Coal Liquefaction Process Streams Characterization and Evaluation

Application of Liquid Chromatographic Separation Methods to THF-Soluble Portions of Integrated Two-Stage Coal Liquefaction Resids

Topical Report

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PROJECT ASSESSMENT

Introduction

Under subcontract from CONSOL Inc. (DOE Contract No. DE-AC22-89PC89883), the National Institute for Petroleum and Energy Research (NIPER) evaluated the use of non-aqueous ion exchange liquid chromatography (NIELC) for preparative-scale separation of residual (non-distillable) coal liquefaction materials. The resultant fractions were further analyzed by nonaqueous titration of the acid and base fractions, infrared spectroscopy, and analytical-scale separation by high-performance liquid chromatography (HPLC). An attempt was made to analyze the acid fractions by ^{13}C -NMR following derivatization with ^{13}C -enriched methyl iodide in order to speciate oxygen groups; however this procedure proved unsuccessful. "Direct" HPLC (i.e., no NIELC pre-separation) was attempted on one THF-soluble whole process oil. This met with limited success. The full report authored by the NIPER researchers is presented here. The following assessment briefly highlights the major findings of the project, and evaluates the potential of the methods for application to residual coal liquefaction materials. These results will be incorporated by CONSOL into a general overview of the application of novel analytical techniques to coal-derived materials at the conclusion of this contract.

Summary

This study demonstrated the feasibility of using non-aqueous ion exchange liquid chromatography (NIELC) for the examination of the tetrahydrofuran (THF)-soluble distillation resids and THF-soluble whole oils derived from direct coal liquefaction. The technique can be used to separate the material into a number of acid, base, and neutral fractions. Each of the fractions obtained by NIELC was analyzed and then further fractionated by high-performance liquid chromatography (HPLC). The separation and analysis schemes are given in the accompanying report. With this approach, differences can be distinguished among samples obtained from different process streams in the liquefaction plant and among samples obtained at the same sampling location, but produced from different feed coals. HPLC was directly applied to one THF-soluble whole process oil without the NIELC preparation, with limited success. The direct HPLC technique used was directed toward the elution of the acid species into defined classes. The non-retained neutral and basic components of the

oil were not analyzable by the direct HPLC method because of solubility limitations. Sample solubility is a major concern in the application of these techniques.

Program Description

This report describes the work performed at NIPER under a subcontract from CONSOL Inc., Research and Development. CONSOL's prime contract to the U.S. Department of Energy (Contract No. DE-AC22-89PC89883, "Coal Liquefaction Process Streams Characterization and Evaluation") established a program for the analysis of direct coal liquefaction derived materials. The program involves a number of participating organizations whose analytical expertise is being applied to these materials. This Participants Program has two main objectives. The broad objective is to improve our understanding of fundamental coal liquefaction chemistry to facilitate process improvement and new process development. The specific approach to achieving this objective is to provide a bridge between direct coal liquefaction process development and analytical chemistry by demonstrating the application of various advanced analytical methods to coal liquefaction materials. The methodologies (or techniques) of interest are those which are novel in their application for the support of coal liquefaction and those which have not been fully demonstrated in this application. CONSOL is providing well-documented samples from different direct coal liquefaction process development facilities to the program participants. The participants are required to interpret their analytical data in context to the processing conditions under which the samples were generated. The methodology employed then is evaluated for its usefulness in analyzing direct coal liquefaction derived materials.

Participant's Methodology

NIPER used non-aqueous ion exchange liquid chromatography (NIELC) for preparative-scale separation of four THF-soluble distillation resid (850°F⁺) and one THF-soluble whole oil. The resultant fractions were further analyzed by non-aqueous titration of acid fractions with the potassium salt of dimethyl sulfoxide (potassium dimsyl), non-aqueous titration of base fractions with HClO₄, infrared spectroscopy, and analytical-scale separation (HPLC). An attempt was made to speciate oxygen functional groups in the strong acid fractions by ¹³C-NMR analysis

of them after O-methylation with ^{13}C -enriched methyl iodide. The product of the methylation reaction was not recoverable in the desired solvent (ethyl ether); this line of analysis was discontinued. The complete analytical scheme is given in Figure 1 (p. 19) in the attached report. The HPLC method used with the NIELC-prepared acid fractions also was used alone, without NIELC preseparation, to fractionate a THF-soluble process oil. This direct HPLC approach met with some success. The HPLC methods used for the base and neutral NIELC fractions could not be applied without preseparation because of the low solubilities of the samples and overlapping elution of chemical compound classes.

The samples were produced at the Wilsonville two-stage direct coal liquefaction facility. A major processing parameter which varied among the Wilsonville runs was feed coal. Samples were taken from two locations in the plant: between the two reactors, and at the recycle oil tank. These samples are expected to represent different extents of coal liquefaction. The resid samples are composites of samples taken over long periods of single runs. The whole oil was obtained from the same run as one of the composite resids, but from a single run period. It was chosen from the same stream as the parent materials of one of the composite resids. The THF-soluble portions of the resids are solids at room temperature; the whole oil is a viscous liquid. The experimental procedures used in this study are described on pages 2-5 of the attached report.

Participant's Major Findings

NIPER reported the following principal observations for the application of nonaqueous ion exchange liquid chromatography to coal liquefaction materials. An expanded discussion can be found in the attached report, pages 5 through 12.

The NIELC scheme, originally developed for the analysis of high-boiling petroleum residues, was used in this work to analyze the direct coal liquefaction process-derived resid samples. This standard procedure, however, resulted in relatively low sample recovery (<90%) for four of five samples. Limited sample solubility proved to be a major problem in the preparative-scale NIELC separation scheme, and in subsequent HPLC and solution IR analyses. Some of the insolubility is attributed by NIPER

to oxidation of the sample during and after the initial NIELC separation procedure. However, the solvents used in the original version of the method may not have been optimum for coal liquids; this appears to be a contributing factor in the limited success of the original NIELC scheme. Modifications were made to the NIELC separation scheme to tailor it for use with coal resids. The modified procedure was employed with the sample that gave the poorest recovery (76%) with the standard procedure; with the modified procedure, recovery improved to near 100%.

Analysis of the base fractions shows that there is a significantly higher proportion of acetyltable bases, mostly primary and secondary amines, in the interstage samples than in the recycle material. It was shown that the acid fractions isolated by NIELC and HPLC are preponderantly multifunctional and that the isolated bases are mostly monofunctional. The weak acids isolated by NIELC contain a large concentration of carbonyl functionality. The presence of the carbonyls may be a result of sample oxidation during handling. As is typically true with petroleums, the weak acids are found to have a greater concentration of nitrogenous acids than of phenolic acids; the reverse of the strong acids. The compositions of the neutral fraction differed very little as a function of sampling point in the liquefaction process. The neutral fraction approximates the "oils" fraction obtained in the conventional analysis for oils, asphaltenes, and preasphaltenes.

Complete direct HPLC analysis of whole process oils was not feasible without pre-separation by NIELC. Solubility of base and neutral fractions and co-eluting compound types were problems in the direct separation of this material.

CONSOL Evaluation

Separation of coal-derived resids into acid/base/neutral classifications is somewhat ambiguous, as it is expected that a large portion of the high molecular weight coal-derived materials are multifunctional. The NIELC technique, however, was shown to have some potential for the analysis of direct coal liquefaction resid samples. It is projected that with full optimization for coal-derived materials, especially those with high molecular weight and polyfunctionality, such as distillation resids, the

technique can be useful in characterizing process streams for process development. This optimization should include better quantitation, better definition of the composition of each fraction, and development of methods that are significantly more rapid. HPLC can be used for a rapid analysis of neutrals or bases; however, a pre-separation with NIELC would be required first to produce the base or neutral fractions from the whole material. Direct application of HPLC (without a NIELC pre-separation) to whole process oils is not possible at this time. The use of solution IR to analyze resultant fractions is limited by sample solubility. Methods for solid sample analysis should be used for this application.

The NIELC technique is time-consuming and relatively costly on a per-sample basis. The following table, supplied by NIPER, provides costs and manpower requirements for the techniques employed in this work.

EQUIPMENT AND COST BREAKDOWN FOR COAL LIQUID ANALYSES

Analysis	Capital Equipment/\$	Expendables/\$	Time, hrs/Personnel ¹
Preparative separation into acids, bases, neutrals	Columns/500 Soxhlet extractors/200 Rotary evaporator/1000	Solvents/20 Ion exchange resins/50	40/Tech
Analytical-scale separations	HPLC + Data system/60K	Column/300 ² Solvent/10	16 Setup/Res. Chem. ³
A. Acids			2/Chem.
B. Bases			2/Chem.
C. Neutral-aromatics			1/Chem.
D. Saturates			1/Chem.
IR	IR spectrophotometer/ 20-60K	Cells/150 Solvent/2	2/Chem.
Nonaqueous titrations	Automatic titrator/20K Microbalance/7K Drybox/5K ⁴	Electrodes/300	16 Setup/Chem. ³
A. Acids		Reagents/5	3/Tech.
B. Bases		Reagents/5	3/Tech.
NMR	NMR spectrometer/300K	Reagents/50	18 Res. Chem.

- 1) Technician, chemist (BS), research chemist (BS,MS).
- 2) A separate column is required for each HPLC method.
- 3) About 2 days is required to set up, calibrate, and optimize each HPLC and titration method.
- 4) Required for titration of acids only.

Further Development

There are a number of avenues for further development of the separation techniques for the examination of coal liquefaction derived resids that were employed in this study. They include the following suggestions made by the researchers at NIPER: 1) NIELC methods development, such that samples and resultant fractions are protected from oxidation. 2) HPLC detectors should be evaluated for uniformity of response. Recommended types for trial include FID or light-scattering detectors. 3) Improvement of sample solubility (possibly via derivatization techniques) should be explored on a range of resid samples and their fractions. This would allow infrared analyses, with liquid sampling systems, to be a more useful method for the examination of the chromatographically separated fractions. In addition to these suggested research directions, alternative analyses of sample fractions, inclusive of techniques designed to analyze solid materials, should be explored. Also, automation of the LC procedures (inclusive of multiple column, multiple solvent systems) should be looked into to make this a more user-friendly method for analyzing coal liquefaction process-derived samples. HPLC of whole process streams should be optimized to prevent co-elution of compound types.

Contractor's Statement of Work

The complex mixtures which comprise coal liquids contain polar compounds and many hydroaromatic structures. It is important to gain a better understanding of the influence that the polar compounds and hydroaromatic compounds found in coal liquids have on coal liquefaction. Polar compounds may significantly affect the coal liquefaction process and the refining of crude products to finished products, as such they should be identified and quantified. Hydroaromatic structures, key in the liquefaction of coal as hydrogen donors and shuttlers, should be characterized by methods which can recognize differences between various ring structures. Analysis of coal liquefaction derived materials with a particular emphasis on these two compound classes is therefore important to obtaining a better understanding of the liquefaction process, and falls within the scope of the Participants Program.

NIPER will concentrate its effort on analysis of polar materials and hydroaromatic ring structures found in coal derived liquids. Quantitative preparative-scale separation of coal liquids into strong and weak acid, strong and weak base, and neutral (ABN) fractions will be done on five samples supplied

by CONSOL to NIPER. The separations will be performed by non-aqueous ion-exchange chromatography. The samples will be both tetrahydrofuran (THF) soluble portions of distillation resids and filtered whole process oils, as designated in the attached list. The samples will be separated into five fractions (strong acids, strong bases, weak acids, weak bases, and neutrals). The samples will be supplied with the following information (as available): elemental analyses, ash content, ash elemental analysis, phenolic -OH concentration, calorific value, hydrogen classes by ^1H -NMR, and the full history of the sample (plant, process conditions, age, and storage conditions). Sample size will be minimally 50 g. Aliquots of three of the neutral fractions (as designated in the attached list) will be further separated by analytical high performance liquid chromatography (HPLC) with gradient elution on derivatized silica columns into saturates and aromatic ring classes (mono-, di-, and polyaromatics). The corresponding acid and base fractions will similarly be further fractionated by HPLC. The acid fractions will be separated into phenols, carboxylic acids, pyrroles, and amides. The base fractions will be separated into primary and secondary amines, and aza-aromatics. The remaining portion of the ABN fractions of each sample will be made available to CONSOL for possible distribution to other participants in the Program. Confirmation of the analytical HPLC findings will be made with elemental analyses, non-aqueous titrations, and infrared spectroscopic analysis of the acid and base fractions. In addition to HPLC analysis of the separated ABN fractions, one sample will be analyzed directly by HPLC. NIPER will determine from this direct HPLC analyses if a fast analysis of the acidic and basic components of these materials can be accomplished without preseparation by non-aqueous ion-exchange chromatography.

