SEPARATION OF COAL LIQUIDS BY SIZE EXCLUSION CHROMATOGRAPHY - GAS CHROMATOGRAPHY (SEC-GC)

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Introduction

The high efficiency gel columns packed with 5μm particles have increased the efficiency and decreased the analysis time of size exclusion chromatography (SEC). Since relatively large samples can be separated in a time as short as 20 minutes, SEC can be used as a preliminary separation technique prior to other analytical techniques such as gas chromatography (GC) and gas chromatography-mass spectroscopy (GC-MS). Such SEC separation of coal liquids, petroleum crudes and their distillation cuts into four or five fractions, followed by the analysis of the SEC fractions by GC and GC-MS have been reported elsewhere (1-14). The fraction collection and concentration of fractions were performed manually. This procedure was inefficient, and suspectible to human error. The Automated fraction collection followed by injection of the fraction into the GC reduces analysis time, and offers an option for collecting a desired number of fractions at predetermined time intervals.

The SEC separates coal liquids into fractions containing species with similar linear molecular sizes. Since similar molecular size species in coal liquid happened to have similar functionalities, the size separation enables the separation of fractions containing similar chemical species. When tetrahydrofuran (THF) is used as the mobil phase the coal liquid can be separated into four fractions containing heavy nonvolatiles, long chain alkanes mixed with light nonvolatile, phenols and aromatics. When the number of fractions are increased, less complex chromatograms with fewer peaks are obtained. The results of SEC-GC analysis of coal liquids indicate that the coal liquids are composed of a very large number of species but with similar structural blocks and functional groups. Lumping of similar components into four distinct groups such as nonvolatiles, alkanes (nonaromatic hydrocarbons) alkylated phenols and aromatics is seen as practical means of characterizing coal liquids. The instrumentation, analysis of coal liquid samples including recycle solvents are discussed in detail in this paper.

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Experimental

A Western Kentucky Synthoil and four recycle solvents from the Energy Research Center, University of North Dakota were the samples used for the analysis. Dry additive free tetrahydrofuran (THF) under helium atmosphere was used for preparing sample solutions and as the mobil phase in the size exclusion chromatograph (SEC). Although the synthoil could be injected without dilution, a 50% solution was preferred in order to reduce possible peak spreading and tailing. Since the recycle solvents were very viscous, 25% solutions were used. All the solutions were filtered through 0.5 Millipore filters using modest heat, but not high enough to boil THF, from a hot air gun and 30 psi Nitrogen pressure.

The instrumentation included a liquid chromatograph (LC, Waters ALC/GPC Model 202) equiped with a 60 cm, 5µm 100 Å PL gel column (Polymer Laboratories) and a refractive index detector (Waters Model R401) a Varian Chromatographic system (GC, VISTA 44) equiped with a 30 meter x 0.32 mm ID DB-5 capillary column (bonded phase fused silica column manufactured by J&W Scientific Co.) an autosampler (Varian 8000), a flame ionization detector (FID) and a nitrogen specific detector (thermionic ion specific - TSD) and a microcomputer system (IBM CS 9000) with 1000 K bytes RAM and dual 8" floppy disc drives for collecting raw chromatographic data.

The continuous sample separations on the gel column followed by the GC analysis of selected fractions was achieved by the operation of two sixport valves and a 34 port valve (All from Valco Instrument Company) as illustrated in figure 1. Sample injection into the LC was performed by a sixport valve (V_1) with a 2 ml sample loop and fitted with a syringe-needleport for variable sample size injection. The combined operation of another sixport switching valve and the 34 port valve (V_3) with 16 sample loops (100 µl) enabled the linking of the liquid chromatograph with the autosampler of the gas chromatograph. The autosampler was modified to handle 100 µl samples directly from the fraction collection loops of V_3. When V_2 was turned clockwise, it kept V_3 in line of LC effluents so that the fractions of separated sample could be collected and also the autosampler was bypassed. V_2 at its counter clockwise position kept V_3 in line with the autosampler for sample injection but bypassed the LC stream. Generally 0.1 µl sample size was used for GC analysis. The stream from the capillary column was split (50/50) for the simultaneous monitoring by the FID and TSD. The real time monitoring of the GC was possible on both Varian and IBM systems and the raw chromatographic data were stored on the 8" floppy discs. The fraction collection, sample injection into the GC as well as the data collection was performed by the integrated system composed of a Varian Automation System (VISTA 401) and the IBM microcomputer (CS 9000). For each sample injection into the GPC column, up to 16 fractions were collected and analyzed by the GC using appropriate gas chromatographic porgrams stored in the memory without any manual interaction.

