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Reconfigured, Close-Coupled Reconfigured, and Wyodak Coal Integrated Two-Stage Coal Liquefaction Process Materials from the Wilsonville Facility: Chemical and Toxicological Evaluation

C. W. Wright

March 1987

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
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RECONFIGURED, CLOSE-COUPLED RECONFIGURED, AND WYODAK COAL INTEGRATED TWO-STAGE COAL LIQUEFACTION PROCESS MATERIALS FROM THE WILSONVILLE FACILITY: CHEMICAL AND TOXICOLOGICAL EVALUATION

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Pacific Northwest Laboratory
Richland, Washington 99352

FOREWORD

This document reports the results of the chemical analysis and toxicological testing of process materials sampled during the operation of the Advanced Coal Liquefaction Research and Development Facility (Wilsonville, AL) in the reconfigured, integrated (RITSL run #247), the close-coupled, reconfigured, integrated (CCRITSL run #249), and the Wyodak coal integrated (ITSL run #246) two-stage liquefaction operating modes. Chemical methods of analysis included proton nuclear magnetic resonance spectroscopy, adsorption column chromatography, high resolution gas chromatography, gas chromatography/mass spectrometry, and low-voltage probe-inlet mass spectrometry. Toxicological evaluation of the process materials included a histidine reversion assay for microbial mutagenicity, an initiation/promotion assay for tumorigenicity in mouse skin, and an aquatic toxicity assay using *Daphnia magna*. The results of these analyses and tests are compared to the previously reported results derived from the Illinois No. 6 coal ITSL and nonintegrated two-stage liquefaction (NTSL) process materials from the Wilsonville facility.

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EXECUTIVE SUMMARY

The chemical composition and toxicological activity of the coal liquefaction products and internal process stream materials from the reconfigured, integrated two-stage liquefaction (RITSL) process, the close-coupled, reconfigured, integrated two-stage liquefaction (CCRITSL) process, and the integrated two-stage liquefaction (ITSL) process using a sub-bituminous Wyodak coal as a feedstock have been evaluated as part of an effort to define the potential health effects of advanced coal liquefaction technology. All coal-derived liquids were produced at the Advanced Coal Liquefaction Research and Development Facility in Wilsonville, AL. The RITSL process configuration consisted of a first-stage thermal liquefaction unit followed by a second-stage hydrotreater unit with critical solvent deashing after the second-stage. The CCRITSL process was operated the same way as the RITSL process, except that no cooling down or heating up of products occurred prior to the second-stage in the close-coupled mode. Critical solvent deashing was prior to the second-stage hydrotreater reactor in the ITSL process.

Chemical analyses were performed using the following methods: proton nuclear magnetic resonance spectroscopy, adsorption column chromatography, high resolution gas chromatography, gas chromatography/mass spectrometry, and low-voltage probe-inlet mass spectrometry. Toxicological activity was determined using the standard histidine reversion microbial mutagenicity assay, an initiation/promotion mouse skin tumorigenicity assay, and a static bioassay with the freshwater invertebrate *Daphnia magna.*

Chemical analyses and mutagenicity testing of the RITSL and CCRITSL product and internal process stream coal liquids indicated there were generally no significant differences between the samples from the close-coupled versus the non-close-coupled configuration. There was, however, slight evidence of retrograde reactions occurring in the RITSL process as compared to the CCRITSL process probably due to the cooling down step in the former versus the latter process. The first-stage products of both processes had compositions generally higher in nitrogen-containing polycyclic aromatic compounds (NPAC) and hydroxy-substituted polycyclic aromatic hydrocarbons (hydroxy-PAH) and had compositions generally lower in aliphatic hydrocarbons (AH) and hydroaromatic hydrocarbons than did the second-stage products. These results corresponded to slightly increased mutagenic responses in the first-stage products versus the second-stage products. Increased tumorigenic response was also noted for the hydrotreater feed (a first-stage internal process stream coal liquid) versus the second-stage heavy distillate product. The coal liquids of higher boiling ranges (particularly the bottoms products) had increased NPAC and hydroxy-PAH contents with correspondingly decreased AH contents as compared to the lower boiling range materials from the same process.

