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CHARACTERIZATION OF VACUUM BOTTOMS FROM THE
P-99 COAL LIQUEFACTION UNIT

By
R. G. Lett
C. E. Schmidt
D. H. Finseth
M. R. Hough
T. A. Link
R. F. Sprecher
H. L. Retcofsky

Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

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Spectroscopy Section

Analytical Chemistry Branch

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ABSTRACT

A composite sample of vacuum bottoms has been analyzed by structural sensitive techniques applicable to high molecular weight, highly functional coal-derived materials. The utilization and limitations of X-ray diffraction, infrared, high resolution and ^{13}C -CP/MAS nuclear magnetic resonance, high resolution and field ionization mass spectrometry, and electron spin resonance are discussed. Particular emphasis is given to the characterization of methylene chloride soluble fractions, isolated by a combination of mild extraction and functionality-specific procedures, in terms of heteroatom functionality, molecular weight and carbon number distributions, and mean structural parameters. This nondistillate but soluble material is primarily a complex mixture of high molecular weight polynuclear aromatic and heterocyclic components with short alkyl substituents. The vacuum bottoms are low in phenolic OH functionality compared to typical SRC-II distillates.

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

INTRODUCTION

There has recently been a demand for detailed structural information on coal-derived vacuum bottoms or residua fractions that can be used in thermo-physical property correlations. A better knowledge of the nature of these fractions, particularly with regard to functionality and molecular weight distribution, is required to understand and predict their behavior in coal-conversion systems. During FY-83, a program was started at PETC to address this need.

The work summarized in this report was initiated to provide the basis for constructing an analytical scheme for the characterization of soluble but nondistillate (850°F+) fractions of coal conversion products. This includes a description in terms of mean structural parameters, heteroatom functionality, molecular weight, and carbon number distribution. Advanced structure-specific analytical techniques currently available were applied to a typical coal liquefaction vacuum bottoms product. Limitations of these techniques are discussed and areas where additional analytical development may be necessary are indicated. Similar analytical approaches are also applicable to the analysis of products resulting from short contact time or mild reaction conditions.

EXPERIMENTAL

Sample Origin

The sample analyzed was removed from drum 123 of composite vacuum bottoms obtained by the Coal-Conversion Engineering Branch from Gulf Research & Development Company (GR&DC), Harnarville, Pennsylvania. This material was collected during operation of the P-99 coal liquefaction PDU at GR&DC in a vacuum column receiver at 354°C over about a one hour period during SRC-II runs using Powhatan No. 5 bituminous coal. Compositional data supplied with the sample are summarized in Tables 1 and 2. As evident from Table 2, about 97 wt% of the vacuum bottoms sample is nondistillate range (900°F+) material. The ash content is high compared to most coal-conversion products, and about 60 wt% is pyridine soluble. Consequently, standard solvent analysis procedures and techniques requiring appreciable sample volatility, such as gas chromatography or conventional mass spectrometry, will have limited applicability. Because of the inhomogeneous nature of the as-received sample, most analyses were performed on a more representative sample prepared by finely grinding about 150 grams with a mortar and pestle.

Separations

Without further separation, the total vacuum bottoms are rather intractable from the standpoint of most structure determination techniques. Two distinct procedures were applied to (1) separate soluble from insoluble constituents and (2) separate the solubles into base, acid, and neutral fractions.

The methylene chloride solubles were extracted by a combination of dialysis and Soxhlet procedures as outlined in Figure 1. Using a procedure recently described,¹ the vacuum bottoms were dialyzed through a latex rubber membrane to generate a particulate-free, methylene chloride soluble

Table 1. Elemental composition of composite
P-99 vacuum bottoms, as received.^a

<u>Element</u>	<u>wt %</u>
C	64.35
H	3.73
N	1.28
S	3.36
O (Total)	12.7
Ash	27.8

^aAnalyses supplied by Gulf Research and Development Company.

Table 2. Distillation and solubility data on
composite P-99 vacuum bottoms as received.^a

<u>Distillate Component</u>	<u>Fraction (wt %)</u>	<u>Cumulative (wt %)</u>
500°F-	---	---
500° - 550°F	---	---
550° - 600°F	---	---
600° - 650°F	---	---
650° - 700°F	---	---
700° - 750°F	---	0.0
750° - 800°F	1.19	1.19
800° - 850°F	1.19	2.38
850° - 900°F	1.19	3.57
900°F+, Pyridine Soluble	56.79	60.36
IOM	8.78	72.2
Ash	27.8	100.0
Sp. Gr. 77/77°F	1.435	
Melting Pt., °F	329	

^aSupplied by Gulf Research and Development Company.

Figure 1. General scheme for separation of vacuum bottoms into methylene chloride soluble and insoluble fractions.

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dialyzate and a residue fraction. The dialysis proceeds very slowly on this type of sample, but after ten days, nearly 40 wt% of the vacuum bottoms had been extracted. The dialysis extraction also has the property that lower molecular weight material is preferentially extracted first. The dialysis could be speeded somewhat by using a mixed solvent system with pyridine on the sample side of the membrane, but this would preclude long periods of unattended operation of the dialysis apparatus.

The dialysis residue was then removed and extracted an additional 4 days in a Soxhlet extractor. Since Soxhlet extracts invariably contain some fine particulate and/or colloidal material, the Soxhlet extract and dialyzate were treated as distinct samples and not combined. Including both the dialyzate and Soxhlet extract, about 43 wt% of the vacuum bottoms were recovered as methylene chloride solubles, as indicated in Table 3. This comprises more than 70% of the pyridine solubles and thus was considered a sufficiently representative sample for initial structural studies.

Considerably more information can be gleaned from most spectroscopic techniques if the sample is further separated into functionality-enriched fractions. The P-99 dialyzate was separated into nitrogen base, phenolic acid, and neutral fractions by the procedure outlined in Figure 2. This unpublished PETC procedure was developed specifically for the separation of heavy direct liquefaction products. Since the starting sample was completely soluble in methylene chloride, and Rotovap (solvent removal) losses were nil due to low sample volatility, recoveries were excellent, as shown in Table 4.

Chemical and Instrumental Analyses

Major element, ash, and molecular weight determinations were made at Huffman Laboratories, Wheat Ridge, Colorado. Elemental analyses were accomplished by microanalytical procedures. Number average molecular weights were determined by vapor phase osmometry (VPO) in pyridine at 80°C.

Several minor elements in the residue remaining after Soxhlet extraction were determined by the Analytical Support Section. Silicon was quantitated by classical gravimetric procedures involving loss of silicon tetrafluoride upon treatment of the residue remaining from nitric and perchloric acid digestion with hydrofluoric and sulfuric acids. Iron, aluminum, calcium, titanium, and potassium were determined by atomic absorption spectroscopy after fusion of the residue from the nitric and perchloric acid digestion with sodium carbonate. Sodium was determined by atomic absorption analysis of an unfused portion of the sample. Concentrations were calculated by comparison with standard solutions.