Results and Discussions

The effluents from the GC capillary column are split into two streams and monitored by a flame ionization detector (FID) and a nitrogen specific detector (TSD). The analysis of a coal liquid derived naphtha (produced from western Kentucky coal-synthoil) is shown in Figure 2. The GC-MS analysis of coal liquid can miss several nitrogen compounds due to complex fragmentation pattern and low concentration. The FID output shows signs of overloading and most peaks are unresolved. Such overloading does not appear to affect the separation of nitrogen compounds. The use of a nitrogen specific detector in addition to FID enables one to identify the nitrogen species easily and GC-MS can be used for their structural identification.

Molecular size parameters such as molecular weight, molecular volume and hydrodynamic volume are used very effectively as the basis for SEC separation of polymers with identical building blocks or monomers (16-21). These molecular parameters need correction factors which vary depending on the individual structure of species (20), in order to use them as the basis for the SEC separation of mixtures of species especially the low molecular size compounds.

The SEC studies on a number of small molecular size species (5) such as alkanes, aromatics, phenols, amines and complex mixtures (15) such as coal liquids (1-11), petroleum crudes and their distillates (12,14), indicate that linear molecular size or the length of the molecule measured from its valance bond structure, is a better basis for explaining the mechanism of size separation by SEC (12). The effective linear molecular size of a species depends on its tendency to hydrogen bond with the solvent resulting in an increase of linear molecular size compared to nonhydrogen bonding species. Tetrahydrofuran, the SEC mobil phase, can increase the length of certain hydrogen bonding species such as phenols, amines and alcohols while the size of compounds such as benzene, pyridine, thiophene and alkanes are unaffected. This phenomenon enables the separation of phenols and aromatics in coal liquid into separate fractions.

SEC separation of recycle solvent obtained by the liquefaction of Wydak coal is illustrated in Figure 3a. The SEC effluents can be divided into four fractions based on elution time. The longer species appears first and are collected in Fraction 1. Since they are not volatile enough for GC-MS analysis, they are termed as heavy nonvolatiles. The second fraction is composed of volatiles, mostly straight chain alkanes (n $C_{14}H_{30}$ - n $C_{44}H_{80}$), and light nonvolatiles. Some olefins whose concentration may depend on the severity of liquefaction process, and branched alkanes such as pristane and phytane are also found in the second fraction. The third fraction is enriched mostly with alkylated phenols, indanols and naphthols. Some long structured aromatics such as biphenyls and binaphthyls may appear in this fraction. If the coal liquids are refined by cracking process resulting in naphthenic materials - a mixture of olefins and cyclic hydrocarbons, the third fraction may contain these materials also. The fourth fraction is composed of alkylated benzenes, indans, naphthalenes and heavy fused ring aromatics such as pyrenes and benzopyrenes.

When valve V_2 and V_3 are engaged the SEC Effluents (Figure 1) can be collected on the sample loops of V_3 at specific intervals. The refractive index detector output shows the effect of such fraction collections as negative peaks (compare Figure 3a and 3b). Although sixteen is the maximum number of fractions, which can be collected at one time, more than sixteen fractions can be collected for a sample by repeating the procedure aimed at different elution times. Figure 4a shows SEC of a synthoil produced from western Kentucky coal. Twentythree fractions were collected. The FID output of 18 fractions, leaving the first three and the last two, are shown in Figure 5. The synthoil sample was analyzed by GC-MS prior to SEC-GC analysis and the major components were identified as alkanes ranging from n $C_{10}H_{22}$ to n $C_{44}H_{80}$, phenols such as alkylated phenols, indanols and naphthols and aromatics such as alkylated benzenes, indans and naphthalenes. The first GC in Figure 5 shows the FID output of SEC fraction 4 of synthoil. All the peaks shown are straight chain alkanes. The next GC shows that the volatiles in fraction 5 are composed of relatively smaller alkanes. As the elution time increases the alkane chain length decreases. The fractions with short alkanes has overlap from heavy phenols (Fig. 5 GC, 6-9). The heavy phenols are not resolved but appear as a base line shift which is due to a large number of phenolic species eluting unresolved. As the fraction number increases smaller phenols appear as well resolved peaks (Fig. 5 GC, 9,14). When the molecular weight of phenolic species are increased by adding alkyl groups the probable number of isomers are increased and more isomers are possible for heavier phenols. The heavy and light aromatics appear in the last fractions (Fig. 5 GC 15-18). The fused ring aromatics such as pyrene and benzopyrenes appear after light aromatics (12).

