

CHROMATOGRAPHIC SEPARATION OF COAL LIQUIDS

By

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INTRODUCTION

Coal liquefaction is a major attempt to meet certain energy requirements and at the same time protect the environment. If coal liquefaction is to be successful, a technology must be developed that provides analytical data on both feed coals and liquid products. Refining procedures could then be altered to accommodate syncrudes of different composition. Thus, efficient processing and utilization require a knowledge of the chemical composition of coal liquids.

Interest in the chemical structure of coal and coal conversion products has increased greatly in recent years. This interest has produced two general approaches to the study of coal liquids. One is the detailed characterization of a particular coal liquid by extensive separation followed by elaborate spectroscopic characterization of the various compound types (1). The other approach emphasizes a rapid and simple method of separation in which fewer fractions are generated (2). The latter is more amenable to on-stream control, where fast procedures are required.

Our approach to the analysis of coal liquids incorporates the most attractive features of the two approaches. Five chemically meaningful fractions are generated from a total coal liquid. These fractions are separated on a chemical functionality basis and are suitable for detailed characterization. Asphaltene and pre-asphaltene fractions are purposefully avoided because of their lack of chemical definition.

This paper describes the separation of a coal liquid into five fractions by liquid chromatography. The fractions are generated by ion exchange, coordination complex, and adsorption chromatography. The nonhydrocarbon fractions account for most of the coal liquid and were emphasized in the characterization work that is reported here.

EXPERIMENTAL

Coal Liquid Sample

The coal liquid used in this investigation was obtained from the Pittsburgh Energy Research Center's Synthoil process (3). The feed was a high-sulfur West Virginia coal slurried in 65 percent product recycle oil. The process used a 14-ft catalytic reactor operated at 450°C and 4000 psig of hydrogen. The liquid product was centrifuged to reduce water and solids.

Apparatus

Infrared spectra were recorded using a Perkin-Elmer 621* infrared spectrophotometer; low-resolution mass spectra were recorded on a Varian CH-5 single-focusing mass spectrometer. The columns used for chromatographic separations were similar to those used by Jewell et al. (4). They were gravity flow columns, 1.4-cm i.d. by 119-cm, with a recycling arrangement that permits the continuous elution of the sample without the need for large quantities of solvent.

Reagents

All solvents were flash distilled. The ion-exchange resins and other chromatographic materials were prepared according to previously reported methods (5).

Routine Methods of Nitrogen, Sulfur, and Oxygen Analyses

Elemental analyses were performed at a commercial laboratory; nitrogen was determined by the micro-Dumas method; sulfur, by combustion followed by titration of oxidation product with barium perchlorate to a colorimetric endpoint; and oxygen, by a modified Unterzaucher method.

Quantitative Infrared Analyses

Quantitative infrared measurements and calculations were performed in a manner similar to that used by McKay et al. (6).

Separation Procedure

The coal liquid (0.5 g) was dissolved in methylene chloride (20.0 ml) and passed through a 10- to 15-micron filter to remove inorganic solids and any undissolved organics. The material retained on the glass filter amounted to less than 2 percent of the total coal liquid. The separation was performed by sequentially passing the coal liquid through four chromatographic columns to obtain five fractions: acids, bases, neutral nitrogen compounds, saturate hydrocarbons, and aromatic hydrocarbons as shown in Figure 1.

Separation of Acids--Anion Exchange Chromatography. - The sample of filtered coal liquid was chromatographed on anion resin (100 g) that had been wet packed in the column with methylene chloride. Unreactive material was washed from the resin with methylene chloride (700 ml) for 3 hours or until the eluant was clear. After the unreactive materials were removed, the reactive compounds (acids) were recovered in two steps. The column was first eluted with 60% benzene-40% methanol (350 ml); the resin was then removed from the column and placed in an extractor; the remaining acid was removed by elution with 60% benzene-40% methanol (350 ml) saturated with carbon dioxide.

Separation of Bases--Cation Exchange Chromatography. - The sample of acid-free coal liquid (about 350 mg) was taken to dryness by evaporation under a nitrogen atmosphere and redissolved in benzene (25 ml). The benzene solution was chromatographed on cation resin (50 g) that had been wet packed in the column with benzene. Unreactive material was eluted from the resin with benzene (500 ml) for 1 hour or until the eluant was clear. The reactive material (bases) was removed from the resin in two steps. The column was first eluted with 60% benzene-40% methanol (350 ml); the resin was then removed from the column and placed in an extractor; the remaining bases were removed from the resin with 54% benzene-38% methanol-8% isopropylamine (200 ml).