Major minerals in the Soxhlet residue were identified by X-ray diffraction. The finely ground sample was packed into a glass cavity with no binder for X-ray analysis. Data were obtained on a computer-controlled Rigaku horizontal goniometer. The X-ray source was a copper X-ray tube operated at 40 kV and 35 mA. Data were collected with a 1° divergent slit and a 0.3-mm receiving slit. The signal was detected by a scintillation counter with a pulse height discriminator following a graphite receiving monochromator.

Table 3. Yields from methylene chloride extraction of
P-99 vacuum bottoms dialyzate.

	<u>wt (gm)</u>
Unextracted P-99 Vacuum Bottoms	107.8
Dialyzate	37.0
Dialysis Residue Removed	2.0
Soxhlet Extract	9.3
Soxhlet Residue	52.9
Recovery	94%

Table 4. Yields of functionality-enriched fractions from
P-99 vacuum bottoms dialyzate.

	<u>wt (gm)</u>
Unseparated Dialyzate	1.00
Bases (N-Bases)	0.19
Acids/Neutrals	0.80
Recovery	99%
Unseparated Acids/Neutrals	0.80
Neutrals	0.51
Acids (Phenols)	0.28
Recovery	99%

Figure 2. Separation scheme for isolation of base, acid, and neutral fraction from methylene chloride solubles.

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Basic nitrogen types in the dialyzate were estimated by a nonaqueous titration procedure developed at PETC in the Analytical Support Section.² The analysis requires three separate titrations in different solvent systems with 0.05M perchloric acid in 1,4-dioxane as titrant. Each titration used about 40 mg of dialyzate in a volume of 4 to 6 mL. Smaller samples could be used if the basic nitrogen content was higher. One titration was carried out in nitrobenzene to determine the total bases except weak bases. A second titration in 20% acetic anhydride/nitrobenzene gave a measure of the heterocyclic bases and total bases including weak bases. A third titration in 2M phthalic anhydride/nitrobenzene was used to determine secondary aromatic amines and heterocyclic bases. Primary amines were estimated by difference.

Infrared survey spectra were recorded on a Digilab FTS-20C FT/IR or a Perkin-Elmer Model 180 double-beam infrared spectrometer. The solid samples were examined as KBr pellets of approximately 0.03-mm thickness. The dialyzate was also run as a thin film prepared by evaporating a concentrated methylene chloride solution on a KBr plate. Each FT/IR spectrum represents the accumulation of 16 interferometer scans made at a rate of 35 sec/scan (sample + reference scan) and then transformed for representation in a standard % transmittance vs. wavenumber format. The Perkin-Elmer 180 spectra were recorded in the "Constant I_0 " mode. Resolution was maintained at 8 cm^{-1} or less over the entire scan range on the FT/IR and at 2 cm^{-1} or less over the entire scan range on the Perkin-Elmer 180.

Quantitative measurements of free O-H and relative N-H concentrations were made on a Cary 17D UV/visible/near-infrared spectrometer by near-infrared spectroscopic procedures developed at PETC.³ Briefly, the samples were prepared as dilute solutions (~2 gm/L) in dry methylene chloride. Using an average O-H molar absorptivity previously determined by running about 20 different phenols as standards, the concentration of oxygen as free O-H can be estimated from the peak absorbance of the O-H band in the sample if the cell path length and sample concentration are known. Absolute quantitation of N-H is more difficult, since N-H absorptivities show a much wider range of variation among different molecules than O-H, rendering standardization a problem on complex mixtures. It is possible to use the ratio of the N-H to O-H peak absorbances as a measure of relative changes in N-H between related samples.

High resolution ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra of soluble fractions were acquired on a Varian Associates XL-100 spectrometer. This instrument is equipped with a 15-inch magnet, a 16K computer, and an interactive disk system. Samples were run as CD_2Cl_2 solutions with TMS added as a reference standard. Internal pulse deuterium lock was employed, permitting very stable operation for long accumulation times. Samples for ^1H NMR were placed in 5-mm tubes and irradiated with a 10- μsec pulse. A 1-KHz spectral width was observed. A flip angle between 70° and 80° and a 3-sec pulse delay were used. For ^{13}C NMR, the dialyzate was placed in 12-mm tubes and irradiated with a 12- μsec pulse. A 5-KHz spectral width was observed. Data were acquired using a 90° flip angle and proton board-band noise decoupling in the suppressed Overhauser mode of operation. A long pulse delay of 100 seconds was employed to insure relatively complete nuclear relaxation and quantitative integrity of the data. An 8K data length was used to provide adequate resolution.

Solid-state ^{13}C NMR spectra were obtained by combined cross-polarization and magic angle spinning (CP/MAS) techniques at Colorado State University, Fort Collins, Colorado. Samples of the unseparated vacuum bottoms, dialyzate, and dialysis residue were run without any further sample treatment. Carbon aromaticities were determined directly from the integrated ratio of the aromatic to total carbon in the spectra.

Electron spin resonance (ESR) spectra were obtained at PETC on a Varian Associates Model E-112 spectrometer equipped with a dual cavity and field/frequency lock module. The resonant frequency of the cavity (~ 9.5 MHz) was measured with an EIP Autohet Model 3500 frequency counter. The spectrometer was interfaced to a Nicolet 1180 computer system, and data were acquired, stored, and reduced by means of custom software written at PETC.⁴ Samples of the vacuum bottoms, dialyzate, and Soxhlet residue were placed in 4-mm-o.d. quartz tubes, degassed to $\sim 10^{-6}$ torr, and sealed. Quantitative intensity measurements were made by comparing the doubly integrated spectrum of the sample to that of a diphenylpicrylhydrazyl (DPPH) standard containing a known number of free spins. Linewidths were calculated from the full width at half maximum intensity ($\Delta H_{1/2}$) of the absorption band using the hyperfine splitting constants of peroxyaminedisulphonate (PADS) as a magnetic field calibration standard. The g-values were determined from the known g-value of the PADS standard and the measured microwave frequency.

Low voltage mass spectra were run on a Kratos MS-50 high resolution mass spectrometer. Samples were introduced either through a heated inlet maintained at 300°C or by a direct probe that can be heated to 350°C . Typical sample sizes were 5 to 7 mg for the heated-inlet system and 60 to 80 μg for direct-probe runs. In either case, spectra are representative only of that material that vaporized at the indicated temperature and 10^{-6} torr. The heated-inlet system is capable of more reproducible, quantitative results, but direct-probe introduction into the mass spectrometer source permits observation of a greater fraction of the less volatile material. Direct-probe runs were kept to an absolute minimum, since carbonaceous deposits rapidly accumulate in the mass spectrometer, necessitating frequent source cleaning.