At the Energy Research Center of the University of North Dakota, anthracene oil distillate was initially used as the solvent for coal liquefaction. The solvent along with dissolved liquefaction products were reused several times and solvent grade products mixed with the original solvents were supplied as recycle solvents. Four recycle solvents derived from four coals were analyzed by SEC-GC. The gas chromatograms of similar SEC fractions of these liquids are shown in Figures 3 and 4. Gas chromatograms of three similar fractions from each of the four solvents are presented in Figure 6. Examination of GCs indicate that these solvents contain similar volatile components.

Conclusions

Although SEC and GC are two powerfull chromatographic techniques, their combined use for analyzing complex mixtures has been limited due to the time consuming steps involved. The two valve interface which links the liquid chromatograph to gas chromatograph and the computer system which automate the system, reduce the analysis time as well as the frequency of manual interaction during the analysis which may take 8-10 hours for a coal liquid sample. By adding a mass spectrometer as a third detector to the GC, an extensive analysis of a rather complex sample such as coal liquid, petroleum crude and their refinery products is possible.

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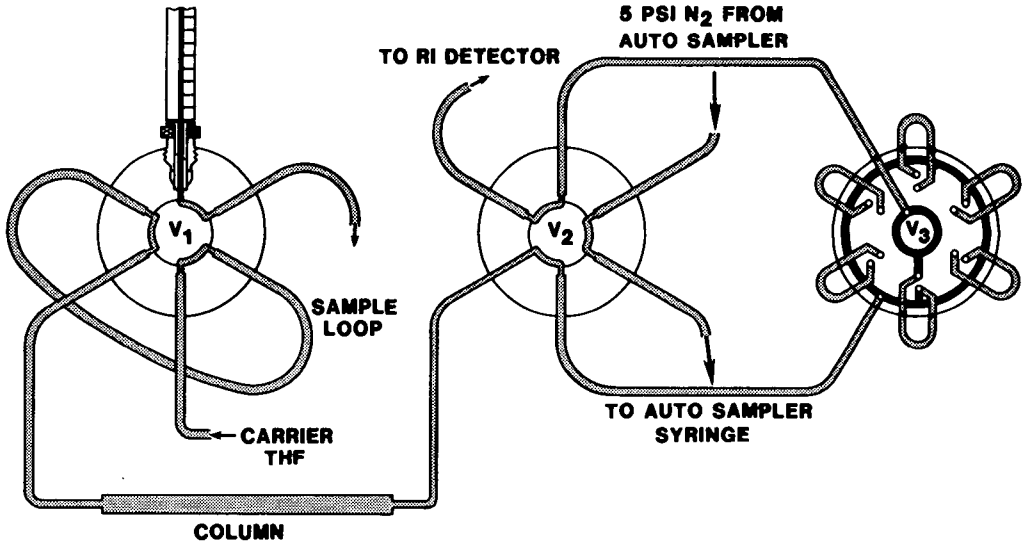

Figure 1. LC - GC inferface. Note: V_3 has sixteen loops instead of six shown.