Separation of Neutral Nitrogen Compounds--Ferric Chloride Coordination Chromatography. - Ferric chloride-Attapulugus clay (80 g) was placed above anion resin (120 g) in a single column. After the column was washed with cyclohexane (100 ml), the acid- and base-free material, freed of benzene and redissolved in cyclohexane (50 ml), was passed through the column. The column was eluted with cyclohexane (300 ml) to remove hydrocarbons. The nitrogen compound-ferric chloride complexes were removed from the clay with 1,2-dichloroethane (200 ml). These complexes were subsequently broken by passing the solution over the anion resin; the ferric chloride salt was retained on the resin, and the neutral nitrogen compounds were recovered in the eluate.

Separation of Hydrocarbons--Silica Gel Chromatography. - The acid-, base-, and neutral-nitrogen-free coal liquid, freed of cyclohexane and redissolved in n-pentane (50 ml), was placed on a silica gel column (150 g). The column was eluted with n-pentane (approximately 500 ml or until UV monitor showed absorbance greater than 10 percent of full scale at 254 nm) to remove the saturate hydrocarbons. The aromatic hydrocarbons were then recovered by elution with benzene (approximately 300 ml).

RESULTS AND DISCUSSION

Recovery and precision data for three different runs are presented in Table 1. Recoveries from 96 to 98 percent may be expected from the separation scheme. The precision data in the last column of Table 1 show a reproducibility of ± 3 wt. percent for each of the five fractions.

TABLE 1. - Three separations showing weight percent and precision for each fraction

Fraction	Weight percent			Precision
	Run 1	Run 2	Run 3	
Acid	27	33	31	30 \pm 3
Base	20	18	22	20 \pm 2
Neutral nitrogen	12	10	11	11 \pm 1
Saturate	10	13	11	11 \pm 2
Aromatics	27	22	23	24 \pm 3
Recovery	96	96	98	97 \pm 1

The data in Table 1 show that for each separation run the acids, bases, and neutral nitrogen compounds represent about 60 percent of the total coal liquid. Acids and bases alone amount to about 50 percent of the total liquid showing the highly polar nature of the coal liquid. This relatively high amount of polar material compared with amounts found in petroleum poses problems in developing separation methods and in processing these liquids into useful fuels.

The saturate and aromatic hydrocarbon fractions represent about 35 percent of the total liquid. The content of aromatic hydrocarbons is about twice that of saturate hydrocarbons, reflecting the aromatic character of the coal feedstock.

Elemental analyses in Table 2 show that oxygen and nitrogen are the primary heteroatoms present in the polar fractions. The acid fraction contains about 5 percent oxygen, primarily due to large amounts of phenolic compounds as discussed later. The bases are high in nitrogen, having about 4 percent nitrogen. Reproducible data for the neutral nitrogen fraction were not obtained so they are not included in Table 2. The saturate hydrocarbons contain only small amounts of heteroatoms, but the aromatic hydrocarbons contain large amounts of oxygen heteroatoms. The aromatic fraction shows 3.4 percent oxygen, which is high for a hydrocarbon fraction. This might be explained by the presence of furan or dibenzofuran-type oxygen compounds that are not removed by the resins or the ferric chloride. Data on sulfur are too limited to determine whether sulfur is evenly distributed among the fractions or whether sulfur compounds are concentrated in any one fraction(s). Molecular-weight data on the total coal liquid and on selected fractions from the separation show average molecular weights ranging from 210 to 250.

TABLE 2. - Elemental analyses and molecular weights of Synthoil and fractions

Sample	Weight percent					Molecular wt.
	Carbon	Hydrogen	Nitrogen	Oxygen	Sulfur	LRMS*
Total Synthoil	86.09	7.4	1.6	3.9	0.7	225
Acid	79.4	6.7	1.0	5.5	0.8	250
Base	81.5	7.4	3.9	1.9	-	225
Saturates	88.1	11.6	0.3	-	-	230
Aromatic	87.6	7.6	0.1	3.4	0.6	210

*Low-resolution mass spectrometry.

Characterization of Acid Fraction

The acid fraction represents about 30 percent of the total coal liquid. This fraction has 5.5 percent oxygen (Table 2) and an average molecular weight of 250. Calculations from these data, assuming one oxygen atom per molecule, show that 86 percent of the molecules contain one oxygen atom. Similarly, one percent nitrogen and a molecular weight of 250 calculates to 15 percent of the molecules containing one nitrogen atom.