Three of the strong acid fractions from above also will be speciated and quantified by 2D-NMR (^1H and ^{13}C) after replacement of the acid protons by $^{13}\text{CH}_3$ groups. The derivatization will be done with $^{13}\text{CH}_3\text{I}$ and KOH in N-methylpyrrolidone solvent. The NMR analysis will be accomplished using four types of measurement: proton NMR, quantitative ^{13}C -NMR with decoupling of protons, distortionless enhancement by polarization transfer (DEPTD) mode, and chemical shift (CHSHF) correlation procedures.

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**APPLICATION OF
LIQUID CHROMATOGRAPHIC SEPARATION METHODS
TO THE SOLUBLE PORTIONS OF
INTEGRATED 2-STAGE COAL LIQUEFACTION RESIDS**

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ABSTRACT

Five coal liquefaction process streams were separated into acidic, basic and neutral classes using nonaqueous ion exchange liquid chromatography (NIELC). Three of the five sets of fractions were subjected to further analysis. The results indicated that primary aromatic amines and multifunctional acidic compounds produced in the initial stage of liquefaction were reduced in concentration after the second stage reactor. Most other compositional parameters, e. g., the distribution of neutral-aromatics by ring-number, were unaffected by the second stage reactor.

Problems with sample solubility limited the applicability of some analytical techniques, particularly the NIELC method, and infrared or NMR-methylation techniques. However the nonaqueous titration and most HPLC methods employed were directly applicable or required modifications which could be incorporated over the course of the work. Many of these techniques could be used routinely for monitoring coal liquefaction processes.

INTRODUCTION

Coal liquefaction process development, optimization, and operation would be facilitated by improved process stream analyses. In particular, analyses capable of predicting operational problems and optimizing conversion of coal and resid are needed. Available techniques include solubility fractionation, distillation, ^1H and ^{13}C NMR, infrared, and microautoclave tests for coal solvation/hydrogen donor capability (1). These analyses, while quite useful for general product characterization, are largely inadequate for purposes stated above.

Analytical methods developed previously at NIPER (2-8) have been applied to a variety of fossil liquids, including coal-derived materials. Many of these were designed to determine particular compound classes or types in complex matrices like coal liquids. The objective of this work was to determine their applicability and usefulness toward analysis of integrated 2-stage process oils and in particular the $>850^\circ\text{F}$ resid portion of those oils.

EXPERIMENTAL

Samples

The samples are identified in table 1. Removal of tetrahydrofuran (THF) insoluble portions of each was performed at CONSOL, prior to shipment to NIPER. The overall scheme for separation and analysis of these materials is shown in figure 1. Methodology referred to in the figure is described below.

Preparative scale separations

Each sample was initially separated into strong acids, strong bases, weak acids, weak bases and neutrals using NIELC [nonaqueous ion exchange liquid chromatography (2)]. Briefly (see Appendix 1 for details), the sample is dissolved in a 4.5:4.5:1 mixture of benzene:THF:ethanol and passed through a strongly basic anion exchange resin followed by a strongly acidic cation exchange resin. Strong acids and strong bases are recovered via extraction of anion and cation resins, respectively. The eluate is rotoevaporated to near dryness, redissolved in 2.5:7.5 benzene:cyclohexane, and passed through a second set of ion exchange resins. Weak acids and weak bases are recovered in a manner analogous to that of strong acids and strong bases; the eluate is defined as neutrals. Since low recoveries were generally obtained with the above standard procedure, reseparation of two samples with modified versions was attempted, as described below.

An additional ion exchange resin, Rohm and Haas Amberlyst A-21 weakly basic $(\text{RN}(\text{CH}_3)_2)$ macroporous resin, was prepared by washing with the following sequence of solvents: 1M NaOH(aq) (2L/454g resin), high purity water (2L/454g), methanol (8L/454g), and 9:1

toluene:ethanol (4L/454g). Aliquots of this resin were packed into 1.5 (i.d.) x 70 cm glass columns, which is the same size column employed in the standard procedure.

A nominal 20 g charge of the 259 V131B resid (ref. no. 3) was successfully dissolved in 50 mL 8:1:1 toluene:ethanol:tetrahydrofuran (THF) and pumped onto a column containing the A-21 resin. Unretained material was eluted with an additional 280 mL of the same solvent mixture. The resin was then transferred out of the column into a fritted glass Soxhlet thimble. Recovery of the retained (acidic) material was initially attempted using a 1:4 pyridine:toluene reflux. After 2 hours, 20 mL *n*-propylamine was added to the extraction mixture which was allowed to reflux overnight. 1.007 g (5.02 wt %) of material was extracted as above. Since visual inspection revealed coal-derived material on the resin even after the above treatment, a second extraction with 30 mL formic acid in 300 mL benzene was performed. A small additional quantity (0.17 g, 0.83 wt %) of material was obtained with this second extraction, which was judged to be generally ineffective.

A nominal 20 g charge of 259 R1235 resid (ref. no. 4) was successfully dissolved in 70 mL 4.5:4.5:1 benzene:THF:ethanol and eluted through a series of three columns containing A-21, MP-1 (strongly basic anion exchange resin) and MP-50 (strongly acidic cation exchange resin) resins, respectively. The solvent mixture and latter two resins are the same as that employed in the standard procedure. 300 mL of the solvent mixture was pumped through all three columns; an additional 200 mL was passed through the last two columns; a final 75 mL was passed through the last (MP-50) column alone. Resins from each column were transferred to Soxhlet thimbles. The MP-1 and MP-50 resins were extracted in the conventional manner (MP-1: benzene-formic acid; MP-50: benzene-propylamine; see Appendix 1). The A-21 resin was extracted initially with 25 mL ethylene diamine in 250 mL toluene. It was later extracted with 250 mL benzene:25 mL formic acid:30 mL THF. The two extracts from the A-21 resin were combined and designated SSA ("super strong acids"). Additional material was also eluted from the MP-1 resin via a second extraction with pyridine. This material was designated SA(pyr) (pyridine extracted strong acids). It was recovered via rotoevaporation of the bulk of the pyridine, dilution of the remaining pyridine with water, followed by filtration.

The strong acid/strong base-free material eluted as described above was later re-separated in the conventional manner to obtain weak acid, weak base, and neutral fractions.

Analytical scale separations

HPLC separation of acid fractions into compound classes on silica was initially attempted using methyl *t*-butyl ether (MTBE) and chloroform-based mobile phases developed previously (3). Neither was successful, owing to the insolubility of the coal-derived materials in either solvent. Extensive modifications resulted in a system which performed satisfactorily. Those conditions, listed in table 2, were applicable to any acid fraction or whole resid. The cutpoints listed in the

table for the various compounds types were defined by elution times of pure compounds of each type and by the appearance of the actual chromatograms of acid fractions.

HPLC separation of base fractions into compound classes was performed as described previously (see table 3 of reference 4), with only minor modifications. Cutpoints for integration of the various types of nitrogen bases were defined solely on elution times of pure compounds, since the chromatograms of the base fractions themselves were usually featureless lumps. Thus, the region between 0-4.5 min was arbitrarily defined as neutral-contaminants/very weak bases, 4.5-18.5 min as secondary aromatic amines, 18.5-41.0 as primary aminoaromatics, and 41-77 min as tertiary amines. Examples of each type include: 1) polycyclic hydrocarbons, 2) diphenylamine, 3) aniline, and 4) pyridine.

HPLC separation of neutrals was performed on two separate systems. The first determined saturates only; the second provided a breakdown of aromatics according to number of aromatic rings present. For determination of saturates, a standard solution (ca. 5%) of each neutral fraction in heptane was prepared with the aid of sonication and heat (60° C). Each was immediately injected onto a 25 x 0.46 (i.d.) cm Dupont 7 µm silica column using a manual injection valve. The saturates were eluted with heptane at 2.0 mL/min and detected using a refractive index detector (Waters Model 401). The soluble aromatics were backflushed after elution of the saturates. The resulting saturate peak area was ratioed against that from a standard hexadecane solution (1%) in order to calculate the quantity of saturates present.

Aromatic ring-number distributions of neutrals were determined via elution from a 2,4-dinitroanilinopropylsilica (charge transfer type) HPLC column. A linear gradient from hexane to dichloromethane and UV-detection at 254 nm was employed. Details of the procedure may be found elsewhere (5). Selection of retention regions corresponding to a given number of rings was based on elution of pure compounds. Raw area data were corrected for variation in UV response for each ring-number class using previously determined response factors (6).

HPLC separation of whole resids was performed as discussed above for acid fractions. Basic and neutral components present were eluted as unretained species under those conditions. The other HPLC methods discussed above were inapplicable to whole resids for reasons of solubility and interference from coeluting compound types.

Other Analyses

Nonaqueous titration of bases was done using perchloric acid in dioxane as the titrant. Separate aliquots of each sample were dissolved in acetonitrile/toluene and acetic anhydride/toluene, and each was titrated potentiometrically. Titration in each solvent enables calculation of the proportion of the bases undergoing acetylation to the corresponding amide in

acetic anhydride. This quantity is an estimate of the percentage of primary/secondary amines present. Other details of the method appear elsewhere (7,8).

Nonaqueous titration of acids was done using potassium dimsyl, the potassium salt of dimethyl sulfoxide (DMSO), as the titrant. Samples were dissolved in DMSO/toluene and titrated potentiometrically. Specially modified electrodes and other apparatus are required for this technique because of the highly reactive nature of the titrant (8).

Infrared (IR) spectra were obtained using a conventional dispersive instrument and liquid sampling cells. Dichloromethane solutions of ca. 10 mg/mL concentration were used in most cases, but a few spectra were also obtained of samples dissolved in THF. The concentrations of OH, NH, C=O and S-O groups present were calculated assuming molar absorptivities of 133 (3580cm^{-1}), 151 (3470cm^{-1}), 607 ($1800\text{-}1640\text{cm}^{-1}$), and 245 (1030cm^{-1}) $\text{L mol}^{-1} \text{ cm}^{-1}$, respectively.

Methylation of acidic functional groups with methyl iodide and ^{13}C -enriched methyl iodide was attempted in basic 1-methyl-2-pyrrolidinone media. Thus, 0.2 g of a strong acid fraction, 0.1 g KOH, and 0.15 g CH_3I were dissolved into about 4 mL 1-methyl-2-pyrrolidinone and heated to 40°C for 1 hour. Water was then added and the reaction product was extracted with ethyl ether. Had this reaction been successful, ^{13}C NMR would have been used to determine the distribution of methylated functional groups present. The major problem encountered was incomplete extraction of the product into ethyl ether (only about 2% of the starting material was recovered).

RESULTS

Preparative scale separation

Table 3 shows mass balances from the preparative scale separations into acidic, basic, and neutral types. As noted in the table, the overall recoveries obtained initially were poor, and significant quantities of insolubles were observed at various points in the separations. However, the results are directionally consistent with known properties of each sample. For example, figure 2 demonstrates the expected inverse correlation between yield of neutrals (table 3A) versus nitrogen content (supplied by CONSOL) for each whole material (see ref. nos. in figure).

Reseparation of the R1235 resid with the modified procedure resulted in a much improved overall mass balance accompanied by significant increases in yields of strong bases, weak acids, and neutrals. It may be speculated that strong bases were lost in the initial separation through association with strong acids on the ion exchange resin. The extraction solvent, which is designed for elution of acids, may have been ineffective at removing coadsorbed bases from the resin, which remained black in color after extraction ceased. The increase in weak acids may reflect partitioning of the insolubles (11.1 wt % in the initial separation) into that fraction. The increase in neutrals may reflect decreased sample oxidation owing to precautions to exclude air taken in the second

separation attempt. In any case, the modified method was obviously superior to the standard procedure in recovery of this sample.