High resolution mass spectral data were collected from the output of an electron multiplier by scanning from $m/e=67$ to $m/e=600$ over a period of approximately 2 1/2 minutes in a direct-probe run or 25 minutes in a heated-inlet run. Resolution was maintained near 1 part in 30,000. Precise masses were determined by the Kratos DS-55 operating system relative to a mixture of halogenated aromatics added as precise markers. Elemental formulas of observed ions are readily calculated by the DS-55 data system for those mass regions in which precise mass calibration data are simultaneously recorded with the sample data. However, some problems have been experienced above $m/e=350$ due to the low intensity of observed ions and lack of sufficiently closely spaced mass markers. Above this point, it also becomes increasingly difficult to unambiguously assign a unique formula to a precise mass even with a mass measurement accurate to within a few millimass units.

Field ionization mass spectra were obtained from SRI International, Menlo Park, California. The SRI spectrometer is equipped to introduce samples at temperatures as high as 450°C , but a maximum temperature of 340°C was used in this work. The material observed will thus include most of the

sample that has any significant vapor pressure under normal liquefaction conditions. Some dehydrogenation and thermal cracking may occur under these conditions. However, most distillate bottoms have already been subjected to relatively high temperatures for extended periods, and sample decomposition is not expected to be serious under rapid vaporization conditions. The field ionization source produces primarily parent ions and yields a mass envelope that is at least reasonably representative of the carbon number distribution of the material vaporized. The SRI spectrometer operates at relatively low resolution, i.e., about 1 part in 1200. The plotted mass spectral profiles were not corrected for ^{13}C contributions.

RESULTS AND DISCUSSION

Elemental Composition

The elemental composition of the P-99 vacuum bottoms was redetermined after receipt by the Spectroscopy Section. The analyses in Table 5 are generally in agreement with those in Table 1 (supplied by GR&DC) with respect to C, H, N, and S. Based upon the data in Tables 5 and 6, the oxygen content is estimated by difference to be 12.7%, which agrees with the value from GR&DC. The data also imply that about 5/6 of the oxygen is associated with the mineral matter. Due to an initial problem with the chlorine determination in the as-received bottoms sample, triplicate analyses were obtained on the unseparated P-99 vacuum bottoms and the Soxhlet residue. The results indicate that the chlorine present in the P-99 vacuum bottoms is quantitatively recovered in the Soxhlet residue. Thus the chlorine content of the soluble fractions is a reliable indication of the extent of methylene chloride solvent removal or incorporation.

There is nothing particularly unusual about the mineral matter. Concentrations of what are termed in coal analyses "major elements in the ash," as determined on the Soxhlet residue, are given in Table 6. X-ray diffraction analysis of the Soxhlet residue indicates the major minerals present are pyrrhotite, kaolinite, and illite (clays), and quartz, as expected. Lower concentrations of calcium sulfate and troilite (FeS) are also present. The presence of troilite in addition to pyrrhotite is consistent with prolonged exposure to elevated temperatures.

Infrared Survey

The vacuum bottoms give a rather poor quality infrared spectrum, which is shown in Figure 1A. The spectrum is typical of that obtained for a mixture of coal-derived carbonaceous material and mineral matter.

The infrared spectrum of the organic material in the vacuum bottoms is exemplified by spectra 2A and 3A. The cast film spectrum is of superior quality, displaying a lower background and scatter than the KBr run, but it also shows a trace of the methylene chloride solvent. The spectra are similar to those of any heavy coal liquid fraction, such as an asphaltene or preasphaltene, derived from a bituminous coal. In the condensed phase, the O-H and N-H bands in the 3500 cm^{-1} region are not resolved because of strong hydrogen-bonding effects. The spectra are characterized by a weak aromatic C-H stretching band near 3050 cm^{-1} , aliphatic C-H stretching bands from 2800 cm^{-1} to 3000 cm^{-1} , intense absorption near 1600 cm^{-1} arising at least

Table 5. Elemental analyses, ash, and molecular weight data.^a

Sample	Elemental Analysis (wt %) ^b						Ash (750°C)	MWC/
	C	H	O	N	S	Cl		
P-99 Vacuum Bottoms (As Received)	64.1	3.7 ₇	-----	1.3	3.3	0.28 ^d	28.2	---
Dialytic Extract	86.1	5.6 ₆	2.5	1.5	0.8 ₃	3.9	< 0.1	440
Soxhlet Extract (CH ₂ Cl ₂) of Dialysis Residue	84.9	5.2 ₂	2.4	1.9	0.8 ₁	4.9	0.4	590
Soxhlet Residue	42.0	2.1 ₈	-----	0.9 ₄	-----	0.46 ^d	48.4	---

^aHuffman Laboratories, Wheat Ridge, Colorado.

^bMicroanalysis.

^cVPO in pyridine (4 points).

^dTriplicate analyses.

Table 6. Major inorganic element analysis of methylene chloride Soxhlet residue from P-99 vacuum bottoms.^a

Element	Concentration (wt %)	
	Soxhlet Residue	Total Vacuum Bottoms Basis
Fe	10.6	5.5
Si	9.8	5.1
Al	5.2	2.7
Ca	1.0	0.5
K	0.4	0.2
Ti	0.4	0.2
Mg	0.2	0.1
Na	0.1	0.05

^aAnalytical Support Section, PETC.

in part from aromatic skeletal vibrations, methylene and methyl deformations at 1450 and 1375 cm^{-1} , and a series of weak aromatic C-H out-of-plane bending absorptions between 750 cm^{-1} and 950 cm^{-1} . The infrared spectrum of the Soxhlet extract of the vacuum bottoms dialysis residue in Figure 5A is similar to that of the dialyzate.

The infrared spectrum of the dialyzate residue in Figure 4A is very similar to that of the as-received vacuum bottoms in Figure 1A. Many of the most prominent features can be attributed to minerals, particularly kaolinite. A typical spectrum of kaolinite has been included as Figure 7A for comparison. The infrared spectrum of the Soxhlet residue, Figure 6A, is similar to that of the dialysis residue, although the organic content has been further reduced. The spectrum resembles that obtained from a bituminous coal char.

The infrared survey spectra are very useful for determining the general nature of the samples, following the course of sample separations, and detecting the presence of any impurities or incomplete solvent removal. Survey spectra of coal-derived organic fractions tend to not be qualitatively very distinctive if run as a condensed phase. Some of the problems encountered in extracting quantitative information, such as poor infrared transmission characteristics, ill-defined baselines, and overlapping bands, are obvious from spectra 1A to 6A.

Carbon Number Distribution

Several low voltage high resolution mass spectrometry runs were made on the vacuum bottoms and dialyzate to determine the carbon number distribution of the more volatile components in the vacuum bottoms. Due to the low sample volatility, these runs were carried out by stepwise heating of the sample in the direct injection probe at 100°C, 200°C, 300°C, and 350°C while recording mass spectra at each step. The results are somewhat similar to those obtained by looking at distillation cuts. Also, since the material is vaporized directly into the mass spectrometer source region, it is rapidly pumped away, necessitating operation under relatively rapid scan conditions for a high resolution mass spectrometer. The results are thus dependent not only on temperature but also on the time of observation after heating to a given temperature. It is possible to add spectral scans to partially compensate for these effects. All of the major mass peaks observed in the mass spectra from the vacuum bottoms and dialyzate can be attributed to condensed aromatic structures with C_1 and C_2 substitution prevalent.