The RITSL, CCRITSL, and ITSL (Wyodak) coal liquids all had the same major individual components present in their isolated fractions as have been identified in other two-stage direct coal liquefaction products, with their concentrations dependent upon the boiling range of the sample. All the coal liquids in the present study expressed low microbial mutagenic activities, also consistent with other two-stage liquefaction materials studied to date. The tumorigenicity of the CCRITSL heavy distillate product was the same as the tumorigenicities of comparable distillate products from the ITSL and nonintegrated two-stage liquefaction (NTSL) processes from the same pilot plant. Similar to other coal liquids, the aquatic toxicities of the RITSL distillate products were related to their water solubility, with the more water soluble coal liquid expressing increased acute toxicity to *Daphnia magna*.

Compared to the ITSL (Illinois No. 6) products, comparable ITSL (Wyodak) products were of a generally lower molecular weight range and had increased AH content and decreased hydroxy-PAH content.

ACKNOWLEDGMENTS

The Pacific Northwest Laboratory (PNL) received support for the chemical and toxicological analyses of advanced coal liquefaction process materials from the U.S. Department of Energy, Office of Fossil Energy under Contract DE-AC06-76RLO 1830. The process materials and engineering information from the reconfigured, close-coupled reconfigured, and Wyodak coal integrated two-stage liquefaction (RITSL, CCRITSL, and ITSL [Wyodak], respectively) modes of operation of the Advanced Coal Liquefaction Research and Development Facility (Wilsonville, AL) were provided by Catalytic, Inc., under subcontract to Southern Company Services, Inc. (Birmingham, AL).

CONTENTS

FIGURES

TABLES

LIST OF ABBREVIATIONS

α =statistical level of significance
AH = Aliphatic hydrocarbon(s)
amu = Atomic mass unit

CCRITSL =Close-coupled, reconfigured, integrated two-stage liquefaction
cm =Centimeter

D. =*Daphnia*
°C =Degrees Celsius
°F =Degrees Farenheit
DOE =U.S. Department of Energy
DMSO =Dimethylsulfoxide

eV =Electron volt(s)

FID =Flame ionization detector

g =Gram(s)
GC =Gas Chromatography
GC/MS =Gas Chromatography/mass spectrometry

h =hours
HP =Hewlett-Packard
HRGC =High resolution gas chromatography
hydroxy-PAH =Hydroxy-substituted polycyclic aromatic hydrocarbon(s)

ID =Inner diameter
I/P =Initiation/promotion
ISTD =Internal standard
ITSL =Integrated two-stage liquefaction

KM: =Refers to Wilsonville pilot plant location

L =Liter(s)
LC_{50} =Lethal concentration for 50% of the organisms
LVMS =Low-voltage probe-inlet mass spectrometry

m =meter(s)
mg =Milligram(s)
μg =Microgram(s)
min =Minute(s)
ml =Milliliter(s)
μl =Microliter(s)
mm =Millimeter(s)
μm =Micrometer(s)
MS =Mass spectrometry