Analysis of base fractions

Table 4 summarizes results from analysis of base fractions. Results from elemental analysis, nonaqueous titration, IR, and HPLC techniques are shown.

Nonaqueous titration of strong base fractions indicated a significantly higher proportion of acetyltable bases (primary and secondary aromatic amines) in the R1235 strong bases than in those from the other two 259 samples. A corresponding decrease in "weak bases" (typically azaaromatics) in the R1235 fraction was also observed. The "very weak base" category determined is probably comprised largely of azaaromatics with either highly condensed aromatic ring systems or neighboring heteroatoms (O or S), both of which decrease the apparent basicity of the nitrogen atom. This class is also enriched in the R1235 strong bases relative to the other samples. The higher proportion of acetyltable bases in the R1235 interstage product indicates that primary or secondary amines may be produced as intermediates during the initial stage of coal liquefaction, and later reduced in concentration in the second stage reactor. Similarly, the reduction in very weak bases going from the R1235 to the V131B product may reflect partial conversion of highly condensed azaaromatic and/or removal of heteroatoms (note the decrease in strong base sulfur content) in the second stage reactor.

The weak base fractions largely contain materials too weakly basic to titrate with perchloric acid. Although ketones and aromatic hydrocarbons serve as common examples of nontitratable compounds found in weak base fractions, comparison of titration and elemental nitrogen data shows that many of the nitrogen compounds also did not titrate. The structure or type of these nontitratable nitrogen compounds is not known.

Average molecular weights of strong base fractions were estimated from titration data and elemental nitrogen content. One nitrogen atom per molecule was assumed in the calculation of molecular weight from nitrogen content, and the equivalent weight was assumed to be equal to molecular weight in the case of titration data. Good agreement between molecular weight estimates from the two methods was obtained. The higher apparent molecular weight of R1235 strong bases from the second separation indicates that the increase in yield of that fraction over the first separation (table 3) resulted mainly from higher molecular weight species. Those higher molecular weight bases may not have been recovered in the initial separation.

Infrared analysis of base fractions qualitatively confirmed the presence of azaaromatics in all strong base fractions as well as the greater abundance of aromatic amines in the R1235 strong bases (first separation). However, IR bands corresponding to those species are not suitable for quantitation. Only bands corresponding to carbonyl and sulfoxide species were used for

quantitative calculations, as shown in table 4. Carbonyl bands in both strong and weak base fractions are tentatively assigned to ketone structures. Strong base spectra showed a single band near 1690 cm^{-1} ; weak base spectra exhibited a doublet at 1700 and 1650 cm^{-1} . The latter band could represent either ketone or amide functional groups. Assuming the molecular weights shown in the table, strong base fractions contained only about 5% carbonyl species and weak base fractions up to 20% carbonyl types. A relatively high proportion ($\geq 50\%$) of the sulfur present in weak base fractions appeared to be present as sulfoxides, based on the comparison of IR and elemental analyses.

HPLC analysis of strong base fractions showed the same general trends as the other techniques. For example, R1235 strong bases from the first separation contained the highest apparent concentration of primary plus secondary aromatic amines consistent with the higher level of acetylable bases indicated by nonaqueous titration. Also, the concentration of primary and secondary amines in the second R1235 fraction is lower, consistent with dilution by the additional species isolated in that separation. The HPLC data indicate that primary aromatic amines predominate over secondary amines for all samples, but tertiary amines (i.e. azaaromatics) are the single most dominant class for all strong base fractions. However, since UV response factors were not determined for the various compound types, the HPLC data should be viewed as only semiquantitative.

Although the arbitrary compound type assignments for the various HPLC elution intervals may be reasonable for strong base fractions, they appear to be entirely inappropriate for weak base fractions. For example, nonaqueous titration data show the weak base fractions to actually contain minor proportions of all types of aromatic amines. Thus, much of the HPLC signal in each elution region must actually reflect other compound types (e.g. ketones, sulfoxides) which coelute with the respective amine types listed in table 4. A new set of compound type-elution time correlations would have to be derived in order to make HPLC analysis of weak base fractions meaningful.

Analysis of acid fractions

Results from analysis of acid fractions are shown in table 5. Elemental analysis of acid fractions showed appreciable levels of nitrogen in all fractions. The exceptionally high nitrogen content of the SSA fraction from the second separation of the R1235 resid indicates considerable contamination of the fraction with ethylene diamine, used in its extraction from the A-21 ion exchange resin. The presence of ethylene diamine also introduced error into the nonaqueous titration results for that fraction.

Nonaqueous titrations of acid fractions showed two or three equivalence points. These are expressed as "medium" "weak" or "very weak" acids based on the half neutralization potentials observed. Medium acids exhibited acidities consistent with neutralization of one group on selected

difunctional molecules, thiophenols, carboxylic acids, or selected ketones (8). Weak acids exhibited acidities typical of hydroxyaromatics or pyrrolic benzologs with 3 or more aromatic rings (carbazole, benzocarbazole, etc.). Very weak acids include a wide variety of compound types with weakly acidic groups (e.g., tetrahydrocarbazole, selected amides, mercaptans), and/or neutralization of the second group on difunctional acids.

The most probable assignments for the various compound types determined by titration varies with the fraction being titrated. For example, "medium acids" are probably difunctional in the case of strong acid fractions and probably ketones (see IR data for $C=O$) in the case of weak acid fractions. "Weak acids" determined by titration are predominantly hydroxyaromatics in the case of strong acid fractions and benzologs of pyrrole for weak acid fractions. "Very weak acids" probably represents neutralization of the second group on difunctional acids in the case of strong acid fractions, and neutralization of very weakly acidic species in the case of weak acid fractions.

The equivalent weights of acid fractions determined by titration are all significantly lower than molecular weights previously estimated for base fractions (table 4). This may indicate a fundamental difference in molecular size for acids versus bases, or a high degree of multifunctionality for acids, in contrast to bases which appeared to be completely monofunctional. HPLC analysis supports the contention of multifunctionality, as up to 80% of the compounds in selected strong acid fractions appeared to contain multiple acidic groups via that technique.

IR analysis of strong acid fractions was only semiquantitative, because of their incomplete solubility in the solvent employed (dichloromethane). The ratio of OH/NH groups provided in the table refers only to CH_2Cl_2 -soluble portions. Spectra obtained in THF exhibited a single band for OH+ NH groups, as previously noted (9). This information was of little utility for evaluation of acid fractions, since the relative proportion of these two groups was of key interest. The insolubility of strong acid fractions in suitable solvents drastically reduced the effectiveness of IR toward their analysis.

Reasonable IR analyses were obtained for weak acid fractions, however. They contained very high proportions of carbonyl groups, as noted in the table. Weak acid carbonyl bands typically exhibited maxima at 1730 and 1670 cm^{-1} . Corresponding bands were absent in spectra of whole materials; therefore, they probably represent oxidation products formed over separation and handling. Very likely, other analyses of weak acid fractions were also significantly impacted by the apparent sample oxidation.

Weak acid fractions contained more NH functionalities than OH, which is typical (8). The majority of hydroxyaromatics partition into strong acids; those found in weak acid fractions are typically sterically hindered. Nitrogen present as NH groups accounted for roughly two-thirds of the total nitrogen present. The majority of the weak acid NH species are probably benzologs of pyrrole. The quantity of sulfoxide forms of sulfur measured was greater than or approximately

equal to total sulfur. The IR response factor used for sulfoxides may be inaccurate for molecules which contain acidic functionalities, or some other functional group may interfere in their determination in this case.

HPLC analysis indicated significant proportions of molecules containing two or more functional groups (designated $\text{Ar}(\text{OH})_y$ in the table) in strong acid fractions. In the case of weak acid fractions, one of the groups in difunctional species probably represents a carbonyl group introduced during isolation and handling as noted above. For example, the weak acid fractions with the highest carbonyl contents determined by IR exhibit the highest relative concentrations of " $\text{Ar}(\text{OH})_y$ " types. The R1235 strong acid fraction from the initial separation contains a higher proportion of $\text{Ar}(\text{OH})_y$ types than those from the other two samples, thereby indicating a reduction of that type during the second stage of reaction. Strong acid fractions from the second separation of the R1235 material also contained high proportions of multifunctional species. The apparent high proportion of unretained species in the R1235 pyridine-extracted strong acids probably reflects an artifact from the ion exchange resin washed out by pyridine.

The proportion of compounds in strong acid fractions containing a single NH group (pyrrolic) is similar to that of monohydroxylated species (ArOH). This finding in conjunction with the IR ratio for NH/OH indicates that the difunctional species present largely contain OH groups, and that multiple-hydroxylated species account for at least 60% (V131B resid and whole process oil) to about 80% (R1235) of the total OH groups present.

HPLC analysis of weak acid fractions showed high proportions of unretained species and pyrrolic compounds. Most of the unretained compounds are probably carbonyl types and hydrocarbons with benzylic hydrogens (8). The NH and OH compounds indicated by IR most likely coelute and are reported as pyrrolic compounds in the HPLC analysis.

Analysis of neutral fractions

Table 6 shows results from analysis of neutral fractions. Analysis of neutrals proceeded smoothly and indicated few unexpected or controversial findings. Perhaps the most significant finding was the higher concentration of saturates in the whole process oil compared to the V131B resid. Compared to the relatively minor differences observed from acid and base compositions, their differences in saturate content and distribution of neutral-aromatic species are quite notable. The compositions of V131B and R1235 resid neutrals differed only slightly, with the R1235 fraction exhibiting a slightly higher concentration of ≥ 5 -ring compounds.

Analysis of whole resids/oils

Results from analysis of whole resids/oil are shown in table 7. In addition, results from HPLC analysis of acid fractions (table 5) are restated on a whole sample basis for comparison to

those determined directly. In the calculation of "unretained" species from data on acid fractions, gravimetric yields for neutral and base fractions (table 3) were added to area percents of unretained components to obtain estimates of total unretained species present in each whole sample. This practice relied on assumptions that 1) base and neutral components would in fact elute as unretained species, and 2) that their UV response would be proportional to their weight. The discrepancies observed in this category between calculated versus directly determined data probably arise mainly from the inexactness of the second assumption.

As with IR analysis of strong acid fractions, IR analysis of whole materials suffered from their incomplete solubility in dichloromethane. Thus, the OH/NH ratios provided refer only to the soluble portion of each sample. Carbonyl bands for whole materials were extremely broad, and were centered near 1700 cm^{-1} . A weak sulfoxide band (1030 cm^{-1}) was also observed. Because of the incomplete sample solubility and difficulties in measuring the C=O and S-O bands, they were not quantitated.

Although different in absolute terms, the trends in HPLC results for whole samples calculated from acid fractions versus those measured directly were comparable. For example, the R1235 resid contained the most multifunctional material, with the V131B resid and whole process oil containing proportionally less in either data set. The quantity of pyrrolic versus monohydroxylated materials was similar for the V131B and R1235 resids, and the pyrrolic types were approximately 50% more abundant in the V131B whole process oil. This observation is consistent with the relatively high abundance of carbazole (b.p. 355°C , 671°F) and its alkyl homologs typically observed in coal liquids (10). The bulk of these species boil below the 850°F cutpoint employed here for distillate versus resid, and thus would contribute to the pyrrolic content of the whole oil but not that of the resid. The HPLC results also follow the same trend as the IR data, assuming that the multifunctional acids contain mostly hydroxyl groups. That is, the R1235 sample exhibited the highest OH/NH ratio determined by IR, and the largest proportion of multifunctional species determined via HPLC.

DISCUSSION

Insolubility and susceptibility to oxidation after separation are major factors limiting the applicability of the preparative separation technique used here, or any other techniques, to these samples. Clearly, development beyond modifications already imposed here would be required to bring the performance of the NIELC technique up to acceptable levels. In particular, removal of solvents under an inert atmosphere should be implemented.