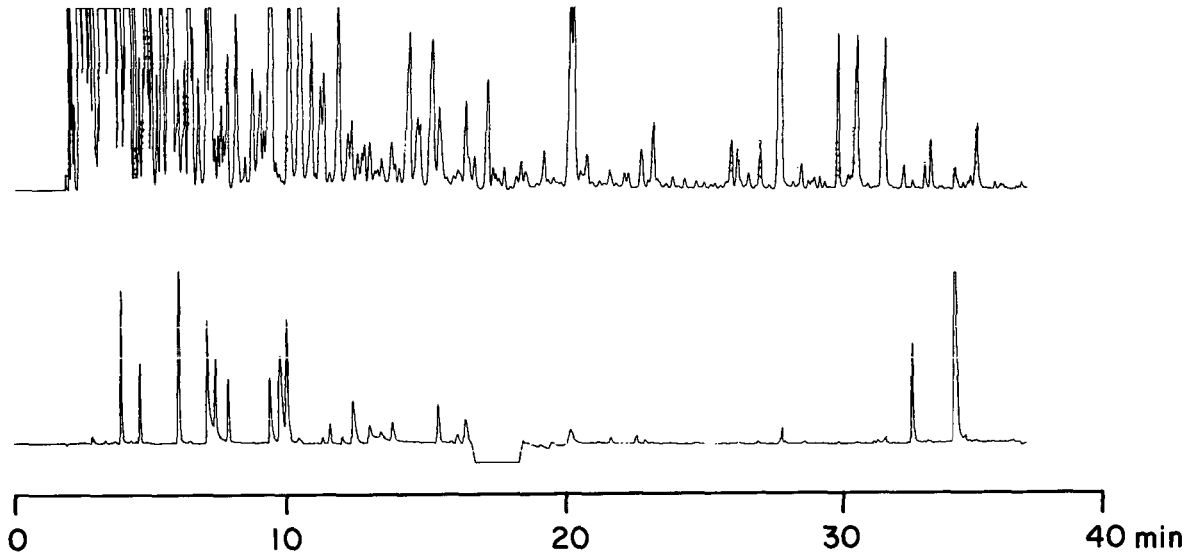

Figure 2. Gas chromatographic analysis of coal derived naphtha with duel detectors. The gas chromatograph is equipped with a bonded phase fused silica capillary column and an outlet stream splitter (1:1). Temperature program: 3 min hold at 40°C, 2°C/min to 80°C, 2°C/min to 120°C and 4 min hold at 120°C. One stream is monitored by an FID detector (top) and the other is monitored by a nitrogen specific detector (bottom).

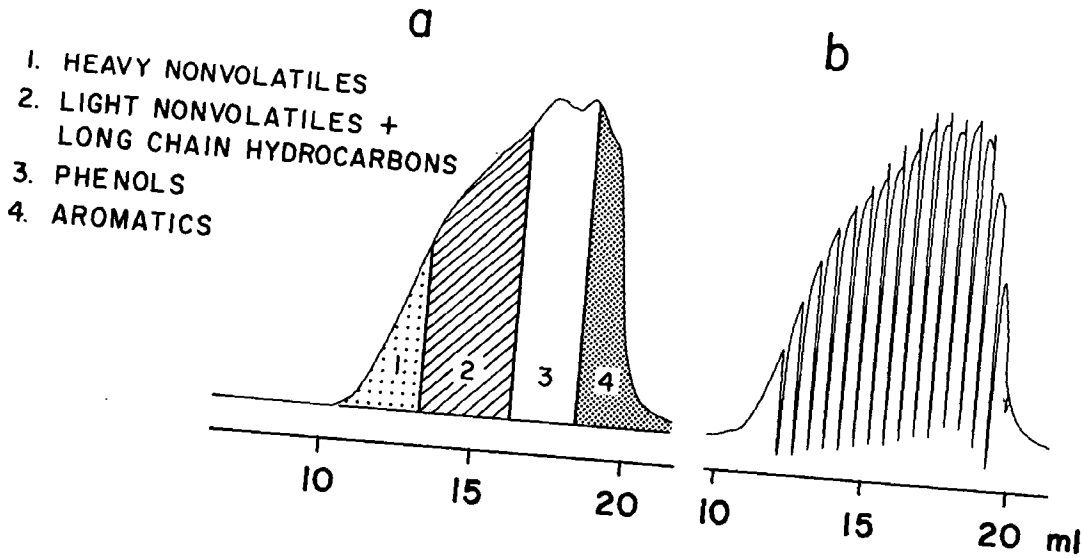

Figure 3. SEC separation of Wydak coal derived recycle solvent (a) LC-GC interface bypassed (b) 16 fraction were collected by LC-GC interface.

