aromatic compounds by means of gel permeation chromatography (GPC), reversed phase chromatography (RPC), and normal phase chromatography (NPC), using the Fractogel, Partisil ODS, and LiChrosorb Si60 column, respectively. The Fractogel polyvinyl acetate column apparently separates by size exclusion, the

TABLE 2

Comparison of Separation of Aromatic Compounds by GPC[1], RPC[2], and NPC[3]

Aromatic Compounds	Retention Volume, mL GPC[1]	RPC[2]	NPC[3]
A. Benzene + 3 carbons			
1,2,3-trimethylbenzene	31.2	9.9	2.5
1,2,4-trimethylbenzene	33.0	11.5	2.5
n-propylbenzene	34.2	10.5	2.5
B. Benzene + 4 carbons			
durene	29.8	13.0	2.5
sec-butylbenzene	33.5	13.0	2.3
C. Benzene + 6 carbons			
1,3,5-triethylbenzene	24.3	21.0	2.3
hexamethylbenzene	29.4	31.0	2.4
D. Diaromatic with 12 carbons			
1,3-dimethylnaphthalene	33.4	14.8	2.4
1,5-dimethylnaphthalene	34.7	14.0	2.5
1,4-dimethylnaphthalene	35.0	14.3	2.5
1,8-dimethylnaphthalene	35.6	13.4	2.5
biphenyl	36.3	11.0	2.9
acenaphthylene	39.6	9.8	3.2

[1]Fractogel column eluted with chloroform-methanol 3:1

[2]Partisil ODS column eluted with acetonitrile-water 1:1

[3]LiChrosorb Si60 column eluted with n-hexane

Partisil ODS by reversed phase principle involving partition, adsorption, and surface tension (9), and the LiChrosorb silica gel column by adsorption principle. In terms of separating group A compounds in Table 2 which contain a benzene ring plus three carbons, GPC works as well as reversed phase, both of which are far superior to the normal phase chromatography. Likewise, for group C where compounds contain a benzene ring plus six carbons,

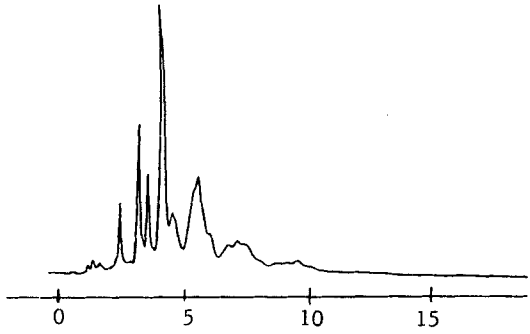

FIGURE 7. Reversed phase chromatogram of HSF of ASO on a Partisil ODS column.

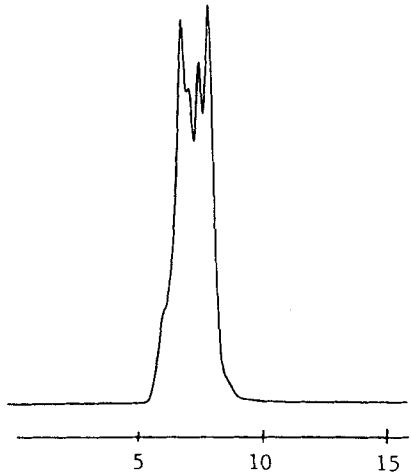

FIGURE 8. Normal phase chromatogram of HSF of ASO on a LiChrosorb Si60 column.

GPC and RPC are just as efficient while NPC is inadequate. For the two group B compounds, benzene plus four carbons, GPC appears to be superior to both RPC and NPC. The last group of compounds are diaromatics containing 12 carbons. In this case, reversed phase chromatography appears to be the best in separating them. Judging from these sets of model compound separations, it would seem that either GPC can be used alone to fractionate H-Coal liquids or that it can be used in combination with the reversed phase method. Figures 7 and 8 show the hexane soluble fraction of ASO when chromatographed by the reversed phase and the normal phase methods, respectively. The chromatogram obtained from the reversed phase ODS column shows a much better spread of the HSF than the silica, hence the ODS will complement the Fractogel column in fractionating the H-Coal liquids.

REFERENCES

1. This is part of a series of reports on the physicochemical properties of liquids derived from Kentucky coal. The research was supported by the Kentucky Institute of Mining and Minerals Research from 1977-1980. The chromatograms in this paper were run by Drs. C. M. Gladstone and M. M. Khan who worked on the project as research associates.

2. (a) Joseph, J. T. and Wong, J. L., Determination of Protonated and Quaternary Carbons in H-Coal Liquids from Quaternary Carbon Suppressed and Nonsuppressed CMR Spectra, Amer. Chem. Soc. Fuel Chem. Div. Preprints, 24, 317, 1979; (b) Joseph, J. T. and Wong, J. L., Fuel, 59, 777, 1980.

3. (a) Wong, J. L., Gladstone, C. M., and Joseph, J. T., Characterization of H-Coal Liquids by FT-NMR Spectroscopy and High Pressure Gel Permeation Chromatography, CHEMRAWN 1, Toronto, Abst. P-19, 1978; (b) Wong, J. L. and Khan, M. M., Gel Permeation Chromatography of H-Coal Liquids, Coal Symposium, Kentucky Academy of Sciences Meeting, 1979; (c) Khan, M. M., Molecular Weight Distributions and Size Fractionations of H-Coal Liquids, Fuel, 61, 553, 1982; (d) Wong, J. L. and Gladstone, C. M., Size Exclusion Chromatography of H-Coal Liquids on Silica, Polyvinylacetate and Polystyrene Columns, Fuel, 62, 000, 1983.

4. Anbar, M. and St. John, G. A., Characterization of Coal-Liquefaction Products by Molecular-Weight Profiles Produced by Field-Ionization Mass Spectrometry, Fuel, 57, 105, 1978.

5. Philip, C. V. and Anthony, R. G., Separation of Coal-Derived Liquids by Gel Permeation Chromatography, Fuel, 61, 357, 1982, and pertinent references cited.

6. Brown, R. S., Hausler, D. W., and Taylor, L. T., Gel Permeation Chromatography of Coal-Derived Products with On-Line Infrared Detection, Anal. Chem., 52, 1511, 1980.

7. Hausler, D. W., Hillgeth, J. W., McNair, H. M., and Taylor, L. T., Size Exclusion Chromatography for the Separation of Whole Coal Liquids, J. Chromatogr. Sci., 17, 617, 1979, and pertinent references cited.

8. (a) Farcasiu, M., Mitchell, T. O., and Whitehurst, D. D., Asphaltols--Keys to Coal Liquefaction, Chem. Tech., 7, 680, 1977; (b) Farcasiu, M., Fractionation and Structural Characterization of Coal Liquids, Fuel, 56, 9, 1977.

9. Horvath, C. and Melander, W., Liquid Chromatography with Hydrocarbonaceous Bonded Phases, J. Chromatogr. Sci., 15, 393, 1977.