The HPLC technique specified in table 2 appeared to perform well on acid fractions as well as whole samples. However, as noted in the Experimental section, considerable modification of the

existing system was required to make it suitable for these materials. As shown in figure 3, this technique provides a clear grouping of the various acidic compound types present within a run time of about 1 hour. To improve quantitation, a detector with more uniform response should be used in place of the UV detector employed here. Either moving belt FID or light scattering detectors may be suitable.

Infrared was found to be of limited value for analysis of strong acid fractions or whole materials because of their insolubility in dichloromethane, or other appropriate solvents. Chemical derivatization (acylation of OH groups) may improve the applicability of IR to these materials via promotion of solubility and elimination of hydrogen bonding effects (11).

HPLC methods for analysis of bases or neutrals require isolation of those fractions to remove interferences. However, the distribution of basic types probably could be determined directly on whole samples via the nonaqueous titration technique, which appeared to give comparable information to that of the HPLC technique for strong base fractions. Weak base fractions were a relatively small proportion of the whole material and could be neglected. Information on neutrals could be obtained via a "quick and dirty" removal of acids and bases on disposable columns, followed by HPLC analysis of the eluate.

A combination of the above techniques would provide much of the information obtained from the more laborious analyses performed here. In addition, benzylic hydrogens in neutral fractions could be estimated via titration of neutrals with potassium dimsyl, if that parameter is of interest. Titration of whole materials with potassium dimsyl would provide a measure of total acidity, but probably not a distribution of acid compound types owing to the considerable overlap in relative acidities observed. Total acidity determined in that manner may correlate with the "total OH content" currently measured by CONSOL (1). The latter clearly includes a significant contribution from NH groups in the case of these samples.

The degree of interpretation of results from group type methods such as these would be improved if the detailed composition of each group were better understood. Thus, it may be of value to analyze one process stream in detail to determine the composition of each type present. This would enable more intelligent interpretation of fine structure of HPLC chromatograms and spectra to obtain the most detailed and complete information possible.

However, even at the rather elementary levels of interpretation employed here, it was possible to differentiate the three samples from run 259 to some degree. For example, the interstage resid (R1235) was found to contain higher levels of primary aminoaromatics and multifunctional acids than the whole oil or resid from the second stage reactor (V131B). The distribution of acidic and basic types within the V131B whole process oil was similar to that of the corresponding resid, but their total acid and base contents were noticeably different. The whole oil also had significantly higher concentrations of saturates and smaller-ring aromatics than the recycle resid. These findings

indicate that much of the lower boiling material in the whole process oil is neutral in character, and that it is significantly less aromatic.

Over all the samples investigated, the dominant polar compound type was strong acids. This fraction appears to generally contain high proportions of multifunctional species, which probably contribute heavily to asphaltene and preasphaltene solubility classes currently measured by CONSOL. Similarly, the neutrals class determined here approximates "oils" determined by CONSOL; for example, the concentration of either in the recycle resid from run 257 is significantly higher in resids from runs 259 or 260.

RECOMMENDATIONS

Although the main focus of analytical method development should be on rapid methods for routine monitoring, modification of the NIELC technique towards attainment of quantitative material balances and minimal sample alteration in separation of coal liquefaction resids should also continue. The resulting fractions would be a valuable resource for analysis and determination of physical/chemical properties, including liquefaction behavior, of the five compound types produced in the separation. Existing HPLC detectors should be evaluated for sensitivity and uniformity of response toward coal-derived materials. Detector optimization is critical to obtaining quantitative data from the HPLC methods discussed here or with any alternate HPLC procedure.

Generally, a better understanding of detailed composition of coal liquids is needed, both to improve interpretation of routine analyses and to understand compositional factors which limit conversion of resid to distillate products. A detailed comparison of resids from the first versus second reactor stages in integrated 2-stage systems would be a logical first step toward this goal.

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TABLE 1. - THF-soluble samples supplied by CONSOL

Ref. No.	Coal Feed	Source/Conditions	Comments
1	Black Thunder	W; Run 260	>850° F Recycle oil resid (V131B)
2	Illinois No. 6	W; Run 257	>850° F Recycle oil resid (V131B)
3	Pittsburgh seam	W; Run 259	>850° F Recycle oil resid (V131B)
4	Pittsburgh seam	W; Run 259	>850° F Interstage oil resid (R1235)
5	Pittsburgh seam	W; Run 259 G	Whole process oil (V131B)

TABLE 2. - Conditions for HPLC separation of acidic compounds

Column: 25 x 0.46 (i.d.) cm Dynamax (Rainin Inst., Woburn, MA) 60 A, 8 μ m SiO₂ with Guard Module

HPLC Instrumentation: Waters (Milford, MA) Model 6000 pumps (2), Model 680 gradient controller, Model 710B injector, Model 440 UV detector (280 nm).

Peak Integration: IBM AT-based P-E Nelson (Cupertino, CA) Software. Each chromatogram was baseline subtracted (solvent blank). Retention interval (min) assigned for each compound type was as follows: very weak acids/neutral or basic contaminants (1.0-8.5); pyrrolic benzologs (8.5-20); monohydroxylated aromatics (20-37); multiple hydroxylated aromatics or other multiple-functional acids (37-54). Quantitation was based on area percent (280 nm).

Solvent Program (linear gradient segments):

Time (min.)	Volume <u>A</u>	Percent <u>B</u>
0	96	4
3	96	4
35	75	25
49	0	100
55	0	100
56	96	4
71	96	4

A: methyl t-butyl ether (MTBE)

B: 30:30:40 MTBE:THF:Methanol containing 0.015% tetramethylammonium hydroxide

Flow rate: 2mL/min throughout

TABLE 3A. - Mass balances (wt%) from initial liquid chromatographic separations							
Ref. No.	Sample No.	Strong Acids	Strong Bases	Weak Acids	Weak Bases	Neutral	Recovered Insolubles
1	260 V131B (Recycle oil resid)	31.0	7.1	7.4	1.34	39.0	85.8 4.5 ¹
2	257 V131B (Recycle oil resid)	31.1	6.4	8.5	0.70	50.7	97.4 4.9 ¹
3	259 V131B (Recycle oil resid)	29.1	8.3	2.90	1.45	34.7	76.5 13.4 ²
4	259 R1235 (Interstage oil resid)	27.8	10.5	8.0	0.67	28.5	75.5 11.1 ²
5	259G V131B (Whole process oil)	18.3 ³	6.2	6.3	0.49	57.1	88.4 7.9 ²

TABLE 3B. - Mass balances (wt%) from reseparator using modified procedure ⁴							
Ref. No.	Sample No.	Strong Acids	Strong Bases	Weak Acids	Weak Bases	Neutral	Recovered Insolubles
4	259 R1235 (Interstage oil resid)	5.5 (SSA) 17.0 (SA) 5.4 (SA-pyr.) 27.9 (Total SA)	15.6	18.1	1.76	37.6	101.0 -

¹ Insolubles were observed in the strong acid fraction.

² Precipitation of insolubles occurred when the strong acid/strong base-free material was redissolved prior to separation of weak acids, weak bases and neutrals.

³ Duplicate determination resulted in a yield of 18.1% strong acids for this sample.

⁴ See experimental.

TABLE 4. - Analyses of base fractions from run 259

TABLE 4. - Analyses of base fractions from run 259														
Ref. No.	Sample No.	Separation	Fraction	Elemental Analysis (wt %)					Nonaqueous Titration Data (mole %)				IR (wt %)	
				C	H	N	S	H/C ¹	Weak	Acetyltable	Very Weak	Nonitratable	C=O	S(SO)
3	V131B resid	1	strong weak	84.2	6.45	2.29	1.19	0.91	47.8	25.9	26.3	-	0.15	-
				88.6	7.07	0.90	0.34	0.95	7.6	1.4	10.9	80.1	0.57	0.35
4	R1235 resid	1	strong weak						7.9	45.3	46.9	-	0.17	-
									10.3	3.3	15.1	71.3	0.48	0.20
		2	strong weak	83.8	6.68	2.09	0.43	0.95						
				82.9	6.31	1.41	0.52	0.91						
5	V131B whole process oil	1	strong weak	84.8	6.80	2.95	1.09	0.96	52.6	23.9	23.5	-	0.16	-
				79.9	6.26	1.05	0.41	1.05	4.3	7.1	16.9	71.7	0.68	0.18

TABLE 4. - Analyses of base fractions from run 259 (continued)

Ref. No.	Sample No.	Separation	Fraction	Average MW		Elemental N	HPLC Analysis (%)				Estimate ² of "Acetyltable bases"
				Titration			unretained	secondary amines	primary amines	tertiary amines	
3	V131B resid	1	strong weak	581	611		0.3 0.4	1.5 16.3	21.3 51.8	76.9 31.5	22.8 -
4	R1235 resid	1	strong weak	527			0.1 0.0	4.9 13.1	27.1 46.5	67.9 40.3	32.0 -
		2	strong weak		670		0.1 0.0	2.6 9.1	19.4 33.2	77.9 57.8	22.0 -
5	V131B whole process oil	1	strong weak	487	475		0.0 0.4	4.8 19.4	19.8 42.5	75.5 37.8	24.6 -

¹ Atomic ratio.² Secondary amines + primary amines.

Dash indicates not applicable, no entry indicates analysis not performed.

TABLE 5. - Analyses of acid fractions from run 259

Ref No.	Sample No.	Separation Fraction	Elemental Analysis (wt %)				Nonaqueous Titration Data (mole %)				IR (wt %)			
			C	H	N	S	H/C ¹	Medium	Weak	Very Weak	OH/NH ^{1,3}	N (NH)	O (OH)	S (C=O)
3	V131B resid	1 strong weak	89.2	7.10	0.89	0.18	0.95	9	91	-	300	2.1	-	-
								4	96	-	350	0.27	0.58	0.31
4	R1235 resid	1 strong weak	84.0	6.56	1.18	0.72	0.93	5	95	-	290	3.6	-	-
			83.7	7.22	0.61	0.22	1.03	23	-	77	287	0.30	0.49	0.15
	2 SSA ⁴	strong	66.5	7.56	7.2	0.24	1.35	-	24	76	294	-	-	-
		strong	76.5	6.46	1.25	0.66	1.01	27	-	73	195	-	-	-
		strong (pyr)	79.0	4.98	0.84	0.69	0.75	-	44	56	474	-	-	-
		weak	81.8	6.80	1.07	0.36	0.99	28	-	72	273	-	-	-
5	V131B whole process oil	1 strong weak	78.4	6.94	0.94	0.18	1.06	14	67	19	298	1.9	-	-
								35	-	65	246	0.64	0.60	0.50

TABLE 5. - Analyses of acid fractions from run 259 (continued)

Ref No.	Sample No.	Separation Fraction	HPLC Analysis (%)			
			Unretained	Pyromic	ArOH	Ar(OH) _y
3	V131B resid	1 strong weak	6.4	23.9	34.1	35.6
			72.2	26.6	0.0	1.1
4	R1235 resid	1 strong weak	4.5	17.1	26.2	52.2
			58.0	25.2	0.0	16.8
	2 SSA	strong	3.1	14.3	0.0	82.6
		strong (pyr)	1.9	1.8	19.0	77.3
		weak	68.7	0	0	31.3
5	V131B whole process oil	1 strong weak	8.9	34.4	29.9	26.9
			50.7	28.7	0.0	20.6

¹ Atomic ratio. ² Equivalent weight (g/eq). ³ IR data for strong acid fractions refer only to CH₂O₂ soluble portions.⁴ High N content of this fraction reflects incomplete removal of ethylene diamine used in its extraction (see Experimental).

Dash indicates not applicable; no entry indicates analysis not performed.