ng =Nanogram(s)
nmr =Nuclear manetic resonance
No. =Number

NPAC	=Nitrogen-containing polycyclic aromatic compound(s)
NPD	=Nitrogen-phosphorus detector
NTSL	=Nonintegrated two-stage liquefaction
P-	=Refers to Wilsonville pilot plant location
PA_1	=Aliphatic hydrocarbon(s) fraction, picric acid-coated alumina separation
PA_2	=Hydroaromatic compound(s) fraction, picric acid-coated alumina separation
PA_3	=Dihydro-PAH and <three-aromatic-ringed PAH fraction, picric acid-coated alumina separation
PA_4	=>Three-aromatic-ringed PAH and some polar polycyclic aromatic compound(s) fraction, picric acid-coated alumina separation
PAC	=Polycyclic aromatic compound(s)
PAH	=Polycyclic aromatic hydrocarbon(s)
PNL	=Pacific Northwest Laboratory
ppm	=Parts per million
ppt	=Parts per thousand
rev	=Revertant(s)
RITSL	=Reconfigured integrated two-stage liquefaction
S.	=*Salmonella*
S9	=Metabolic enzyme system used in microbial mutagenicity assay
sec	=Second(s)
TA98	=Designation for strain of *Salmonella typhimurium* used in microbial mutagenicity assay
TC	=Total carbon
TIC	=Total ion current
TMS	=Tetramethyl silane
V	=Volt(s)
V-	=Refers to Wilsonville pilot plant location
VG	=Vacuum Generators
WSF	=Water soluble fraction(s)
Wt	=Weight
Wt %	=Weight percent

INTRODUCTION

The U.S. Department of Energy (DOE) has supported the chemical analysis and toxicological evaluation of coal liquefaction products to better define the potential health effects and industrial hygiene concerns of coal liquefaction technology. This research has been performed as a component of research and development into advanced coal liquefaction technology as a means of utilizing domestic supplies of coal to produce petroleum-substitute fuels. The purpose of this report is to present data from the chemical and toxicological characterization of products and internal process stream materials from three different configurations of the Advanced Coal Liquefaction Research and Development Facility in Wilsonville, AL. The three configurations of the pilot plant included the reconfigured, integrated two-stage liquefaction process (RITSL, run #247), the close-coupled, reconfigured, integrated two-stage liquefaction process (CCRITSL, run #249), and the integrated two-stage liquefaction process with a subbituminous Wyodak coal used as feedstock (ITSL, run #246). Results from the analyses of these process materials will be compared to the results obtained from ITSL process materials derived from a bituminous Illinois No. 6 coal reported by Later (1985). Evaluations of process considerations will be made for the following conditions: critical solvent deashing placement either prior to or after the second-stage hydrotreater reactor (ITSL versus RITSL process materials); close-coupled versus non-close-coupled mode (CCRITSL versus RITSL process materials); and feedstock coal rank (ITSL process materials derived from Illinois No. 6 versus Wyodak coals).

Chemical analyses were performed to determine the compositions of the materials produced from the different two-stage, direct coal liquefaction processes. Gross chemical compositional differences were determined by proton nuclear magnetic resonance (nmr) spectroscopy and fractionation using adsorption column chromatography. Fractions of aliphatic hydrocarbons (AH), polycyclic aromatic hydrocarbons (PAH), nitrogen-containing polycyclic aromatic compounds (NPAC), hydroxy-substituted PAH (hydroxy-PAH), and hydroaromatic compounds were among the chemical class fractions isolated from the RITSL, CCRITSL, and ITSL (Wyodak) products and internal process materials. Selected fractions were analyzed by high resolution gas chromatography (HRGC), gas chromatography/mass spectrometry (GC/MS), and low-voltage probe-inlet mass spectrometry (LVMS) to determine the qualitative and quantitative composition of the individual constituents present in the fractions.

Three toxicological assays were used on selected crude products and chemical class fractions to better identify the potential overall environmental hazard of the coal-derived liquids. Three assays were chosen since each one tends to be sensitive to the presence of particular classes of compounds. For example, microbial mutagenic activity of coal liquids generally predominates in the NPAC, particularly the amino-substituted PAH (Later *et al.* 1982, Wilson *et al.* 1980). The microbial mutagenicity of the RITSL, CCRITSL, and ITSL (Wyodak) coal-derived liquids was measured using the standard histidine reversion assay with *Salmonella* (*S.*) *typhimurium,* TA98. The tumor initiating activity was evaluated using the initiation/promotion (I/P) assay for mouse skin tumorigenicity. Generally, increased tumorigenicity has been noted to correspond to increased boiling range and increased PAH content of coal liquids (Wright *et al.* 1985). The ecotoxicity of the water-soluble fractions (WSF) of two RITSL distillate products was evaluated using a static bioassay with *Daphnia* (*D.*) *magna.* The toxicological properties of the coal liquids' WSF mainly reflect the presence of highly soluble phenolic constitutents (Dauble *et al.* 1982, 1983).