The bulk of the material observed by the high resolution mass spectrometer vaporized between 200°C and 300°C. Figure 1B is a nominal mass plot of the ion distribution from the vacuum bottoms observed at 300°C. This plot is computer-synthesized from the high resolution data, which is output separately as a lengthy listing of precise masses and possible molecular formulas, by co-adding the ion intensities at each nominal mass. The material vaporized at 300°C has an average molecular weight of about 310. There is a relatively sharp cutoff of parent ion peaks below $m/e=200$; consequently, this region was not displayed. The most intense peaks at $m/e=276$, 290, 304, and 330 are indicative of condensed 6-ring structures, such as benzoperylenes, dibenzopyrenes, anthanthrenes, and alkylated derivatives.

It is instructive to consider the material that vaporized at 200°C and 350°C. These spectra have been plotted such that the strongest peak is full-scale; thus the plots are not directly intercomparable with respect to ion intensities without additional information on total ion currents, etc. The major peaks in the nominal mass plot of material vaporized from the dialyzate at 200°C in Figure 2B arise from 4-ring aromatics (pyrenes, chrysenes), 5-ring aromatics (benzopyrenes), and some 6-ring aromatics (benzoperylene, anthanthrenes). According to Figure 3B, the additional material vaporized between 300°C and 350°C consists largely of 7-ring aromatic structures (dibenzoperylene, etc.).

A better representation of the carbon number distribution of the material with significant vapor pressure at liquefaction temperatures is provided by the medium resolution field ionization mass spectra. The FIMS profiles have been generated by co-adding spectra, weighted according to total ionization, at one-minute intervals while increasing the sample temperature to 340°C. Compared to low voltage high resolution mass spectrometry using an electron impact source, ionization by the FIMS source is a less sensitive function of compound type and aromatic ring number. The disadvantage of this technique is that it is difficult to identify the specific types of structures being observed without additional information from other sources. Field ionization mass spectra of the P-99 vacuum bottoms and dialyzate are shown in Figures 7B and 8B. Both mass spectra are similar, ions being observed to $m/e=800$. The number average molecular weight of the material vaporized from the total vacuum bottoms at 340°C is about 440 vs. about 420 for the dialyzate. However, virtually all (~95 wt%) of the dialyzate vaporized, while only about half (~45 wt%) of the vacuum bottoms vaporized. The percent vaporized is nearly equal to the methylene chloride solubility of the sample. The presence of intense fragment ions at masses lower than $m/e=200$ would be indicative of some thermal cracking. If this becomes excessive for a given sample, the only recourse, other than lowering the vaporization temperature, is probably to try a technique, such as field desorption mass spectrometry, that is not totally dependent upon thermal heating to vaporize the sample.

Acid and Base Functionality

Information on the phenolic acid and nitrogen base content is particularly relevant if the behavior of a coal-derived material under process conditions is to be predicted. These data are difficult to obtain directly by analysis of an unseparated vacuum bottoms sample. Attempts to estimate the free O-H concentration by dilute-solution near-infrared analysis of the total vacuum bottoms were unsuccessful owing to poor methylene chloride solubility and the relatively low O-H content.

Considerable information on the oxygen and nitrogen functionalities in the dialyzate can be obtained without further separations. As indicated in Table 7, dilute-solution near-infrared spectroscopy indicates that about 20% of the oxygen in the dialyzate is present as free O-H. This is in contrast to a typical coal hydrogenation product, where about half of the oxygen is present in the form of free O-H. Most of the remaining oxygen is probably present in ether structures. Any tightly internally bonded O-H would also not give a discrete O-H absorption at the same frequency as the free O-H in the infrared. There is no evidence for C=O in the infrared spectra, nor is

any expected because of the reducing environment in the liquefaction unit. A crude estimate of the pyrrolic-N-H nitrogen has also been included in Table 7.

The basic nitrogen content of the dialyzate and Soxhlet extract of the dialysis residue was determined by nonaqueous titration procedures. The results in Table 8 indicate that 0.90 wt% of the nitrogen is titratable as basic nitrogen, predominantly heterocyclic nitrogen bases. The remaining nitrogen (0.58 wt% in the dialyzate) is presumed to be in pyrrolic-type structures. This is in agreement with the infrared estimate for the dialyzate. The results suggest that the increased nitrogen content of the Soxhlet extract relative to the dialyzate is because of an increase in pyrrolic nitrogen, not in basic nitrogen. The interpretation of the different types of titratable basic nitrogen given in Table 8 is not as firmly established as the total basic nitrogen determination. The low primary amine content is determined by difference and may have only qualitative significance.

Additional insight into the nature of the functional groups can be obtained by the analysis of functionality-enriched fractions. Since these fractions were only isolated in mg quantities, analyses were of necessity somewhat limited. Based upon a basic nitrogen content of 0.90 wt% and weight average molecular weight of 450, isolation of 19 wt% of the dialyzate in the base fraction is low for a fraction containing one basic nitrogen per molecule. Although this could result from failure to completely elute all of the bases from the cation exchange resin in the separation procedure, it is more likely an indication that the bases are high in multifunctional components. The latter explanation is consistent with the infrared spectral data. The recovery of 28 wt% of the dialyzate in the acid fraction appears high for a material with 0.5 wt% to 0.6 wt% oxygen as free O-H.

Infrared survey spectra in Figure 8A of the dialyzate fractions are all virtually identical and indicate the fractions are relatively solvent-free. Near-infrared determinations of free O-H are summarized in Table 7. The base fraction, since it is isolated first from a cation exchange resin, will contain some O-H in the form of bifunctional (amphoteric) molecules with both basic and acidic groups. Some carbazole N-H will also appear in the base fraction due to the presence of bifunctional nitrogen species (about one molecule in ten of the bases). The cation exchange procedure should be relatively specific in eliminating any molecules containing an amine or pyridinic nitrogen from the acid and neutral fractions.

The near-infrared results indicate the neutral fraction is almost free of the O-H functionality. Most of the carbazoles are expected to elute in this fraction. The acid fraction appears a bit low in O-H but high in N-H. Since the acid fraction is eluted from alumina last, using a mixed $\text{HCOOH/MeOH/CH}_2\text{Cl}_2$ solvent system, this suggests that in this particular sample, some of the higher molecular weight, weakly acidic, pyrrolic material is not eluting with the neutrals but is being removed from the column when a more polar solvent is introduced. This causes no particular problems in most analyses as long as one is aware that this type of material is present in the phenolic acid fraction. It is possible to "fine-tune" the separation for a given sample to generate a carbazole-enriched fraction if required.

Table 7. Near-infrared analysis of P-99 vacuum bottoms dialyzate and functionality-enriched subfractions.