TABLE 6. - Analyses of neutral fractions from run 259

TABLE 6. - Analyses of neutral fractions from run 259																
Ref No.	Sample No.	Separation No.	Elemental Analysis (wt %)					HPLC Analysis (%)								
			C	H	N	S	H/C ¹	Saturates			Aromatics					
								1-ring	2-ring	3-ring	4-ring	5-ring	6-ring	7-ring	>7-ring	
3	V131B resid	1	91.4	8.07	0.036	0.087	1.05	9.8	0.8	6.9	24.3	28.0	13.9	11.1	3.9	1.2
4	R1235 resid	1	91.5	7.80	0.044	0.14	1.02	10.6	0.7	4.2	23.1	27.5	15.7	12.2	4.2	1.8
		2	91.0	7.70	0.074	0.14	1.01	10.3								
5	V131B whole process oil	1	91.4	8.03	0.022	0.044	1.05	30.0	0.7	12.3	26.0	20.0	5.9	4.4	0.7	-

¹ Atomic ratio.
Dash indicates not applicable, no entry indicates analysis not performed.

¹ Atomic ratio.

Dash indicates not applicable, no entry indicates analysis not performed.

TABLE 7. - Analyses of whole resids/oils from run 259

TABLE 7. - Analyses of whole resids/oils from run 259										
Ref No.	Sample No.	IR Analysis OH/NH ¹	HPLC Analysis (%)			Calculated HPLC Analysis (%) ²				
			Unretained	Pyrolic	ArOH	Ar(OH) _y	Unretained	Pyrolic	ArOH	Ar(OH) _y
3	V131B resid	1.4	45.6	18.9	16.0	19.5	61.8	7.7	9.9	10.4
4	R1235 resid	1.9	35.5	21.3	17.5	25.7	56.7	6.8	7.3	15.9
5	V131B whole process oil	1.1	46.9	22.2	14.4	16.5	76.5	8.1	5.5	6.2

Atomic ratio

¹ From analysis of acid fractions (table 5). R1235 results are from first acid fraction.

¹ Atomic ratio.² From analysis of acid fractions (table 5). R1235 results are from first separation.

Figure 1. Scheme for separation and analysis.

Figure 2. Correlation of total nitrogen content with yield of neutrals via NIELC

**Figure 3. HPLC chromatograms of whole resids/oils from Run 259.
See table 2 for experimental conditions.**

APPENDIX 1

SEPARATION OF LIQUID FOSSIL FUELS INTO ACID, BASE AND NEUTRAL CONCENTRATES

Separation of liquid fossil fuels into acid, base and neutral concentrates

1. An improved nonaqueous ion exchange method

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An improved method is presented for nonaqueous ion exchange separation of liquid fossil fuels into acid, base and neutral fractions. Improvements over previous procedures have been made in the areas of ion exchange resin activation, elution of the neutral compounds, extraction of acids and bases from the resins, and in a better definition of the overall properties, strengths and weaknesses of the method. A detailed procedure for applying the method to separations of fuels is presented. In addition, results of its application to different types of fuels and model compound mixtures are included, as well as other data relating to the mechanism of acid-base retention on resins and overall optimization of the usual chromatographic variables.

(Keywords: fossil fuels; ion exchange separation; model compounds)

In 1978, the authors began an evaluation of methods for separating and concentrating polar compounds present in fossil fuels. Initial work focussed on improving existing liquid-liquid extraction techniques. However, it soon became clear that liquid-liquid extraction methods worked well only with low boiling (<350°C) distillates – especially those from coal-derived liquids. The main problem encountered during extractions was poor solubility of larger, more hydrophobic, polar molecules in either an aqueous or an aqueous-alcoholic phase as evidenced by the emulsions, precipitates and poor recoveries observed. As supporting evidence, Tomkins and Ho¹ found that 1-aminopyrene (MW = 217) was near the upper limit of extractable amino-PAH compounds, yet McKay *et al.*² estimate the average molecular weight of nitrogen bases in 370–535°C petroleum distillates to be ≈ 400 . Hence, extraction techniques cannot be expected to work well with mid- or high-boiling distillates or residues. Furthermore, extensive alkyl substitution, often found in petroleum, further aggravates the hydrophobicity problem. Detailed results of the extraction work will be reported later.

Subsequent work in this laboratory has dealt mostly with use of macroporous polystyrene-divinylbenzene ion exchange resins for making acid-base-neutral (ABN) separations. Munday and Eaves³ first reported using ion exchange resins for fuel separations in 1959. They employed cross-linked gel-type resins, since they were all that were available at the time, although these are not well suited for nonaqueous media. Webster *et al.*⁴, first used macroreticular resins for separation of polar materials from fuels, although Snyder and Buell⁵ published an elaborate scheme including macroreticular resin-based separations only a year later. Workers at the Laramie

Energy Technology Center^{2,4-16} have applied the technique to a large number of fossil fuels including coal-derived liquids, shale oils and tar sands, as well as petroleum. In fact, a major advantage of nonaqueous ion exchange chromatography is its wide applicability to virtually all samples and boiling ranges.

In spite of this extensive work with ion exchange ABN separations, very little information about the technique itself has been published. For example, information about chromatographic efficiency, overlap between fractions, artifacts produced from the resins, compound recoveries from resins, optimum eluent type and amount for a given sample, etc., has not been published. In fact, the work of Sawatzky *et al.*¹⁷ represents one of the very few critical examinations of the method. They experimented with different eluents for ABN separation of bitumen, and characterized fractions in terms of elemental analysis plus mass balance, and compared the results with those from a silica-alumina separation method. Among other things they showed that the 'exhaustive elution' approach originally published by Jewell *et al.*⁶ was wrong; only modest amounts of eluent were needed to elute neutral compounds.

Thus, the objective of this Paper is to critically examine the method itself and to provide enough information such that the reader can:

1. select and properly prepare ion exchange resins;
2. select the optimum eluent for a given type of sample;
3. obtain good recovery of all three fractions;
4. regenerate the resins for reuse; and
5. be aware of the problems and most critical factors with ABN separations.

Side issues such as characterization of the fractions and/or

fuels, comparison of resins from different vendors and separation of the more exotic species such as organometallics will be published later.

EXPERIMENTAL

Apparatus

Separation of fuels by nonaqueous ion exchange chromatography requires a pump, two water-jacketed glass columns connected in series and a water bath with circulating pump. In addition, Soxhlet extractors with glass thimbles, rotary evaporators and ordinary glassware are required. Table 1 lists dimensions of three sizes of columns along with the approximate sample loading for each. Most of the work reported here was carried out on the 74 × 0.9 cm columns. Several chromatography and general supply vendors sell the above equipment.

Materials

The ion exchange resins were macroreticular styrene-divinylbenzene polymer type bonded with strong base or acid groups. They were purchased (BioRad Laboratories, Richmond, CA, USA) in four particle size ranges and were designated MP-1 (anion) and MP-50 (cation) by the vendor. The 200–400 mesh (37–75 μm) particle size resin was used for most of this work. Also, solvents were obtained from Fisher Scientific, Pittsburgh, PA, USA, and were h.p.l.c. or similar grade. The extraction reagents, formic acid and 1-propylamine, were ACS reagent grade (MCB, Gibbstown, NJ, USA) and 99 + % (Fluka, Huppauge, NY, USA), respectively.

Activation of ion exchange resins

Table 2 shows the optimized sequence of solvent washes for preparing ion exchange resins. This method, as discussed later, was derived from a trial-and-error approach to produce resins with the highest activity and lowest blank. After washing was complete, the resins were transferred as a cyclohexane slurry to amber storage bottles with airtight caps.

Packing columns and running samples

A packing reservoir with a volume about three times

Table 1 Ion exchange experimental apparatus

Columns	Length x i.d. (cm)	Approximate acid or base capacity (g)	Usual charge wt(g)	Flow rate (ml min ⁻¹)
Glass, with adjustable plungers	74 x 0.9	1.0–1.5	10	1–2
Glass, with adjustable plungers	70 x 1.5	2.5–5	25	2–4
Glass, with adjustable plungers	100 x 2.5	10–20	100	5–10

Sample to adsorbent (wt/wt) ratio 1:4

Pumps

Requirements: 1–10 ml min⁻¹, low dead volume, 150 psi (1 MPa)

Temperature bath

40 ± 1°C

Soxhlet extraction

Thimble size = 2 X resin volume. Glass thimbles with fritted filters work best.

Separation of liquid fossil fuels: J. B. Green et al.

Table 2 Sequence of solvent washes for preparing anion exchange resins

Order	Reagent	Amount (dm ³ /1.5 kg resin)
1	1–2 N HCl	25
2	water	4
3	1–2 N NaOH	25
4	water	12
5	1:1 propanol-water	25
6	propanol	25
7	ethyl ether	Soxhlet, 24 h (N ₂)
8	n-pentane	Soxhlet, 24 h (N ₂)

Note: Steps 1–6 are done while the resin is in a large Buchner funnel. For 7–8 the resin is transferred to a large extraction apparatus. For steps 5 and 6, 1- or 2-propanol may be used when activating anion resins. Anion resins should be protected from CO₂ once they are in the hydroxide form (steps 3–8). For activation of cation resins, steps 1 and 3 are reversed and 35 dm³ each of HCl and NaOH are used. 1-Propanol should be used for step 6 when activating cation resins.

that of the column being packed was connected to the column via a specially fabricated junction. The junction had ends suitable for sealing with both the column and packing reservoir and a stopcock in the middle. The storage bottle containing the resin was shaken vigorously to resuspend the resin in the cyclohexane and an appropriate amount was poured into a graduated cylinder. The column was filled with cyclohexane and the junction stopcock was closed. The resin in the graduated cylinder was transferred to the packing reservoir with cyclohexane, and an 80 psi (550 KPa) helium source connected to the reservoir top. The stopcock was quickly opened and the helium pressure allowed to pack the column. After packing, the stopcock was closed, the helium line disconnected, the reservoir removed from the column, and the appropriate plunger or end fitting inserted into the column. For efficient use of time, enough columns of each resin type were packed to enable running 3–5 samples as a group.

The columns were equilibrated with four void volumes of mobile phase before use. Usually, the columns settled slightly during equilibration, in which case the column plungers were pushed down to remove any visible voids. Then, each pair of anion and cation columns were connected, the water jackets plumbed to the temperature bath, and pumps used to charge dissolved samples onto the column pairs (after temperature equilibration at 40 ± 1°C). Preweighed charges were dissolved in a 4:1 excess of mobile phase. Usually, the total charge volume nearly equalled the void volume of the resin columns. All residue samples were filtered prior to charging to check for complete dissolution and to remove ash and other particles. Elution of the neutral fractions was effected by pumping 2.5 times the void volume of the anion-cation column pair; then the anion column was disconnected and an additional 0.5 void volume was pumped through the cation column alone. The void volume of a given column configuration was determined by injecting 10–20 μl of pentane and monitoring the effluent with a refractive index detector.

After elution of the neutrals, the plungers were removed from all the columns and 5–10 ml of methanol was added to the tops of all resin beds. The top of the bed was stirred with the methanol to break up the hard crust which usually formed – especially with synfuel samples. Then, each column was inverted over a glass Soxhlet thimble

placed in a beaker, and a pump running at 10–20 ml min⁻¹ was used to unpack the column (usually with benzene solvent) into the Soxhlet thimble. After unpacking, the columns and plungers were rinsed with methanol to transfer the last traces of resin into the Soxhlet thimbles.

After all columns were unpacked, the thimbles were placed in Soxhlet extractors and the liquid in the beakers holding the thimbles was transferred with benzene to the Soxhlet boiling flasks. Extra benzene was added, if necessary, to fill the Soxhlet pots two-thirds full. For extraction of acids, 0.2 ml formic acid was added per ml of resin (10 ml for a 0.9 × 74 cm column). The entire quantity was added to the Soxhlet pot at once since the benzene-formic acid azeotrope provided for a slow, steady exposure of resin in the thimble to the acid. The 1-propylamine (b.p. 48–9°) had to be added in slow increments, however, to avoid overly vigorous neutralization of the cation resin in the thimble. The simplest way to do this was to dilute the amine 1:2 with benzene and add it via a slowly dripping addition funnel using a 2-neck flask for the extraction. Otherwise, manual periodic addition in 1–2 ml increments for a total of 0.2 ml/ml resin was necessary.