ENGINEERING AND SAMPLES

A schematic diagram of the RITSL and CCRITSL processes is shown in Figure 1. Briefly, these direct coal liquefaction processes consisted of a first-stage ebullated bed thermal liquefaction unit followed by a second-stage hydrotreater unit with critical solvent deashing after the second-stage. Sample locations are enumerated in the figure and refer to the descriptions and sample numbers given in Table 1. Both the Pacific Northwest Laboratory (PNL) identification numbers and the Wilsonville pilot plant identification numbers are given for all samples. The RITSL samples were from run #247 of the Wilsonville pilot plant. The CCRITSL samples were from run #249 of the same plant. Both runs were with bituminous Illinois No. 6 coal. The operating conditions of the CCRITSL process were the same as the RITSL process, except the former was run in the close-coupled mode with no cooling down or heating up of products prior to the second-stage. The ITSL (Wyodak) samples were from run #246 of the Wilsonville pilot plant operated in the ITSL mode using a sub-bituminous Wyodak coal. In this mode, the critical solvent deashing step was after the first-stage reactor and prior to the second-stage reactor. The analyses of ITSL products and a description of the process conditions when using a bituminous Illinois No. 6 coal as feedstock were given by Later (1985). All samples studied were from pilot plant origin, and, as such, may not be considered to be representative of commercial products.