The infrared spectrum of the acid fraction, Figure 2, shows a strong band of free phenolic O-H stretching vibration at 3590 cm^{-1} . The lack of significant absorption in the carbonyl region ($1650\text{-}1750\text{ cm}^{-1}$) indicates the absence of carboxylic acids. Quantitative infrared analysis shows that approximately 85 percent of the fraction is represented by the phenolic O-H stretching band. The remaining material can be accounted for by quantitative analysis of the N-H absorption at 3460 cm^{-1} , showing the presence of pyrrolic nitrogen compounds.

Two different methods give the same values for oxygen compounds (phenols) and for nitrogen compounds (pyrroles). Thus, the elemental analysis suggests 86 percent oxygen compounds, and infrared shows that these compounds, 85 percent of the fraction, are phenols. Similarly, elemental analysis shows 15 percent nitrogen compounds and infrared shows about the same amount of pyrrolic nitrogen compounds.

Characterization of Base Fraction

The base fraction represents about 20 percent of the coal liquid. A nitrogen content of almost 4 percent reflects a successful attempt to concentrate nitrogen compounds. From the average molecular weight and the nitrogen content it appears that about 70 percent of the molecules contain one nitrogen atom. This is not as easy to substantiate with infrared spectroscopy as it was in the acid fraction. The problem results from overlapping bands, as shown in Figure 3. Pyrrolic N-H stretching at 3460 cm^{-1} overlaps with amide-type N-H stretching at 3410 cm^{-1} , prohibiting quantitative determinations by infrared spectrometry. The infrared spectrum shows carbonyl absorption in the region $1650\text{-}1700\text{ cm}^{-1}$, which may be due to small amounts of amides. A shoulder on the low-frequency side of the 1600 cm^{-1} band may indicate the presence of pyridines in this fraction.

Neutral Nitrogen Fraction

This fraction represents only about 10 percent of the total coal liquid. The infrared spectrum of this fraction is given in Figure 4. The spectrum shows an absorption band at 3460 cm^{-1} due to pyrrolic N-H stretching vibrations and a shoulder around 3410 cm^{-1} probably due to N-H stretching of amide types. Carbonyl absorption between $1700\text{ and }1750\text{ cm}^{-1}$ also suggests the presence of amides.

Saturate Hydrocarbon Fraction

Saturated hydrocarbon compounds comprise 11 percent of the total coal liquid and less than one-third of the total hydrocarbon material. A gas chromatogram of this fraction is presented in Figure 5. The figure shows that normal paraffins, ranging in carbon number from 13 to 35, are major components of this fraction.

Aromatic Hydrocarbon Fraction

About one-fourth of the total coal liquid is defined by the separation method as the aromatic hydrocarbon fraction. However, this fraction has been shown to have over 3 percent oxygen. The compound types containing oxygen have not been defined in this work. Calculations using 3.4 percent oxygen and an average molecular weight of 210, assuming one oxygen atom per molecule, show that about 45 percent of the molecules contain oxygen. This oxygen is probably of the furan or dibenzofuran type which is nonreactive to resins or ferric chloride. Thus, these compounds are isolated with aromatic hydrocarbons in the final separation step.

SUMMARY

A Synthoil coal liquid that had not been solvent deasphalted was separated into fractions of acids, bases, neutral nitrogen compounds, saturate hydrocarbons, and aromatic hydrocarbons using ion exchange, coordination, and adsorption chromatography. The separation method is reproducible, and recovery of material was better than 95 percent. The method separates compounds according to chemical functionality and generates fractions that are suitable for detailed characterization. The Synthoil coal liquid used in this investigation contains about 30 percent acids and 20 percent bases, according to the ion exchange resin definition of acids and bases. The acids were characterized as being about 85 percent phenolic compounds and 15 percent compounds containing pyrrolic nitrogen. The bases were found to be largely pyridine and pyrrolic nitrogen compound types. The saturate hydrocarbons were 11 percent of the total coal liquid, and the aromatic hydrocarbons were about 24 percent; however, oxygen compounds, probably of the dibenzofuran type, were also found in the aromatic hydrocarbon fraction. The average molecular weight of the coal liquid sample was determined by low resolution mass spectrometry to be about 225.