For most samples, extraction was complete in 3–10 h. For samples with acids and bases marginally soluble in benzene, a volume of tetrahydrofuran equivalent to one-half of the Soxhlet thimble volume was added. This often would greatly speed up the extraction of residue samples. However, there is a potential danger of resin-promoted polymerization of the relatively unstable THF; therefore, it was used sparingly and only with the most difficult samples. Completion of the extraction was visually determined. With distillate samples, the resin returned to their original colour; however, residues often left the resin with a dingy grey or even black appearance. Resins returning to their proper colour were reused, others were discarded.

All extractions must be performed under nitrogen. A simple manifold was constructed with plastic tubes placed over the ends of the Soxhlet condensers. These in turn were connected in series to a nitrogen tank on one end, and a tube placed in mineral oil (for pressure regulation and indication of flow) at the other.

Solvent was removed under vacuum from all fractions using a rotary evaporator. To ensure complete removal of water and formic acid from acid and base fractions, they were redissolved in benzene or toluene and reevaporated 2–3 times to azeotrope out entrained polar solvents. The mass balance of each separation was determined gravimetrically. High boiling (>400°C) samples were taken to constant weight in a vacuum drying oven at 60–80°C, 5–10 torr, (0.6–1.2 kPa). Low boiling samples (<400°C) were taken down to 10–20% solvent; then the remaining solvent was determined by g.c. and subtracted to get the final fraction yield. The g.c. conditions were: column, 2 m AT-1000 on Graphpac GC (Cat. 8542, Alltech Associates, Deerfield IL, USA) in 1/8" (3 mm) o.d. nickel tubing; T = 70°C (1 min), 24°C min⁻¹ to 220°C, hold (backflush) for 16 min; flow rate, 20 ml/min He, FID detector at 250°C, and 0.5 µl injected (250°C). In addition, a four-way valve was added to backflush the sample components off the front of the column after the solvent peaks had eluted. An internal standard (toluene or some other solvent not present) was used to quantitate the solvent analyses.

Notes on general procedures

Most of the solvents used for ion exchange separations are highly toxic and/or carcinogenic (benzene). Thus, all steps of the procedure were performed in fume hoods. In addition, the column-packing procedure requires a safety shield between the operator and packing reservoir.

Occasionally, an acid- or base-saturated resin was difficult to remove from the column. In this case, methanol was used instead of benzene to pump the material from the column. This problem is greatest with the smallest particle packings. Thus a 50–100 or 100–200 mesh resin is best for samples containing very high levels of strong acids and bases.

Specific procedures

Quality control on resin activation. Each batch of resin activated according to Table 2 was checked for activity and cleanliness. Activity was determined by separating a 10 g portion of a Wilmington, CA, USA, 370–535°C distillate¹⁸, and comparing the acid and base yields to those of previous batches of resins. This sample was selected for checking activity because it contains relatively large amounts of very weak acids and bases^{19,20}. Hence, acid or base yield falls off rapidly as resin activation decreases.

Model compound experiments. To help elucidate the behaviour of different classes of compounds in ABN separations, several members of a given class were spiked into a portion of Wilmington 370–535° neutral fraction, and the composite was separated into ABN fractions via the general procedure. Individual model compounds were spiked at the 0.5–1.0 wt% level, relative to the total weight of Wilmington 370–535° neutral oil plus total model compounds. The sum total of spiked compounds never exceeded 10 wt%. After isolation of the ABN fractions, each was spiked with an internal standard and analysed by low voltage (10 eV) mass spectrometry, capillary g.c., h.p.l.c., or a combination of these techniques. The results showed the relative distribution of each compound in each fraction, and the overall recovery of each compound.

Procedure for rapid mobile phase optimization. During preliminary screening of different eluents for ion exchange separations, it was often expedient to rapidly determine the retention of various test compounds without going through the elaborate procedure outlined above. For this work, a dual pump h.p.l.c. apparatus with u.v. and refractive index detectors was used (Waters Associates, Milford, MA, USA). This equipment was also used for determining void volumes of the various sized columns.

I.r. spectroscopy. I.r. spectroscopy was used for both qualitative and quantitative analysis of fractions. All spectra were recorded using 0.5 mm NaCl or KBr cells and a double-beam Perkin Elmer (Norwalk, CT, USA) model 283 spectrophotometer with nitrogen purge of the optics and cell compartment. Ethylene dichloride was used as the solvent for quantitative work; carbon tetrachloride was usually used for qualitative scans. Carbazole and 1,2,3,4-tetrahydrocarbazole were used as standards for determining N–H compounds. 9-hydroxyfluorene and 2-naphthol were used as standards for O–H compounds. Beer's law plots were linear for concentrations up to 0.05 M.

RESULTS AND DISCUSSION

Comparison of methanol- and 1-propanol-activated resins

A major conclusion from this work is that preparation and activation of resins is the most crucial step to obtaining satisfactory ABN separations with nonaqueous ion exchange chromatography. For example, the particular alcohol used in step 6, Table 2, has a surprisingly large effect on the resulting activity of a given batch of resin.

An example of this alcohol effect may be seen in Figure 1, which contrasts the 'neutral' fraction of Wilmington 370–535°C distillate from ion exchange resins activated using methanol (Figure 1a) and 1-propanol (Figure 1b). All other aspects of the resin preparation were the same; the only variation was the alcohol used in steps 5 and 6 in Table 2. To obtain data for the plots in Figure 1, the neutral fraction was collected in 10–20 ml subfractions, and were: 1. evaporated and weighed (total gravimetric concentration); 2. analysed for total N with a chemiluminescent nitrogen analyser (Antek, Houston, TX, USA); and 3. analysed for N–H compounds by i.r. spectroscopy. As

Figure 1 Elution of neutral and weakly polar species in Wilmington 370–535°C distillate from methanol (a) and 1-propanol (b) activated resins. ○, total gravimetric elution profile; △, total N; ●, N–H compounds determined by i.r. The numbers in circles refer to the number of column void volumes of eluent at a given point. Note the much higher ability of the 1-propanol-washed resins to retain weakly polar species

shown in Figure 1a elution of both N–H (i.r.) and total N begins simultaneously with the appearance of the first sample components in the effluent of the column pair activated using methanol. Figure 1b shows that retention of these very weak acids and bases is much improved with the 1-propanol-activated resins. In Figure 1b, N–H compounds are not even detected until after the great majority of neutral compounds have been eluted; even then, their concentration in the effluent is quite low. A moderate amount of non-N–H nitrogen compounds is eluted from even the 1-propanol-activated resins. As will be shown later, neutral nitrogen compounds such as *N*-alkylated-pyrroles are not retained by ion exchange resins.

Figures 1a and 1b show clearly that most of the neutral components elute before two void volumes of eluent have passed through the columns, and that a substantial portion of the material eluting after two void volumes is weakly polar material. This observation agrees with that of Sawatzky *et al.*¹⁷ Calculations based on data in Figure 1a show that at least 5% of the effluent from the methanol-activated resins was nitrogen compounds even before one void volume of eluent had passed through the columns. Considering that the bulk of the sample elutes during this period, the total weight of nitrogen compounds eluting from methanol-activated resins into the neutral fractions is significant.

Table 3 compares ABN mass balances from three different types of fuels separated with 1-propanol- and methanol-activated resins, and aqueous-alcoholic extraction. The major difference between the two sets of ion exchange results is in the yield of acids. The more active 1-propanol-activated resins trap weak acids which elute into either the base or neutral fractions with methanol-activated resins. As seen in the table, the effect of using more active resins is greater with the Wilmington petroleum sample. In general, petroleum samples contain more of the very weak acids and bases, and hence are more difficult to separate into ABN fractions. With the exception of the Wilmington 370–535°C data, the agreement between the results of the authors and those of McKay *et al.*¹⁵ is poor. Since many factors affect the yields of acids and bases from high boiling materials, speculation on the reasons for the discrepancy in results seems pointless. Finally, as alluded to in the introduction the overall performance of the extraction method was poor, especially on high boiling petroleum samples. The extraction procedure used was similar to others reported in the literature^{21–23}, except that methanol was added to the aqueous phase to improve solubility of hydrophobic acids and bases.

Separation of PAHs and weak acids and bases

Another important aspect of ABN separations is the separation of weak acids and bases from neutral species. Naturally, this relates to the preceding discussion on resin activation, since high activity is necessary for effective retention of weak and very weak acids or bases. However, other factors such as eluent type, elution volume, and the degree of aromaticity of the neutral components present in the sample have significant effects on the overall quality of the ABN separation. Optimization and study of these parameters was carried out largely with model compounds.

For example, Figures 2a–b and 3a–b show reconstructed chromatograms of polycyclic aromatic hydro-

Table 3 Results from ABN separations using ion exchange and extraction methods on a wide variety of samples

Sample, boiling range (°C)	Separation method									
	IE: ^a 1-Propanol-activated resins					IE: Methanol-activated resins				
	Acids	Basess	Yield (wt%)	Neutrals	Total	Acids	Basess	Yield (wt%)	Neutrals	Total
Wilmington, CA, petroleum										
<370	2.24	1.24	94.7		98.2	1.40	1.40	1.40		100.5
370-535	10.1	8.0	81.8		99.9	8.5	6.0	88.0		100.5
						5.6 ^d	6.8 ^d			
535-675	14.7	14.1	70.6		99.3	5.54	10.8	85.1		101.4
						9.3 ^d	12.7 ^d			
>675	13.1(s) ^b	27.6(s)	34.7		99.3	4.24(s)	41.3(s)	42.9		102.2
	10.7(w)	13.2(w)				4.48(w)	9.3(w)			
	23.8(T)	40.8(T)				8.7(T)	50.6(T)			
						18.0 ^d	19.0 ^d			
OSCR 76-552 shale oil, >200	12.3(s)	16.5(s)	65.4		100.2	3.93(s)	18.9(s)	68.1		97.3
	4.02(w)	2.01(w)				5.19(w)	1.17(w)			
	16.3(T)	18.3(T)				9.1(T)	20.1(T)			
PMCM 77SR12 SRC II coal-derived liquid										
>325	18.0(s)	13.6(s)	54.7		100.4	17.2(s)	14.5(s)	58.4		100.1
	12.8(w)	1.36(w)				6.7(w)	1.29(w)			
	30.9(T)	14.9(T)				25.9(T)	15.8(T)			

^a IE = Nonequeous ion exchange. Resins were BioRad MP-1 and MP-50 200-400 mesh^b (s), (w), and (T) indicate strong, weak, and total acids or bases, respectively. Strong and weak acids and bases were isolated using different eluents as described later in text^c These data are estimated based on the results obtained from extracting a 325-425°C SRC II distillate^d Data from ref. 15; they also reported neutral nitrogen fraction yields of 4.2, 21.3, and 41.0 wt% for the three boiling ranges. Elemental compositions (%C, %H, %N, %S and %O [difference]) - Wilmington crude: 85.6, 11.6, 0.63, 1.6, 0.6. Dried shale oil: 83.7, 11.8, 1.4, 2.6, 0.5. Whole SRC II: 87.0, 8.4, 1.1, 0.25, 3.3

Figure 2 Elution profiles of model compounds spiked into a Wilmington 370–535°C oil matrix on 1-propanol-activated resins. Mobile phases are cyclohexane (a), and 20% (vol/vol) benzene in cyclohexane (b). See Table 4 for codes to numbered compounds

carbons (PAH), weak acids and weak bases eluting from 1-propanol- and methanol-activated resins. Figures 2a and 3a, and 2b and 3b depict chromatograms obtained with the following mobile phases, respectively: cyclohexane and 20% (vol/vol) benzene in cyclohexane. Table 4 lists the compounds in Figures 2 and 3. The material eluting from the resins, the neutral fraction, was collected in sub-fractions in order to study each compound's elution profile. As explained in the Experimental section, this mixture of compounds was run in a matrix of Wilmington 370–535°C acid-base-free distillate. Since the amount charged to the ion-exchange columns, both in terms of total weight and volume, is far greater than most other types of chromatography, the sample components themselves take part in the elution process. Thus, to obtain model compound data representative of actual conditions, the Wilmington matrix is needed.