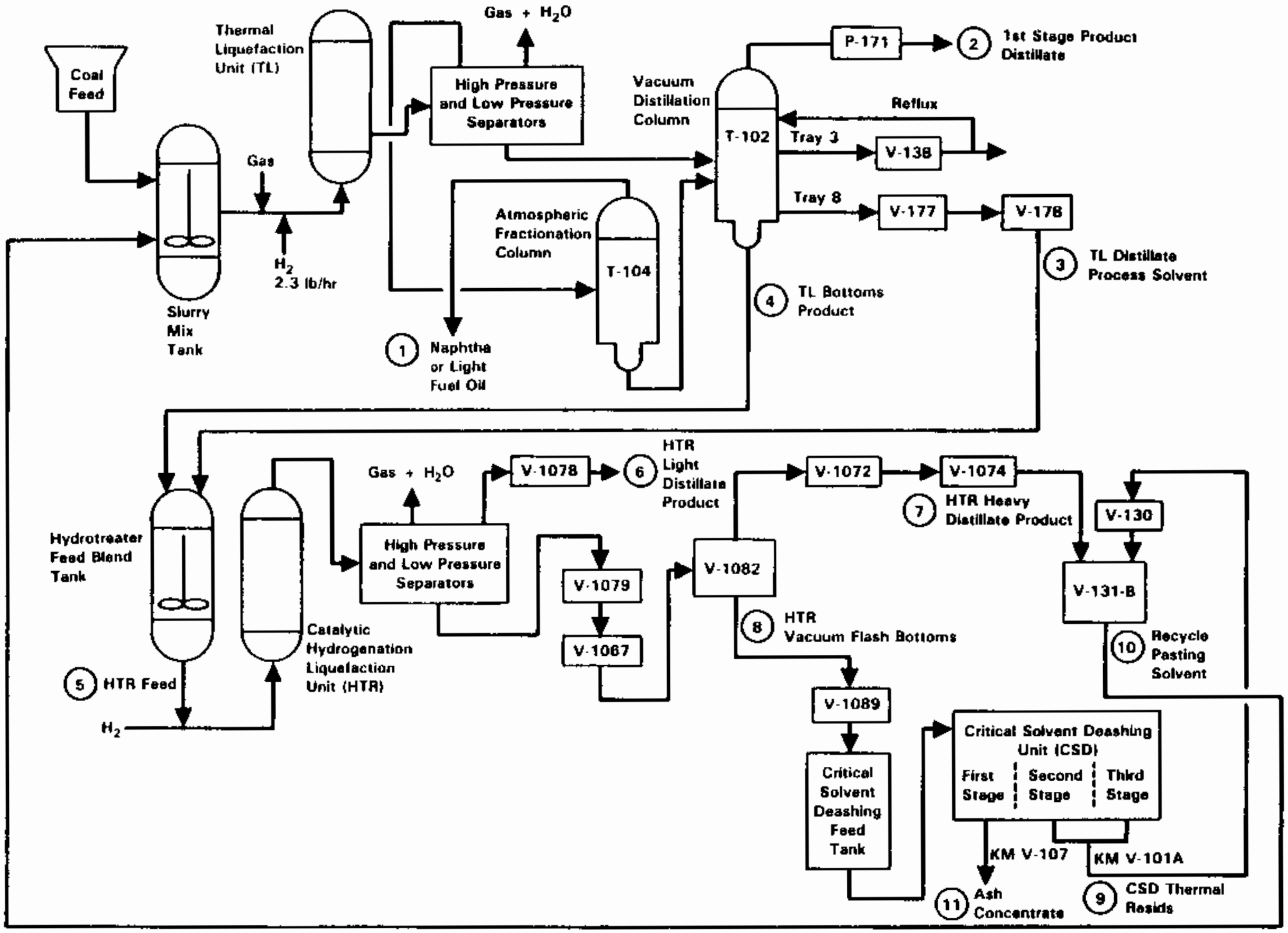

FIGURE 1. Schematic Diagram of the Reconfigured, Integrated Two-Stage Coal Liquefaction Process. Circled Numbers Represent Sampling Locations. Samples are Described in Table 1 for the Reconfigured, Close-Coupled Reconfigured, and Wyodak Coal Integrated Two-Stage Liquefaction Processes. P-, T-, and KM- Numbers Refer to Pilot Plant Identifications.

TABLE 1. Reconfigured, Integrated Two-Stage Coal Liquefaction Sample Descriptions

		PNL Number (50378-); Pilot Plant Number		
No.[a]	Sample Description	RITSL Run #247[b]	CCRITSL Run #249[c]	ITSL (Wyodak) Run #246[d]
1	Naphtha or Light Fuel Oil; T-104; V-170; Overheads	-093; 40688	-136; 53483	
2	First-Stage Distillate Product; T-102, P-171; Overheads	-094; 40690	-135; 53481	-111; 35582
3	Thermal Liquefaction Unit Distillate Process Solvent; T-102; Tray 8; V-178	-095; 40689	-137; 53485	
4	Thermal Liquefaction Unit Product; T-102; Bottoms	-096; 40691	-142[e]; 53501 -143[f]; 53512	
5	Hydrotreater Unit Feed; V-1064; Blend Tank	-097; 40692	-146; 53489 -147[g]; 53522	-112; 35579
6	Hydrotreater Unit Light Distillate Product; V-1078; <500°F	-098; 40693	-148; 53492 -149[h]; 53608	-113; 34370
7	Hydrotreater Unit Heavy Distillate Product; V-1074; >500°F, Less Resids and Ash	-100; 40694 -101; 40695	-139[i]; 53491	
8	Hydrotreater Unit Vacuum Flash Bottoms; V-1082; Resids and Ash; Critical Solvent Deashing Feed	-099; 40696	-144[e]; 53497 -145[f]; 53456	

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[a] Numbers refer to sampling points shown in Figure 1