CONCLUSIONS

This separation method, a modification of a previous method, may be useful for separating other coal liquids according to chemical functionality. An important advantage of this method over other separation schemes used for coal liquids is that the total coal liquid is separated and a minimum number of fractions is generated. A practical application of the separation scheme may be found in monitoring the amounts of acids and bases produced in coal liquification processes. Such information is important because acids and bases are known to cause both chemical and physical problems in the processes.

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*Mention of specific brand names or models of equipment is made for identification only and does not imply endorsement by the Department of Energy.

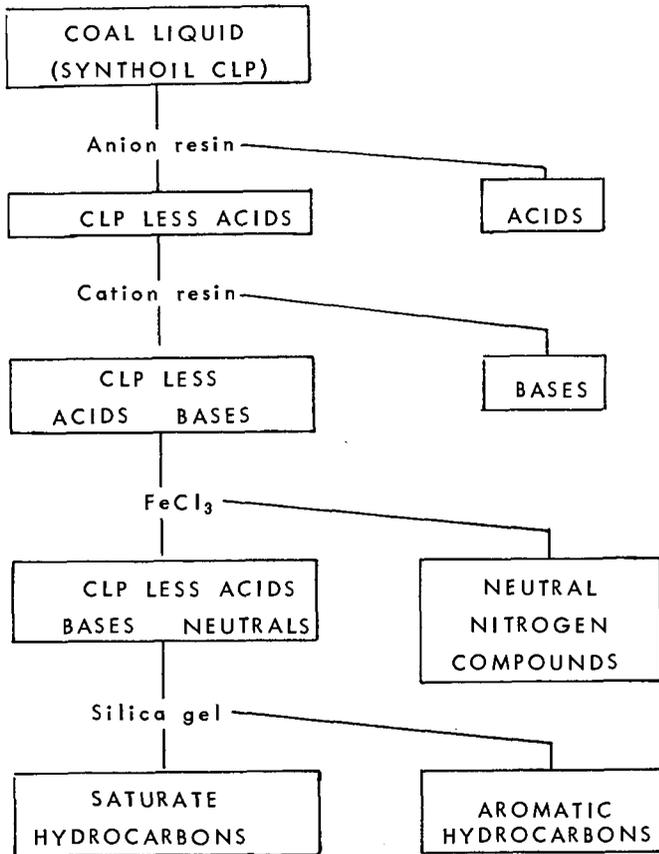


Figure 1- SEPARATION PROCEDURE

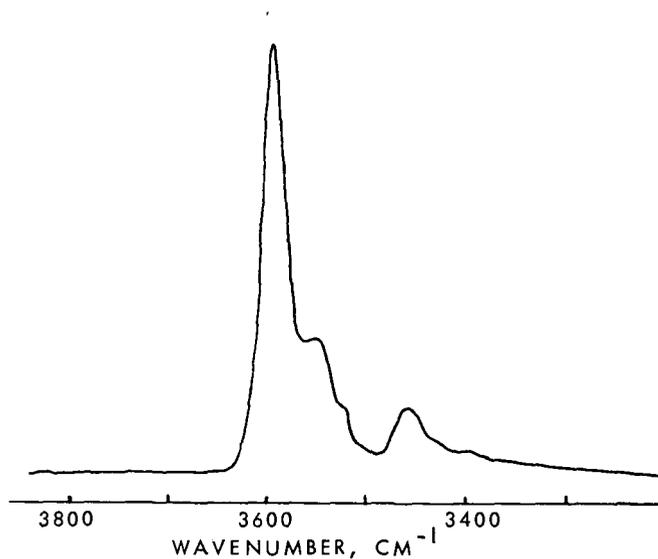


Figure 2- PARTIAL INFRARED SPECTRUM OF ACID FRACTION

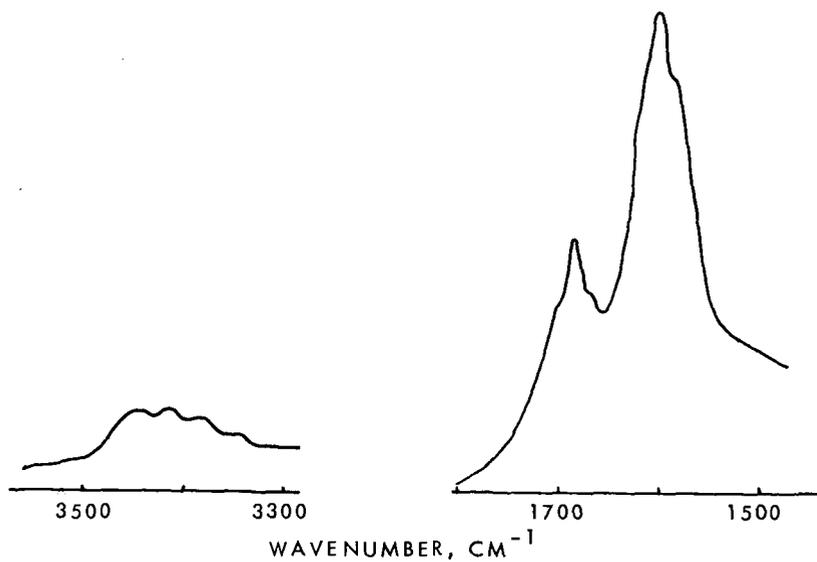


Figure 3 - PARTIAL INFRARED SPECTRUM OF BASE FRACTION

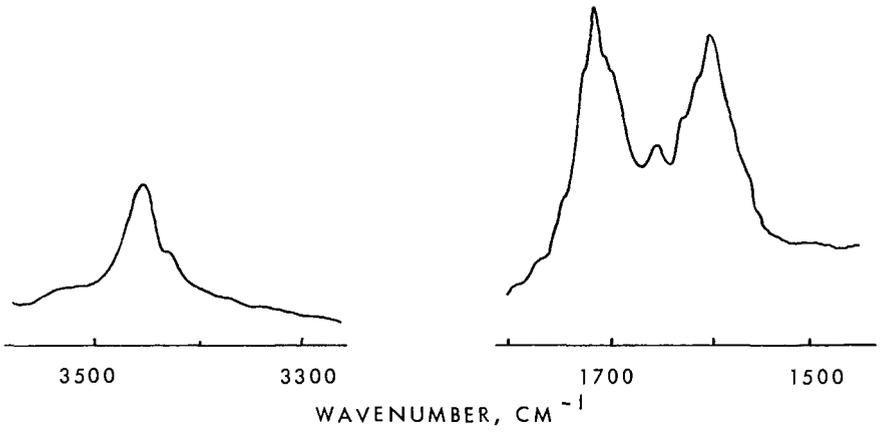


Figure 4 - PARTIAL INFRARED SPECTRUM OF NEUTRAL NITROGEN FRACTION

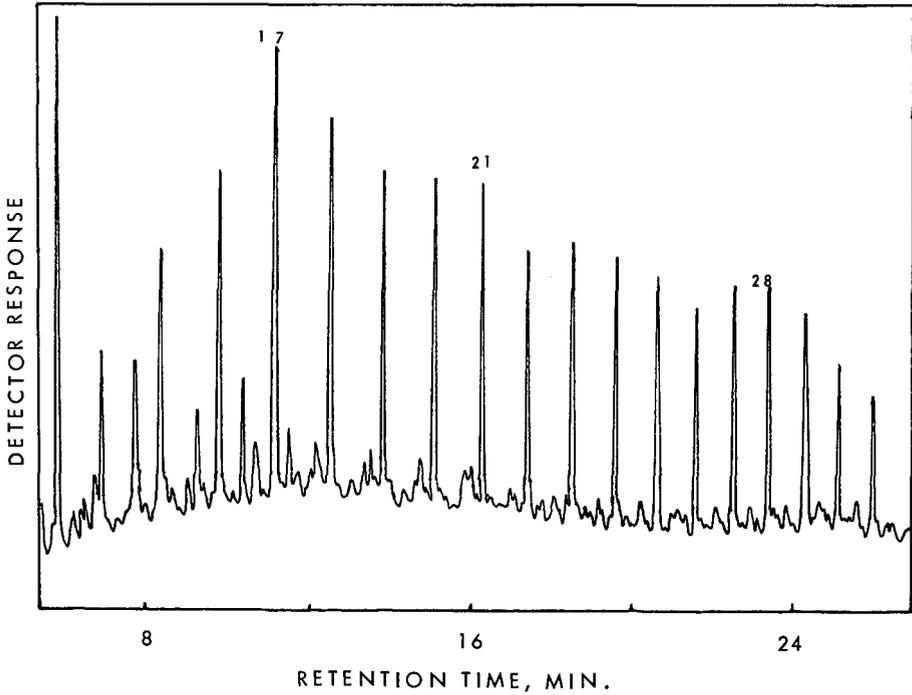


Figure 5 - GC CHROMATOGRAM OF SATURATE FRACTION