Several conclusions were drawn from separations of mixtures containing PAHs and weak acids and bases. The two most important are: 1. the best compromise volume for elution of the neutral fraction is 2.5 void volumes (not counting the volume of the charge); and 2. the quality of the separation between PAH compounds and weak acids

or bases does not change with increasing eluent strength. With regard to the first conclusion and as also pointed out in the discussion of Figure 1, virtually all neutral compounds which are going to elute properly have done so after 2–2.5 void volumes of eluent have passed through the columns. Further elution is fruitless, and in fact merely washes weak acids and bases into the neutral fraction. In reference to the second conclusion, a highly condensed-ring PAH such as coronene requires a fairly polar eluent for effective elution, as discussed in the next section. Of course, the more polar eluents cause larger amounts of weak acids and bases to elute also. Hence, the overall separation between highly condensed ring PAHs and weak acids and/or bases is a limiting factor in ion exchange separations. Thus, when optimizing eluent strength for a given type of sample the authors took the following approach: the weakest eluent was selected which will elute > 50% of the largest, most condensed ring PAH estimated to be present, based on the boiling range and origin of the sample. In most cases, the PAH compounds contaminating the acid and base fractions can be later separated during their subfractionation on silica^{24–26}. In no case have the authors observed a PAH content > 1–2% in any polar fraction.

As expected, Figures 2 and 3 show that ion exchange

Figure 3 As for Figure 2 except that the resins used were activated using methanol

Table 4 Model compounds in Figures 2 and 3

Compound No	Name	Type	Comments
1	Carbazole	Weak acid	Partly eluted from methanol activated resins with 20% dichloromethane-80% cyclohexane eluent. Otherwise retained on anion resin.
2	1,2,3,4-Tetrahydrocarbazole	Weak acid	Partly eluted in Figure 3b and from methanol activated resins with 20% dichloromethane-80% cyclohexane eluent. Otherwise, retained on anion resin.
3	1-Azapyrene	Medium base	Retained on cation resin in all runs.
4	1-Methylpyrene	PAH, neutral	Eluted within 2.5 void volumes in all runs.
5	Chrysene	PAH, neutral	3% recovered in base fraction, Figure 2a. Otherwise totally eluted in all Figures.
6	Benzanthrone	Ketone, acid or neutral	Retained in acid fraction, Figure 2a and b. Otherwise eluted into neutrals.
7	Benz[a]pyrene	PAH, neutral	About 10% retained in acids and bases with cyclohexane eluent. Otherwise 100% eluted.
8	3-Methylcholanthrene	PAH, neutral	Eluted within 2.5 void volumes in all runs.
9	Dibenz[a,c]phenazine	Weak base	Eluted in 3b. Retained on cation resin in other runs.
10	Coronene	PAH, neutral	Poorly eluted by cyclohexane. 70-80% eluted with more polar solvents.
11	2,3,4,5-Tetraphenylpyrrole	Very weak acid	Retained in 2a, 2b, 3a. Eluted in others.
12	1,2,3,4-Tetraphenyl-naphthalene	PAH, neutral	No detectable retention or peak tailing.
13	9-Ethylcarbazole	Neutral nitrogen	Not present in 3a and 3b. Elution profile similar to 1-methylpyrene.
14	N,N-Diethyl-m-toluamide	Weak base	Retained on cation resin in all runs.

resins activated with 1-propanol have superior ability to retain very weak acids and bases. The 1-propanol-activated resins are even able to retain the highly hindered 2,3,4,5-tetraphenylpyrrole and the ketone benzanthrone with eluents as polar as 25% benzene-75% cyclohexane (Figures 2a and 2b). However, 9-ethylcarbazole was not retained at all by either resin. *N*-Alkylated-pyrroles and higher benzologs probably make up part of the luting non-N-H nitrogen observed in Figure 1b.

Finally, a third set of data similar to that in Figures 2 and 3 was obtained using 20% dichloromethane-80% cyclohexane eluent. The resulting chromatograms were similar to Figures 2b and 3b with somewhat faster elution of weakly polar compounds. In addition, an experiment similar to 3a was run with methanol-activated Rohm and Haas (Philadelphia, PA.) A-29 (anion) and A-15 (cation) resins. These resins were used in much of the previous ion exchange work described in the Introduction. The results from that experiment were similar to those shown for the BioRad resins in Figure 3a, except that the weak acid, 2,3,4,5-tetraphenylpyrrole, was not retained by the Rohm and Haas resins and benzanthrone was eluted even more poorly than in Figure 3a.

Separation of medium strength acids and bases

The purpose of the experiments in this section was to verify the separation behaviour of medium strength acids and bases normally found in fuels. Thus, aliquots of Wilmington 370-535°C neutral oil were spiked with 10-20 polar compounds and separated into ABN fractions. Experiments were run with both methanol- and propanol-activated resins. For brevity, only the results from the 1-propanol-activated resins are reported in detail.

Table 5 lists the compounds and eluents used. A few of the compounds in Figures 2 and 3 were repeated as a cross check. Also, the usual column order, anion first - cation second, was switched in one experiment. Finally, since the main interest was in the polar fractions, the neutral fraction was not subfractionated in this series of runs.

The distribution among ABN fractions of selected groups of the model compounds as a function of mobile phase and resin order is shown graphically in Figures 4-6. The actual (except Figure 6) per cent of each type of compound recovered in each of the three fractions is plotted versus aromaticity (Figures 4 and 5) or individual compound number (Figure 6). Recoveries (typically ranging from 80-120%) were normalized to total 100% in Figure 6 to improve legibility of the curves. Also, the compounds in Figure 6 are arranged in the order of decreasing acidity, as indicated on the figure. Finally, run numbers 0-4 on the figures refer to experimental conditions specified in Table 5. A zero run number denotes a pure cyclohexane eluent and anion-cation resin order.

Figure 4 merely summarizes what was said earlier about elution of PAH compounds. That is, PAHs ≤ 4 ring are eluted by all eluents, but elution of PAHs > 4 ring requires eluents at least as strong as 25% benzene-75% cyclohexane. For example, even in run 3, where 100% benzene eluent was used, 1-3% of the coronene (6-rings) spiked into the mixture was found in both acid and base fractions.

Figure 5 shows the surprising affinity of the amino-PAH family for the anion resin. Although basic by virtue of the free electron pair from the nitrogen atom, the amino-PAH class also exhibits acidic (proton donating) behaviour which increases with the number of condensed aromatic rings and decreases with *N*-alkylsubstitution. For example, only in run 4, where quite polar eluent was used, did the 3- and 4-ring amino-PAHs pass completely through the anion column to be retained on the cation column. All amino-PAHs were retained in the base fraction in run 2 because the cation column was placed first in that run.

Since in most schemes it is desirable to have the amino-PAHs in the base fraction, samples suspected of containing them should be processed with the quite polar 45% benzene-45% tetrahydrofuran-10% ethanol eluent used in run 4. (Experiments leading to the development of that eluent are described later.) However, that eluent also

Table 5 Model compounds and experimental conditions for Figures 4-6

Compound No	Name	Type	Chromatographic behaviour
1	<i>n</i> -Decanoic acid	Acid	Always retained on anion column.
2	2,7-Dihydroxynaphthalene	Acid	Retained on cation column - run 2. Otherwise retained on anion columns.
3	2-Naphthol	Acid	Retained on cation column - run 2. Otherwise retained on anion columns.
4	2,6-Dimethylphenol	Hindered acid	Always retained on anion column.
5	2,4-Dimethyl-6- <i>t</i> -butyl phenol	Hindered acid	Always retained on anion column.
6	Carbazole	Weak acid	10% retained on cation column - run 2. Otherwise retained on anion column.
7	2,3,4,5-Tetraphenyl pyrrole	Weak acid	8% retained on cation column - run 2. Retained on anion column - runs 1 and 3. Eluted into neutral - run 4.
8	1,2,3,4-Tetrahydrocarbazole	Weak acid	100% retained on cation column - run 2. Retained on anion column - runs 1 and 3. Eluted into neutral - run 4.
9	Iminostilbene	Weak base	93% retained on anion column - run 1. Otherwise retained on cation column.
10	9-Hydroxyfluorene	Very weak acid or base	Variable behaviour.
11	Diphenylamine	Weak base	10% retained on anion column - run 1. Otherwise retained on cation column.
12	<i>p</i> -Ethylaniline	Base	Retained on cation column - all runs.
13	2,6-Diethylaniline	Hindered base	Retained on cation column - all runs.
14	2,6-Di- <i>p</i> -tolylpyridine	Hindered base	Retained on cation column - all runs.
15	1-Naphthylamine	Amino-PAH	Variable.
16	2-Aminofluorene	Amino-PAH	Variable.
17	1-Aminanthracene	Amino-PAH	Variable.
18	6-Aminochrysene	Amino-PAH	Variable.
19	1-Heptanethiol	Neutral	Never recovered.
20	Phenyl benzoate	Neutral	Virtually never recovered.
21	Benz[<i>a</i>]pyrene	Neutral	<2% in acids and bases in all runs.
22	Coronene	Neutral	70-80% in neutral - runs 1 and 2. 95% run 3. 100% run 4.

Run No.	Eluent ^a	Resin order
1	75% Cyclohexane-25% Benzene	Anion - cation
2	75% Cyclohexane-25% Benzene	Cation - anion
3	Benzene	Anion - cation
4	45% Benzene-45% THF-10% Ethanol	Anion - cation

^a The zero (0) run number in Figure 4 denotes a cyclohexane eluent.

washes some of the weaker acids and bases into the neutral fraction. For example Figure 6 shows carbazole to be the weakest acid still to be retained by the anion resin in run 4. Other weak acids such as 1,2,3,4-tetrahydrocarbazole and 2,3,4,5-tetraphenylpyrrole are eluted into the neutral fraction. Hence, the most significant conclusion from this series of runs is that coal-derived liquid residues and other types of samples likely to contain amino-PAHs should be processed twice: first with 4.5:4.5:1 benzene-THF-EtOH eluent, and then with 3:1 cyclohexane-benzene eluent through a fresh pair of columns to obtain strong acid, strong base, weak acid, weak base, and neutral fractions (see Table 3).

One way around the problem of amino-PAHs contaminating the acid fraction would be simply to switch the usual order of the ion exchange columns and pass the sample through the cation column first. However, as Figure 6 shows, this procedure causes additional problems. First and foremost is the unexpected retention of the hydroxynaphthalenes, compounds 2 and 3, by the cation resin. Also, members of the pyrrole family split between the acid and base fractions depending on their relative acidity, whereas before they were almost exclusively contained in the acid fraction. Thus, except for very special applications, the anion-cation order is preferred.

Finally, Figure 6 once again shows the exceptional ability of the propanol-activated resins to retain weakly

polar compounds. Even with eluents as strong as 100% benzene, the only polar compound found in the neutral fraction was 9-hydroxyfluorene, a benzylalcohol. The low affinity of resins for alcohols may result from their retention of water and alcohols used during their activation; i.e., they may be 'alcohol saturated'.

Recovery of model compounds

Although the previous discussion of Figures 2-6 has dealt with the relative partitioning of compounds into ABN fractions, as mentioned in the experimental section, the overall recovery of each compound was also determined. Generally, recoveries ranged between 80 and 120%, which is within experimental error of 100% recovery in most cases. A few significant deviations were observed, however. For example, low recovery of amino-PAH and hydroxynaphthalene compounds was observed whenever an eluent containing dichloromethane was used. In addition, a decline in anion exchange capacity with time was noted during the period when an older method of resin activation²⁴ involving a dichloromethane extraction was in use. For these reasons, dichloromethane is no longer used in any step of the authors' ion exchange procedure.

In general, recovery within a given class of compounds lowers with increasing degree of aromaticity. For example, slightly lower recoveries were observed for dibenz[*a,c*]phenazine and 1-azapyrene than for the

Figure 4 Partition of PAH compounds into ABN fractions as a function of experimental conditions. See Table 5 for conditions for runs 0-4. The 'number of aromatic rings' label on the abscissa refers only to condensed aromatic rings, e.g., diphenyl-naphthalene would have a value of 2. The resins were activated with 1-propanol.

monoaromatic bases. Also, Figures 4 and 5 show this same downward trend in recovery with increasing aromatic ring number. This trend probably reflects the decreased resistance of the compounds themselves toward oxidation and photochemical reactions induced by room lights.