[b] Sampled 11/13/84

[c] Sampled 8/20/85 unless otherwise noted

[d] Sampled between 6/13/84 and 8/8/84

[e] Sampled at 1500 hours

[f] Sampled at 2300 hours

[g] Sampled 8/21/85

[h] Sampled 8/22/85

[i] Sampling point V-1072

TABLE 1. Continued

No.[a]	Sample Description	RITSL Run #247[b]	CCRITSL Run #249[c]	ITSL (Wyodak) Run #246[d]
		PNL Number (50378-); Pilot Plant Number		
9	Critical Solvent Deashing Thermal and Light Thermal Resids; KM: V-101A	-102; 40698	-140[e]; 53517 -141[f]; 52504	
10	Recycle Pasting Solvent; V-131B; Blend of 7 and 9	-103; 40699	-138; 53486	-114; 35591
11	Critical Solvent Deashing Ash Concentrate; KM: V-107	-104; 40697	-150[g]; 53514 -152[h]; 53510	

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[a] Numbers refer to sampling points shown in Figure 1

[b] Sampled 11/13/84

[c] Sampled 8/20/85 unless otherwise noted

[d] Sampled between 6/13/84 and 8/8/84

[e] Sampled at 0330 hours

[f] Sampled at 1630 hours

[g] Sampled 1500 hours

[h] Sampled 2300 hours

METHODS

CHEMICAL ANALYSIS

Proton Nuclear Magnetic Resonance Spectroscopy

Proton nmr spectra were obtained on a Varian XL-300 instrument for the crude RITSL and CCRITSL heavy distillate products. Aliquots of the crudes were dissolved in about 20 µl of deuterated chloroform and sealed in 1.7-mm capillary tubes. Chemical shifts are reported in parts per million (ppm) with respect to tetramethylsilane (TMS).

Adsorption Column Chromatography

Alumina

All RITSL, CCRITSL, and ITSL (Wyodak) samples were fractionated by chemical class according to the method described by Later *et al.* (1981) and Later and Lee (1983). Approximately 100 mg were sequentially eluted from standardized alumina (1.5% H_2O; Later, Wilson and Lee 1985) with 20 ml hexane, 50 ml benzene, 70 ml chloroform:ethanol (99:1 v:v), and 50 ml methanol. The chemical class fractions produced were AH, PAH, NPAC, and hydroxy-PAH. The weight percent contribution of each fraction was determined gravimetrically. The critical solvent deashing ash concentrates were solvent extracted in a Soxhlet extractor for 24 h with approximately 180 ml benzene:methanol (3:1 v:v). The dried and weighed extracts were then separated on neutral alumina as above. The organic extractables in the ash were approximately 25% by weight.

Picric-Acid-Coated Alumina

The hydroaromatic compounds were isolated from the RITSL and CCRITSL hydrotreater feeds, heavy distillate products, and recycle pasting solvents using a layered adsorption column of 15% picric-acid-coated alumina over alumina as described by Wozniak and Hites (1983). Samples were sequentially eluted with 10 ml hexane to obtain the AH (PA_1), 40 ml methylene chloride:hexane (3:97) to obtain the hydroaromatic compounds (PA_2), 30 ml methylene chloride:hexane (3:17) to obtain the dihydro-PAH and <three-aromatic-ringed PAH (PA_3), and 25 ml benzene to obtain the >three-aromatic-ringed PAH and some polar compounds (PA_4). The weight percent contribution of each fraction was determined gravimetrically.