<u>Sample</u>	<u>wt % Oxygen As Free OH</u>	<u>Absorptivity Ratio A_{N-H}/A_{O-H}</u>	<u>Relative wt % Nitrogen As N-H</u>
Dialyzate	0.56	0.85	~ 0.6
Base Fraction	0.16	2.0	~ 0.3
Acid Fraction	1.5	0.39	~ 0.6
Neutral Fraction	<0.05	>15	~ 0.4

Table 8. Nonaqueous titration of basic nitrogen in P-99 dialyzate and Soxhlet extract of the dialysis residue.

<u>Type</u>	<u>wt % Nitrogen</u>	
	<u>Dialyzate</u>	<u>Soxhlet Extract</u>
Primary Aromatic Amines	0.10	0.08
Secondary Aromatic Amines	<0.02	<0.02 Basic
Heterocycles	0.80	0.82
Total Bases ($pK_a < 3$)	0.90	0.90

Although the vaporization characteristics are poor, low voltage high resolution mass spectrometry does provide confirmatory evidence regarding the nature of the separated fractions. Spectra of the volatiles from the base and neutral fractions are shown in Figures 4B and 5B. The observed spectra consist primarily of background and reference peaks below $m/e=200$. The major peaks in the mass spectrum of the base fraction are readily assignable to simple aza-aromatics and alkylated aza-aromatics, specifically azapyrenes, azachrysenes, and azaphenanthrenes. The major peaks in the mass spectrum of the neutral fraction can be associated with pyrenes (or fluoranthenes), chrysenes, and benzopyrenes. There is little evidence for the presence of hydroaromatic species, partially as a result of coincidences in mass of alkylated and hydroaromatic species. Also present are a series of sulfur compounds beginning with naphthodibenzothiophene ($m/e=234$). A few carbazoles were also detected, namely benzo- and dibenzocarbazole. These fractions are thus relatively free of volatile contaminants and appear to be correctly designated.

The phenolic fraction contained insufficient volatile material to yield an acceptable low voltage high resolution mass spectrum with the heated-inlet system at 300°C . Consequently, a qualitative probe run was made in which the temperature was stepped in the sequence $100^{\circ}\text{C} - 200^{\circ}\text{C} - 300^{\circ}\text{C} - 350^{\circ}\text{C}$. A composite spectrum is shown in Figure 6B. The results verify the fraction is primarily material with phenolic (even mass) and pyrrolic (odd mass) functionalities. Phenols and alkylated phenols are observed from the phenol through C_{30} phenols. Four-ring (benzocarbazoles) through 7-ring carbazoles and alkylated carbazoles are prominent. The largest nitrogen-containing peak at $m/e=267$ corresponds to dibenzocarbazole. Comparison with the field ionization mass profile of the dialyzate in Figure 8B suggests that only 10 to 20 wt% of the fraction is being observed by the high resolution mass spectrometer. Since little additional information would be gained, direct-probe runs were not made on the other fractions.

Field ionization mass spectral profiles of the separated base, neutral, and acid fractions are shown in Figures 9B, 10B, and 11B. Mass spectral profiles of the base and acid fractions are similar, with maxima near 470 amu and 430 amu, respectively. Both profiles are reasonably symmetric, although displaying a low mass cutoff at $m/e=200$ and a high mass tail. In contrast, the mass profile of the neutral fraction is highly asymmetric, with a maximum ion content near $m/e=280$, followed by a steady decrease with increasing mass.

Both number average and weight average molecular weights can be calculated from the field ionization mass profiles. The results summarized in Table 9 indicate that the base and acid fractions contain heavier material than the neutral fraction. This may in part reflect a higher probability of a molecule containing a polar group with increasing mass. However, as previously noted, there is indirect evidence from the separation yields and O-H measurements that some of the higher molecular weight neutrals may have been eluted with the acid fraction. Based upon the separation yields in Table 4, a weight average molecular weight of 457 can be estimated for the total dialyzate from the weight average molecular weight of the fractions. Agreement with the field ionization mass spectrometry estimate of 449 from the spectrum of the total dialyzate is well within the precision of the field ionization mass spectral data and separation yields. The data on the

Table 9. Average molecular weights from field ionization mass spectrometry profiles of the P-99 vacuum bottoms dialyzate and of base, neutral, and acid fractions.

<u>Sample</u>	<u>Weight Percent Vaporized</u>	<u>Number Average Molecular Weight</u>	<u>Weight Average Molecular Weight</u>
P-99 Vacuum Bottoms Dialyzate	95	420	450
Bases	69	480	510
Neutrals	95	400	420
Acids	77	450	480

fraction vaporized indicates the volatility of the separate base and acid fractions is less than that of the neutral fraction or unseparated dialyzate. This may be the result of some association of the polar material subsequent to separation and solvent removal or possibly of an increased tendency of the separated polar fractions to char rather than vaporize into the mass spectrometer. In order to provide sufficient sample for elemental microanalyses, it would be necessary to repeat the separation.

Average Structural Parameters

In a sample that is a complex mixture of high molecular weight components, such as the organic material in liquefaction bottoms, a characterization in terms of average structural parameters is more appropriate than an attempt to identify specific compounds. One structural parameter that can be determined relatively directly is the fraction of aromatic carbon, or carbon aromaticity (f_a). Aromaticities of the P-99 vacuum bottoms, dialyzate, dialysis residue, and Soxhlet extract of the dialysis residue are all very high (see Table 10). The result on the as-received P-99 bottoms appears to be too low and should be redetermined. It is not clear at this time whether the problem is because of the nature of the sample or because of the analysis procedure. The small difference in the carbon aromaticity of the dialyzate as determined by high resolution ^{13}C -NMR in CD_2Cl_2 solution vs. ^{13}C -CP/MAS on the solid is within experimental error. One problem in determining the aromaticity of highly aromatic materials from ^{13}C NMR spectra is evident from the dialyzate spectra in Figures 1C and 2C. The relatively low concentration of aliphatic carbon results in rather noisy spectra of the aliphatic region, particularly in solution, and may cause integration errors. Under these circumstances, the aromaticity estimate from ^1H NMR and elemental analysis data may be more accurate than that by ^{13}C NMR if the sample is soluble. The ^{13}C -CP/MAS spectrum of the dialysis residue shown in Figure 2C is probably broadened by the presence of relatively high concentrations of paramagnetic material.

Proton NMR data recorded on the P-99 vacuum bottoms, dialyzate, and Soxhlet extract of the dialysis residue are summarized in Table 11a. The spectrum of the as-received vacuum bottoms could only be recorded in methylene chloride after filtering out insoluble material. The higher molecular weight and more limited solubility of the Soxhlet extract compared to the dialyzate is evident in the poorer resolution of the Soxhlet extract spectrum shown in Figure 3C. The integrated proton spectra in Figure 3C were divided into four separate regions designated as $\text{H}_{\text{ar}+\phi}$ (7 - 10 ppm, aromatic and phenolic protons), H_α (~2.0 - 4.5 ppm, aliphatic protons α to an aromatic ring), H_β (~1.1 - 2.0 ppm, aliphatic protons β to an aromatic ring), and H_δ (~0.5 - 1.1 ppm, methyl protons δ or further removed from an aromatic ring). The data in Table 11a indicate that the distribution of aliphatic protons is very similar in each of the three samples. The fraction of aromatic protons is slightly higher in the Soxhlet extract than in the dialyzate. This is consistent with the higher carbon aromaticity and molecular weight of the Soxhlet extract.