Finally, some compounds were actually decomposed by the resins or resin extraction reagents. They are listed in Table 6. For example, phenyl benzoate hydrolysed to phenol and benzoic acid. Low recoveries were also observed for phenyl salicylate during earlier work with methanol-activated resins. In addition, 1-heptanethiol was never recovered; presumably, it formed the disulphide. Finally, amino-PAHs gave low recoveries whenever they were retained by the anion resin (runs 1 and 3).

Ion exchange resins are not suited for work with very sensitive molecules; but, all evidence indicates that they do not cause major alteration of fuels. Also, in every case where degradation of a compound has been observed, equal or greater degradation occurred during its solvent extraction with HCl and/or NaOH. Thus, the strong acid and base group on the resins probably caused the observed degradations. Similar alterations have been observed during separations on silica and alumina²⁷; thus, virtually no separation technique is free from this fault.

Model compound work with methanol-activated resins

The model compound experiments with methanol-activated resins will not be described in detail in this report. However, results are cited below for a few types of compounds not included in Figures 2-6 or Tables 4-6. As expected from the previous results obtained for members of the pyrrole family, the anion resin retained all amides with at least one active hydrogen. Similarly, benzimidazole, which is basically a pyrrolic compound with an extra nitrogen in the ring, was retained as an acid. The cation resin retained thiazoles as expected, but let benzonitrile elute. It is difficult to predict whether a 1-propanol-activated cation resin would retain benzonitrile.

Reproducibility of resin activation

The results in this section indicate the approximate batch-to-batch variability of resins activated according to Table 2. Table 7 shows yields from Wilmington 370-535°C distillate obtained with different batches of resins. Cation resins activated with 2-propanol showed inferior activity, otherwise reproducibility was within $\pm 3\%$ (relative average deviation).

Figure 5 Analogous plots to Figure 4 for amino-PAH compounds. Note the strong affinity of these compounds for the anion resin shown in runs 1 and 3.

Figure 6 Partitioning of acidic compounds into ABN fractions as a function of mobile phase and resin order. See Table 5 for codes for run conditions and compounds numbers. See text for explanation of curves.

Table 8 shows blanks (benzene charge, see Experimental) obtained for different batches of resins and different mobile phases. Neither the particular alcohol used for activation nor the type of mobile phase used for elution of the benzene had any large effect on the weights of blanks. However, long-term storage causes increased blanks due to build-up of small amounts of resin and solvent decomposition products. Nevertheless, assuming that 10 g of sample with a 10% acid and 10% base content were charged to a pair of 0.9×74 cm columns (see Table 1), all fractions would contain <2% relative impurities from resins, solvents, etc. Realistically, methods for characterization of full fractions are not often good enough to detect impurities at such low level. Similarly, subfraction of the ABN fractions, usually necessary in detailed analysis, often removes resin impurities altogether.

Optimization of the polar mobile phase used for synfuels and petroleum residues; chromatographic efficiency of resins

The three component mobile phase (45% (vol/vol) benzene, 45% (vol/vol) THF, 10% (vol/vol) ethanol) used in run 4 of Figures 4–6 resulted from a study of the elution behaviour of amino-PAHs, hindered phenols, amides, and other N–H compounds. The 'procedure of rapid mobile phase optimization' described in the Experimental section was used.

Table 9 shows retention data for 6-aminochrysene and a few selected compounds as a function of mobile phase

composition. The 45:45:10 solvent combination was selected because it eluted 6-aminochrysene with a capacity factor <2, did not elute various hindered phenols within a capacity factor of 5, and dissolved most real samples very well.

Columns packed with the smaller mesh size resins had reasonable chromatographic efficiencies and typically yielded peaks with asymmetry factors in the range 1.1–1.2. For example, the anion column used to generate the data in Table 9 had a theoretical plate height of 2 mm and an asymmetry factor of 1.1 for 6-aminochrysene at $k' = 1.7$. A plate height of 2 mm is equivalent to 500 plates/m – far below the theoretical efficiency attainable with particles in the 75–38 μ m size range. However, this efficiency is adequate for the purpose and, considering the broad size range of the particles, faster than optimum flow rate, etc., is reasonable. For comparison, a similar experiment with elution of a neutral species from columns packed with commercial grade (≈ 20 –50 mesh) Rohm and Haas resins yielded a plate count of only 54 plates/m.

Table 8 Compounds with low per cent recoveries under one or more elution conditions

Compound	Fraction where found	% Recovery				
		Elution condition number ^a				
		0	1	2	3	4
Benzanthrone	Acid	23	21			
1-Heptanethiol			0	0	0	0
2-Aminofluorene	Acid, base ^b	29	106	67	92	
Phenyl benzoate ^c		0	0	0	19	
9-Hydroxyfluorene	Acid, base, neutral	97	13	87	75	
6-Aminochrysene	Acid, base	42	68	83	54	65

^a See Table 5

^b When 2-Aminofluorene was found partly or entirely in the acid fraction (numbers 1 and 3), its recovery was low

^c Peaks with g.c. retention times corresponding to benzoic acid and phenol were found in the acid fractions in runs 1–3 and in the neutral fraction in run 4

Table 7 Acid–base–neutral yields of Wilmington 370–535°C distillate from tests of different batches of ion exchange resins

Anion resin batch number	Cation resin batch number	Acids	Wt% bases	Neutrals	Total
21D	21D	10.06	7.53	81.73	99.72
21D ^a	21D ^a	10.10	8.00	81.61	99.71
26A	26A	10.76	7.44	81.79	100.0
248 ^b	26C	10.12	8.40	81.79	100.31
248 ^b	248 ^b	10.68	6.26 ^b	82.35	99.29
–	27A ^b	–	5.61 ^b	–	–
Mean ^c		10.3	7.9	81.8	99.8
Average deviation		0.3	0.3	0.2	0.2

^a Run after one month storage. Resins appear to be stable for at least six months if kept covered with solvent in an air tight container

^b Activated using 2-propanol. Results from 2-propanol-activated cation resins were excluded from the above mean value for base yield

^c Cyclohexane was used as the eluent in all resin quality control runs. Wilmington 370–535°C distillate: %C, 85.8; %H, 11.6; %N, 0.5; %S, 1.6; and %O (difference), 0.5

Table 8 Analytical blanks from BioRad resins activated with different alcohols

Anion resin batch number	Cation resin batch number	Alcohol used for activation	Mobile phase used for elution	Weight (mg) ^a		
				Acids	Bases	Neutral
17C	17C	Methanol	Cyclohexane	14.4	6.7	1.4
21B	21B	Methanol	Cyclohexane	3.5	11.4	0.6
24B	24B	2-Propanol	Cyclohexane	3.2	9.1	1.0
26A	26A	1-Propanol	45% Benzene, 45% THF, 10% EtOH	13.9	7.2	2.5
21D ^b	21D ^b	1-Propanol	45% Benzene, 45% THF, 10% EtOH	19.9	19.7	10.7

^a Absolute weights of impurities obtained from resin packed in a 0.9 x 74 cm column. These columns have a capacity for 1–1.5 g acids or bases.

^b These resins had aged 5 months prior to running this blank. All others were only 1–2 weeks old.

Table 9 Capacity factors (*k'*) for 6-aminochrysene on MP-1 anion resin using a variety of polar eluents

Eluent composition (vol%)				
benzene	THF	Ethanol	<i>k'</i>	Solute
100	0 ^a	0	>6	6-aminochrysene
80	0 ^a	10	3.1	6-aminochrysene
80	0 ^a	20	2.6	6-aminochrysene
80	0 ^a	50	3.0	6-aminochrysene
0	100	0	>6	6-aminochrysene
5	90	5	1.98	6-aminochrysene
0 ^b	90	10	1.25	6-aminochrysene
15	70	15	0.97	6-aminochrysene
81	9	10	2.9	6-aminochrysene
45	45	10	1.89	6-aminochrysene
45	45	10	0.82	1-aminonaphthalene
45	45	10	0.00	naphthalene
45	45	10	0.21	coronene
10	80	10	1.11	6-aminochrysene
0 ^c	0	0	>6	6-aminochrysene

^a Poor peak shape was observed when no THF was present.

^b Substandard peak shape was observed when no benzene was present; but not nearly so bad as when THF was absent.

^c 100% acetonitrile.

CONCLUSIONS

Based on the information given here as well as some unpublished data from i.r. characterization of ABN fractions, Figure 7 summarizes optimum mobile phases for different types of fuel samples. The basic premises underlying Figure 7 are summarized below.

1. Residue samples of all types need to be separated twice – once with a polar eluent and once with a weak eluent. Usually, solubility considerations alone necessitate using a strong eluent on the first pass. Also, separation of strong and weak polars usually facilitates characterization of residues. Because of the probable presence of highly condensed ring PAHs in a residue, use of a benzene-cyclohexane eluent in the second pass is necessary for their elution into the neutral fraction.
2. Raw synfuel distillates boiling > 300°C potentially contain amino-PAHs. Processing them like residues ensures that the amino-PAHs will end up in the base fraction.
3. Very high boiling petroleum distillates likely contain some greater than four-ring PAHs (b.p. ⁷⁶coronene = 525°C, b.p. ⁷⁶chrysene = 450°C). Thus, separation of petroleum distillates boiling > 500°C requires a 3:1 cyclohexane-benzene eluent.

Petroleum and hydrotreated synfuel distillates boiling < 500°C

500–700°C petroleum distillates and < 300°C non-upgraded synfuel distillates

> 700°C petroleum residues and > 300°C synfuel distillates and residues

Figure 7 Optimum eluents for various types of samples. See 'Conclusions'.

4. Cyclohexane eluent (cyclopentane is better for volatile samples) maximizes retention of very weak acids and bases. Thus, samples more likely to contain weak acids and bases than large PAH molecules, such as petroleum and hydrotreated synfuel distillates, are best processed with a pure cycloparaffin eluent.

In all probability, there are numerous samples which will not fit neatly into the categories of Figure 7. In such cases, study of the data presented should also allow the reader to modify procedures to obtain fractions best suited for his own work.

Again, the most critical step in the procedure is preparation of the ion exchange resins. Preparation of quantities appropriate for a six-month supply enhances both separation reproducibility and time utilization efficiency. Each batch of resin should be tested for excessive blank and sufficient activity.

Except perhaps for special applications, the anion resin should be the first to contact the sample.

Two to 2.5 void volumes of eluent are all that is necessary to elute the neutral fraction from both resin columns. Excessive elution merely washes weak acids and bases into the neutral fraction.

Finally, although the procedure presented here improves significantly upon older versions of ion exchange ABN separations, the method is still laborious, requires a lot of equipment and laboratory space, and uses many toxic and/or noxious reagents. Its virtues include: 1. nearly universal applicability; 2. ability to handle a wide range of sample sizes; and 3. production of fractions that have at least some chemical uniqueness or meaning. In contrast, separation of 'asphaltenes' and 'preasphaltenes', for example is nearly as laborious and also requires toxic solvents, but yields fractions of uncertain composition or utility and is restricted as to sample size and other experimental variables. In addition, the present work showed ion exchange to be much more applicable than liquid-liquid extraction methods, and the work of Finseth, *et al.*²³ showed ion exchange to be superior to HCl precipitation methods also. Similarly, Burchill, *et al.*²⁹ recently found that nonaqueous ion exchange compared favorably with other methods for isolating basic nitrogen compounds from coal tars. With regard to the flexibility of the method: Rosset, *et al.*³⁰ used cation exchange chromatography to concentrate nitrogen compounds from 40 dm³ of naphtha containing 0.012 ppm nitrogen into 14 ml, whereas the authors have applied the method to charges as small as 1 g and samples with nitrogen contents as high as 2-3 wt%. Thus, in the authors' experience nonaqueous ion exchange chromatography represents a superior and versatile method for breaking most samples into gross compound types prior to more detailed fractionation and/or spectroscopic examination.

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