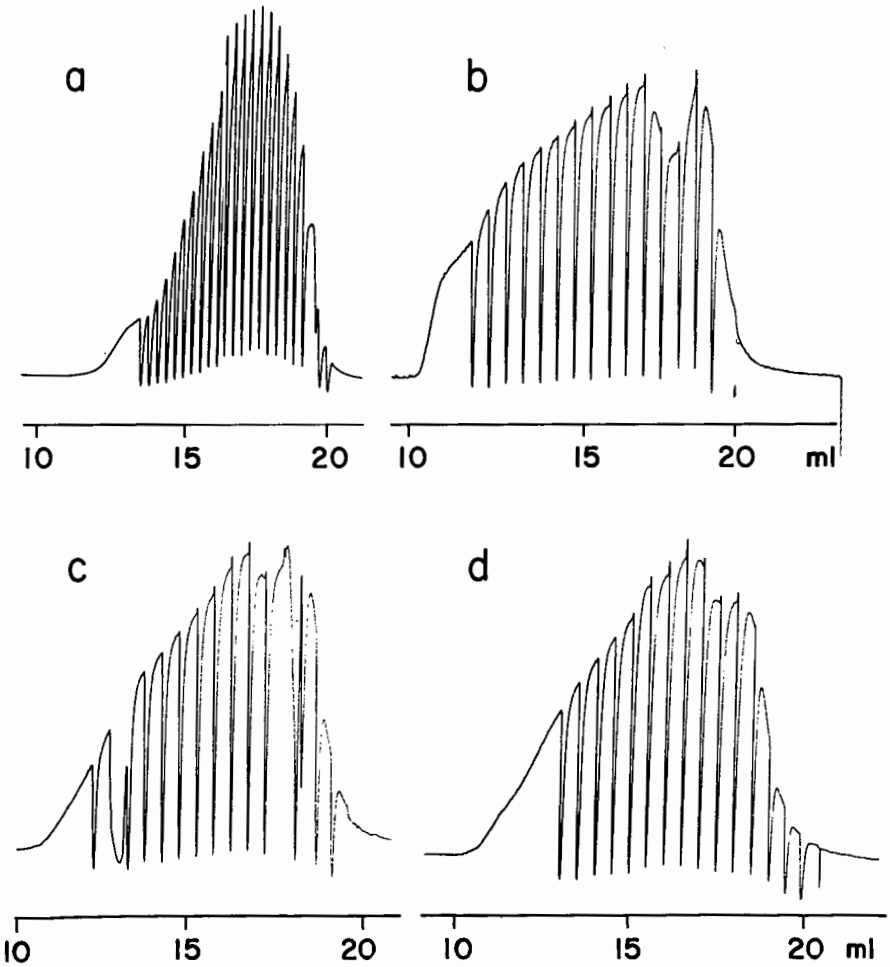

Figure 4. 100 µl fractions are collected from the SEC effluents (a) Western Kentuck Synthoil. Recycle Solvents (b) Texas Big Brown (c) Beulah (d) Zap-2.