A proton NMR spectrum of the Soxhlet residue was also obtained in pyridine after filtering out insolubles. The weak spectrum obtained represents the fraction of the P-99 vacuum bottoms soluble in pyridine but insoluble in methylene chloride. The results in Table 11b are again consistent with a

Table 10. Carbon aromaticities determined by carbon-13 nuclear magnetic resonance spectroscopy.

Sample	f_a
P-99 Vacuum Bottoms	0.76 ^a
Dialyzate	0.79 ^a , 0.83 ^b
Dialysis Residue	0.80 ^a

^a¹³C-CP/MAS NMR.

^bHigh Resolution NMR in CD₂Cl₂.

Table 11a. Proton NMR data on methylene chloride soluble fractions of P-99 vacuum bottoms, dialyzate, and extract of the dialysis residue.

Sample	Relative Integrated Areas			
	H* _{ar+φ}	H* _α	H* _β	H* _γ
P-99 Vacuum Bottoms, As Received	0.49 ₉	0.30 ₄	0.14 ₂	0.05 ₆
Dialyzate	0.52 ₄	0.28 ₂	0.14 ₂	0.05 ₁
Soxhlet Extract (CH ₂ Cl ₂) of Dialysis Residue	0.56 ₁	0.27 ₁	0.12 ₁	0.04 ₈

Table 11b. Proton NMR data on pyridine solubles in the Soxhlet residue from P-99 vacuum bottoms.

Sample	Relative Integrated Areas			
	H* _{ar+φ}	H* _α	H* _β	H* _γ
Soxhlet Residue- Pyridine Solubles	0.62 ₅	0.21 ₅	0.13 ₈	0.02 ₃

material characterized by a higher aromaticity and molecular weight than the methylene chloride solubles.

By combining elemental analysis, proton NMR, molecular weight, and functional group data, a more extensive list of average parameters of the vacuum bottoms dialyzate and Soxhlet extract can be estimated. For these calculations, the elemental analysis data in Table 12, the proton NMR data in Table 10, the molecular weight data in Table 5, and the phenolic O-H data in Table 7 were employed. The data in Table 12 were derived from Table 5 by assuming that the chloride present represented methylene chloride and re-normalizing after making the appropriate corrections on carbon and hydrogen. The effect of these corrections on the carbon-to-hydrogen ratios is almost insignificant.

The average structural parameters may be estimated by the Brown and Ladner approach.⁵ The usual assumption of 2.0 for the average H/C ratio of aliphatic groups α and β to aromatic rings is reasonably good for most coal-derived solubles and generally results in estimated carbon aromaticities from ^1H NMR spectra that agree with those from more direct ^{13}C NMR measurements. However, the standard treatment acknowledges the presence only of phenolic O-H and totally ignores the presence of other heterocyclic structures. Since the vacuum bottoms are low in phenolic O-H but contain considerable heterocyclic oxygen, nitrogen, and sulfur, some modifications of the usual calculation procedure were considered. The calculated carbon aromaticity is relatively insensitive to most of the assumptions of the Brown and Ladner approach. The fraction of hydrogen bonded to aromatic carbon or hydrogen aromaticity, H_{ar}^* , was calculated by correcting the integrated aromatic proton areas from the NMR spectra for pyrrolic-type N-H and phenolic O-H. Both corrections are small, but in the case of the P-99 vacuum bottoms solubles, the N-H correction is about twice that of the O-H.

The degree of substitution, σ , may be defined in various ways. For the present purpose, it was defined as the number of substituted aromatic carbons divided by the total number of edge carbons on aromatic rings. Pyrrole, pyridine, thiophene, and furan rings were considered as simply aromatic rings containing a heteroatom nucleus. Among substituent types that might be considered for coal-derived materials are aliphatic, phenolic (O-H), primary amino aromatic ($\phi\text{-NH}_2$), aryl-alkyl ether ($\phi\text{-O-R}$), and aryl-aryl ether ($\phi\text{-O-}\phi$). For most coal-hydrogenation products, the contributions due to amines and aryl ethers can be ignored, resulting in the usual Brown and Ladner formula for σ . One can further break this into contributions due to aliphatic groups (σ_{ali}) and phenols (σ_{O-H}). For the P-99 vacuum bottoms fractions, the contribution of phenolic groups to σ is small.

Likewise, the H/C ratio of the hypothetical unsubstituted aromatic nuclei, H_{aru}/C_{ar} , can be defined to include heteroatom group corrections due to hydroxyl, amine, and aryl ether substituents. Again, since only the correction due to hydroxyl is of any significant magnitude for the present samples, the resulting equation is identical to that given by Brown and Ladner. The magnitude of this H/C ratio is a rough index of the size of the average aromatic ring cluster (unit structure).

Table 12. Elemental analysis data used in mean structural parameter calculations.

Sample	Elemental Analysis (wt %) ^a				
	C	H	O	N	S
P-99 Vacuum Bottoms Dialyzate	89.2	5.81	2.6	1.5	0.9
Soxhlet Extract (CH ₂ Cl ₂) of Dialysis Residue	89.3	5.41	2.5	2.0	0.9

^aAsh-free, chlorine-free basis.

A problem arises if published formulas for the calculation of the total number of rings/molecule (R_t) and the average number of aromatic rings/molecule (R_a) are indiscriminately used.⁶ These formulas were originally derived for use in the petroleum industry and are strictly valid only for hydrocarbons. They are not correct for heterocyclic rings. Some published treatments of coal-derived products tend to modify the calculation of some parameters, such as σ and $H_{\text{aru}}/C_{\text{ar}}$, often by formulating rather "unusual" definitions for these quantities without appropriate modification of the ring calculation formulas.⁷ This approach appears somewhat inconsistent. To avoid the conceptual and practical difficulties associated with trying to modify formulas that are exact for hydrocarbons, the following procedure was adopted for determining the ring size parameters.⁸ Strictly for calculation purposes, each heteroatom in a ring was replaced by sufficient carbon and hydrogen to transform the heterocyclic rings into the equivalent six-membered aromatic ring. After correcting the total number of hydrogen atoms/molecule, total number of carbon atoms/molecule, and total number of aromatic carbon atoms/molecule to reflect the substitutions, the total number of rings/molecule and total number of aromatic + heterocyclic rings/molecule were calculated. The number of hydroaromatic rings was estimated by difference. The average number of heterocyclic rings of each type/molecule is readily deduced from the average molecular formula, since it is reasonable to assume that each thiophenic sulfur, pyridinic and pyrrolic nitrogen, and ether oxygen resides in a separate ring.

Some of the mean structural parameters calculated for the methylene chloride soluble fractions are summarized in Table 13. This information must be viewed with some caution, however, since many of the parameters are better used for correlation purposes than treated as well-determined physical properties. It must also be realized that Table 13 is essentially the elemental analysis, proton NMR, and molecular weight information simply recast in a different form. The estimated carbon aromaticity of the dialyzate is in complete agreement with the ^{13}C NMR determinations. The most difficult structural parameters to estimate are those related to the average ring cluster size and the average number of hydroaromatic (and/or naphthenic) rings. Consequently, it is also difficult to deduce with any certainty the relative fraction of the aliphatic protons in hydroaromatic rings vs. alkyl chains. Based on the data in Table 13, the average dialyzate molecule is highly aromatic and contains about 5 aromatic rings grouped in a single ring cluster, one heteroatom constituent (most often ether oxygen) in a heterocyclic ring, possibly one hydroaromatic ring, and/or several short alkyl substituents. The average Soxhlet extract molecule is of slightly higher aromaticity and may contain about 8 aromatic rings in one or two clusters, two heteroaromatic rings, and several short alkyl substituents.

Having calculated the parameters in Table 13 and realizing that some of the parameters, such as the average number of hydroaromatic (and/or naphthenic) rings (R_N), and average number of side-chain carbons per molecule (C_{side}), are likely to be physically meaningless due to cumulative errors and several only partially valid assumptions, it is useful to reconsider the original NMR data in Figures 1C and 3C. It has been noted that most aliphatic carbons in 3- and 4-ring hydroaromatics resonate in the area of 22 to 31 ppm from TMS in the ^{13}C NMR spectrum.⁹ According to this criterion, which may not be strictly valid for the material being analyzed,

Table 13. Mean structural parameters of P-99 vacuum bottoms
dialyzate and Soxhlet extract of the dialysis residue.

Parameter	Calculated Values		Description
	Dialyzate (C _{32.7} H _{25.4} O _{0.73} N _{0.48} S _{0.1})	Soxhlet Extract (C _{43.9} H _{31.5} O _{0.92} N _{0.53} S _{0.2})	
f _a	0.82	0.84	Carbon aromaticity
H* _{ar}	0.52	0.55	Hydrogen aromaticity
σ	0.22	0.21	Degree of aromatic ring substitution (including heteroatoms)
σ _{al}	0.21	0.20	Degree of aromatic ring substitution by aliphatic substituents
²³ H _{aru} /C _{ar}	0.63	0.60	H/C ratio of hypothetical unsubstituted aromatic rings
C _{ar}	26.9	37.0	Average number of aromatic C's/molecule
C _{al}	5.8	6.9	Average number of aliphatic C's/molecule
C _{ar} (u.s.)	20.4	27.0	Number of aromatic C's/average ring cluster assuming kata condensation
n	1.3	1.4	Average number of ring clusters/molecule
R _a + het(u.s.)	4.9	6.8	Aromatic + heteroaromatic ring number/average ring cluster

Table 13. Mean structural parameters of P-99 vacuum bottoms
dialyzate and Soxhlet extract of the dialysis residue. (Continued)

Parameter	Calculated Values		Description
	Dialyzate (C _{32.7} H _{25.4} O _{0.73} N _{0.48} S _{0.1})	Soxhlet Extract (C _{43.9} H _{31.5} O _{0.92} N _{0.53} S _{0.2})	
R _t	7.6	10.8	Total number of rings/average molecule (aromatic + heterocyclic + hydroaromatic)
R _a	5.4	7.7	Average number of aromatic rings/molecule
R _a + het	6.5	9.3	Average number of aromatic + heteroaromatic rings/molecule
²⁴ R _N	~1.1	~1.5	Average number of hydroaromatic and/or naphthenic rings/molecule
n'	~1.7	~1.6	Average chain length of aliphatic substituents
C _{side}	~2.5	~2.5	Average number of side chain C's/molecule

about one-third of the aliphatic carbons in the dialyzate may be present in hydroaromatic structures (about two hydroaromatic rings for every three molecules). The calculated transferable hydrogen, H_s , is then 0.4 wt%, which is low compared to most coal-derived materials. Considering the proton NMR spectrum of the dialyzate, about one molecule in two must contain a methyl γ to an aromatic ring. There are simply not enough β protons to support the existence of long alkyl chains. There is an area of weak broad absorption centered about 4 ppm in the aliphatic region, which may be indicative of bridgehead hydrogens of the type present in fluorene. On this basis, less than one molecule in two contains such a bridgehead carbon. The remainder of the aliphatic proton region is consistent with the average structural parameters calculated. It involves such a complex overlap of different structures that any further attempted resolution into cyclic α , alkyl α , cyclic β , and alkyl β regions, as often done for lower molecular weight solvents, is probably futile and may be misleading. The general appearance of the aliphatic region of the 1H NMR spectra indicates similar numbers of cyclic- and alkyl-type protons are present.

Free Spin Parameters

Electron spin resonance results are summarized in Figure 1D and Table 14. In outputting the data for display in Figure 1D, the spectrometer gain was adjusted to produce resonances of comparable amplitude for each sample. Both the as-received P-99 vacuum bottoms and the dialysis residue give resonances similar to those of a coal-derived char or coke-like material. The free spin population and g-value of the dialysis residue are in the range expected for a bituminous coal. The g-value is typical of that for large polyaromatic free radical species. The only significant difference between the measured free spin parameters of the vacuum bottoms and the dialysis residue is simply the lower spin population in the unseparated vacuum bottoms.

The dialyzate contains about an order of magnitude fewer spins/gm than the dialysis residue. The ESR signal from the dialyzate saturated readily. Consequently, lower microwave power levels were used than in making the measurements on the vacuum bottoms or dialysis residue. The g-value of the dialyzate is rather high and indicative of heteroatom-centered radical species. The linewidth observed for the dialyzate is more like that of a bituminous coal vitrinite or coal-derived asphaltene than a char. This may be at least partially due to the higher hydrogen content of the free radical species in the dialyzate compared to the dialysis residue, and unresolved electron-proton nuclear hyperfine interactions.

CONCLUSIONS

The analytical results indicate that the nondistillate organic material in the P-99 vacuum bottoms has some of the characteristics of a coal pyrolysis product rather than a coal hydrogenation product. It is characterized by a very high aromaticity, short alkyl substituents, and low phenolic -OH content. The number average molecular weight of the material that will vaporize at 340°C is approximately 420, although volatile fragments can be observed with molecular weights as high as 800. The VPO number average molecular weights of the dialyzate and of total methylene chloride

Table 14. Electron spin resonance
parameters at 9.5 GHz.

<u>Sample</u>	<u>Free Spin Population (spins/gm)</u>	<u>g value</u>	<u>Line Width FWHM (gauss)</u>
P-99 Vacuum Bottoms (As Received)	8.6×10^{18}	2.0026 ⁷	2.2
Dialyzate	1.6×10^{18}	2.0032 ⁵	8.6
Dialysis Residue	2.5×10^{19}	2.0026 ⁷	2.4

solubles are ~440 and ~470, respectively. Material of molecular weight less than 200 is essentially absent.