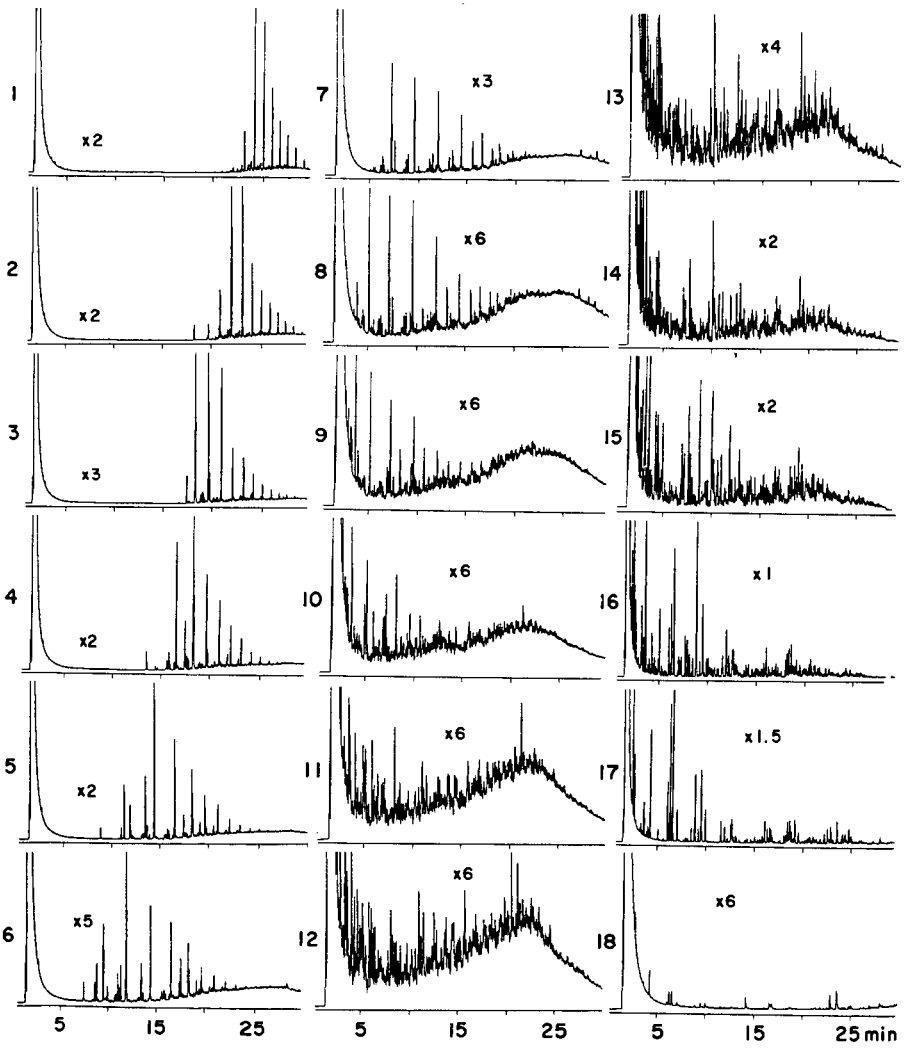

Figure 5. Gas Chromatograms of fractions from Western Kentucky Synthoil (Figure 4a) temperature program: 80-120°C at 4°C/min, 120-280°C at 10°C/min and 4 min. hold at 280°C.

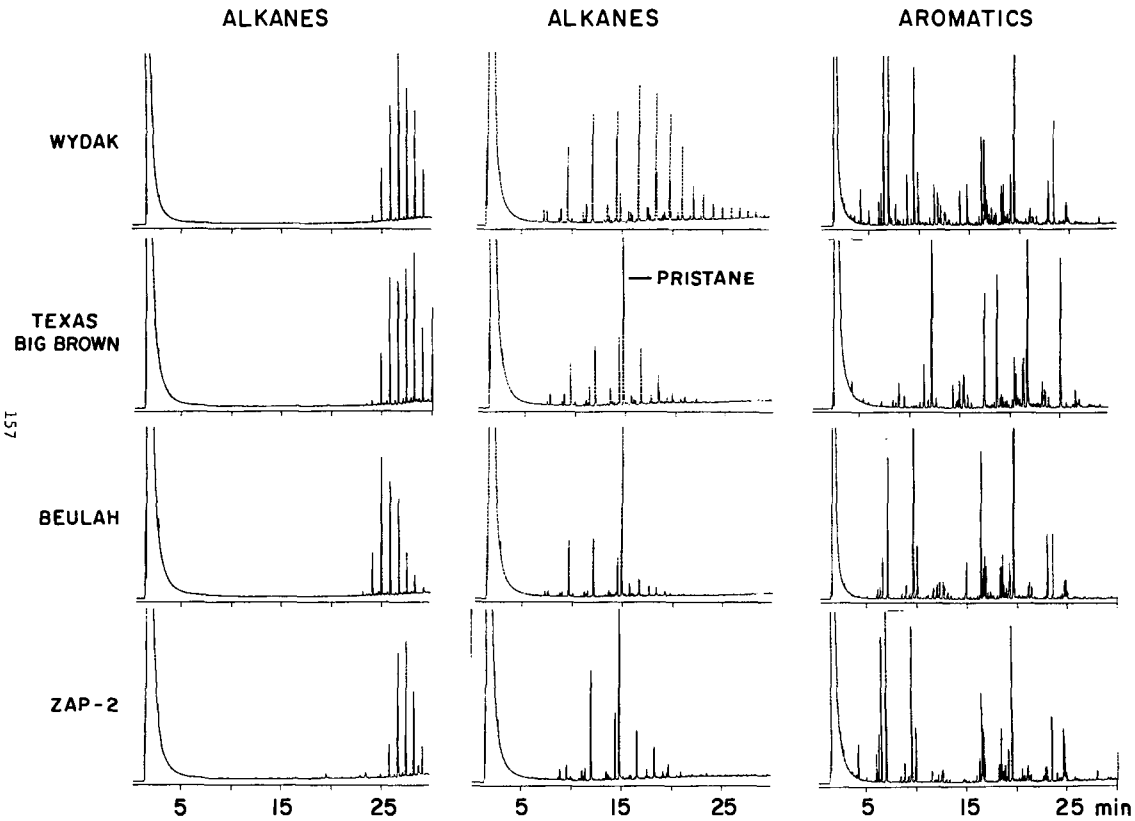

Figure 6. Gas chromatograms of similar fractions of four recycle solvents. GC conditions are same as in Figure 5.