Although methylene chloride solubles can be analyzed in considerable detail, about 10% of the vacuum bottoms are pyridine soluble but methylene chloride insoluble. Much of the additional pyridine-soluble material may actually be microparticulate or colloidal in nature. Some additional characterization of this material is possible by extraction with THF rather than pyridine and subsequent use of GPC and field ionization (or field desorption) mass spectrometry to establish the carbon number distribution. With the exception of a higher molecular weight, the additional pyridine- or THF-soluble material is expected to have average structural parameters similar to those of the methylene chloride solubles. It should also be possible to apply the separation scheme outlined in Figure 2, with minor modifications, to THF-soluble fractions.

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APPENDIX A. Infrared Spectra

- Figure 1A. Infrared survey spectrum of P-99 vacuum bottoms.
- Figure 2A. Infrared survey spectrum of vacuum bottoms dialyzate. (KBr Pellet)
- Figure 3A. Infrared survey spectrum of vacuum bottoms dialyzate. (Cast Film)
- Figure 4A. Infrared survey spectrum of vacuum bottoms dialysis residue.
- Figure 5A. Infrared survey spectrum of Soxhlet extract of vacuum bottoms dialysis residue.
- Figure 6A. Infrared survey spectrum of Soxhlet residue.
- Figure 7A. Infrared spectra of clay minerals in coal.
- Figure 8A. Infrared survey spectra of base, acid, and neutral fractions of the dialyzate.
- Figure 9A. Near-infrared spectra of base, acid, and neutral fractions of the dialyzate.

Figure 1A. Infrared survey spectrum of P-99 vacuum bottoms.

Figure2A. Infrared survey spectrum of P-99 vacuum bottoms dialyzate.

Figure3A. Infrared survey spectrum of P-99 vacuum bottoms dialyzate.

Figure 4A. Infrared survey spectrum of P-99 vacuum bottoms dialysis residue.

Figure 5A. Infrared survey spectrum of Soxhlet extract of P-99 vacuum bottoms dialysis residue.

Figure 6A. Infrared survey spectrum of P-99 vacuum bottoms Soxhlet residue.

Figure 7A. Infrared spectra of clay minerals in coal.

Figure8A. Infrared survey spectra of base, acid, and neutral fractions of P-99 vacuum bottoms dialyzate.

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Figure 9A. Near-infrared spectra of base, acid, and neutral fractions of P-99 vacuum bottoms dialyzate.

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APPENDIX B. Mass Spectra

- Figure 1B. Nominal mass plot of observed ions in the low voltage high resolution mass spectrum of P-99 vacuum bottoms. Direct-probe introduction at 300°C.
- Figure 2B. Nominal mass plot of observed ions in the low voltage high resolution mass spectrum of the P-99 vacuum bottoms dialyzate. Direct-probe introduction at 200°C.
- Figure 3B. Nominal mass plot of observed ions in the low voltage high resolution mass spectrum of the P-99 vacuum bottoms dialyzate. Direct-probe introduction at 350°C.
- Figure 4B. Nominal mass plot of observed ions in the low voltage high resolution mass spectrum of the base fraction of the P-99 vacuum bottoms dialyzate. Heated-inlet introduction at 300°C.
- Figure 5B. Nominal mass plot of observed ions in the low voltage high resolution mass spectrum of the neutral fraction of the P-99 vacuum bottoms dialyzate. Heated-inlet introduction at 300°C.
- Figure 6B. Nominal mass plot of observed ions in the composite low voltage high resolution mass spectrum of the acid fraction of the P-99 vacuum bottoms. Direct-probe introduction at 350°C.
- Figure 7B. Field ionization mass spectrum of P-99 vacuum bottoms.
- Figure 8B. Field ionization mass spectrum of P-99 vacuum bottoms dialyzate.
- Figure 9B. Field ionization mass spectrum of bases from P-99 vacuum bottoms dialyzate.
- Figure 10B. Field ionization mass spectrum of neutrals from P-99 vacuum bottoms dialyzate.
- Figure 11B. Field ionization mass spectrum of acids from P-99 vacuum bottoms dialyzate.

Figure 1B. Nominal mass plot of observed ions in the low voltage high resolution mass spectrum of the P-99 vacuum bottoms. Direct-probe introduction at 300°C.

Figure 2B. Nominal mass plot of observed ions in the low voltage high resolution mass spectrum of the P-99 vacuum bottoms dialyzate. Direct-probe introduction at 200°C.

Figure 3B. Nominal mass plot of observed ions in the low voltage high resolution mass spectrum of the P-99 vacuum bottoms dialyzate. Direct-probe introduction at 350°C.

Figure 4B. Nominal mass plot of observed ions in the low voltage high resolution mass spectrum of the base fraction of the P-99 vacuum bottoms dialyzate. Heated-inlet introduction at 300°C.

Figure 5B. Nominal mass plot of observed ions in the low voltage high resolution mass spectrum of the neutral fraction of the P-99 vacuum bottoms dialyzate. Heated-inlet introduction at 300°C.

Figure 6B. Nominal mass plot of observed ions in the composition low voltage high resolution mass spectrum of the acid fraction of the P-99 vacuum bottoms. Direct-probe introduction at 350°C.

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Figure 7B. Field ionization mass spectrum of P-99 vacuum bottoms.

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Figure 8B. Field ionization mass spectrum of P-99 vacuum bottoms dialyzate.

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Figure 9B. Field ionization mass spectrum of bases from P-99 vacuum bottoms dialyzate.

Figure 10B. Field ionization mass spectrum of neutrals from P-99 vacuum bottoms dialyzate.

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Figure 11B. Field ionization mass spectrum of acids from P-99 vacuum bottoms dialyzate .

APPENDIX C. Nuclear Magnetic Resonance Spectra

- Figure 1C. Carbon-13 nuclear magnetic resonance spectrum (25.2 MHz) of the P-99 vacuum bottoms dialyzate.
- Figure 2C. Carbon-13 CP/MAS nuclear magnetic resonance spectra of the P-99 vacuum bottoms, dialyzate, and dialysis residue.
- Figure 3C. Proton nuclear magnetic resonance spectra (100 MHz) of P-99 vacuum bottoms, dialyzate, and Soxhlet extract of the dialysis residue.

Figure 1C. Carbon-13 nuclear magnetic resonance spectrum (25.2 MHz) of the P-99 vacuum bottoms dialyzate.

Figure 2C. Carbon-13 CP/MAS nuclear magnetic resonance spectra of the P-99 vacuum bottoms, dialyzate, and dialysis residue.

Figure 3C. Proton nuclear magnetic resonance spectra (100 MHz) of methylene chloride soluble fractions of P-99 vacuum bottoms in CD_2Cl_2 .

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APPENDIX D. Electron Spin Resonance Spectra

Figure 1D. Electron spin resonance spectra (9.5 GHz) of the P-99 vacuum bottoms, dialyzate, and dialysis residue.

Figure 1D. Electron spin resonance spectra (9.5 GHz) of P-99 vacuum bottoms, dialyzate, and dialysis residue.

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