High Resolution Gas Chromatography (HRGC)

The AH, PAH, NPAC, and PA_2 fractions isolated from the RITSL, CCRITSL, and ITSL (Wyodak) coal liquids were analyzed at 5.0 mg/ml dilutions in benzene (unless otherwise noted) by HRGC using a Hewlett-Packard (HP; Avondale, PA) 5880A gas chromatograph equipped with a 15- or 30-m x 0.25-mm-ID fused silica capillary column coated with 0.25-µm film thickness DB-5 (J & W Scientific, Folsom, CA). The oven was temperature-programmed to 300°C at 3 or 4°C/min after 2 min isothermal at 50°C. Splitless injection was used with helium as the carrier gas at 50 cm/sec linear velocity. The injection port and flame ionization detector (FID) were operated at 275 and 300°C, respectively. Components were identified by retention index (Lee *et al.* 1979; Vassilaros *et al.* 1982), absolute retention times of standard compounds, and/or GC/MS data. Selected components of the PAH and NPAC fractions were quantified according to the external standard calibration method outlined by Wilson *et al.* (1984) using 2-chloroanthracene as an internal standard (ISTD). Response factors (amount/area) were calculated from standard compounds chromatographed at eight concentration levels, ranging over two orders of magnitude. The response factor of a closely eluting or similar compound was used to quantify components for which standards were not available. PAH and NPAC fractions were analyzed at 10.0, 5.00, and 2.50 mg/ml with averaged results and standard deviations of the mean for selected components reported in parts per thousand (ppt) for each particular fraction. When no quantitative values are reported, either no data was collected or none was detected above approximately 25 ppm in a particular fraction. PAH and NPAC fractions were futher monitored for the presence of nitrogen-containing components by simultaneous injection onto two 15-m x 0.25-mm-ID fused silica columns coated with 0.25 µm film thickness bonded methyl (5% phenyl) silicone gum (Quadrex Corp., New Haven, CT) according to the method of Wright (1984). One column was connected to the universal FID, while the other column was connected to the nitrogen-specific nitrogen-phosphorus detector (NPD).

Gas Chromatography/Mass Spectrometry (GC/MS)

GC/MS analyses were performed on an HP-5985 quadrupole mass spectrometer interfaced with an HP-5840 gas chromatograph equipped with a 15-m x 0.25-mm-ID DB-5 fused silica capillary coumn (J & W Scientific, Folsom, CA). Gas chromatographic conditions were similar to those previously described for the HRGC analyses, except that the oven was temperature-programmed at 8°C/min. The MS was operated in the electron impact mode at 70 eV, and scan rates were typically 100 atomic mass units/sec (amu/sec). AH, PAH, NPAC, and PA_2 fractions isolated from the RITSL, CCRITSL, and ITSL (Wyodak) coal liquids were analyzed.

Low-Voltage Probe-Inlet Mass Spectrometry

The PAH, NPAC, and hydroxy-PAH chemical class fractions isolated from the coal liquefaction materials were analyzed by LVMS using a Vacuum Generators (VG; Manchester, England) ZAB 2-F double-focusing mass spectrometer operated in the electron impact mode with ionizing electron energies of 10-12 eV. Each sample (10 to 20 µg) was loaded into a glass capillary tube, which was then inserted into the source affixed to the end of a direct insertion probe. The probe was heated in a linear fashion from ambient to 250-280°C while the mass spectrometer scanned repeatedly throughout the desorption period. The ZAB 2-F was operated with an accelerating voltage of 6000 or 7000 V, a magnet scan rate of 2 to 3 sec/mass decade, a source temperature of 250°C, and a dynamic resolving power (as determined by the VG 2035 data system) of 1:2000. The intensities of each mass across the entire profile were summed, generating an average spectrum that was representative of the entire sample. Average spectra were composed primarily of signals representing molecular ions rather than fragments or doubly charged ions, due to the low ionization voltage.

TOXICOLOGICAL ASSAYS

Microbial Mutagenicity

Standard agar-plate mutagenicity assays were performed as described by Ames, McCann and Yamasaki (1975) using *S. typhimurium*, TA98 microbial tester strain with optimized levels of Aroclor-induced rat liver (S9) homogenate metabolic activation. Dimethylsulfoxide (DMSO) was used as the solvent. Revertant colonies per petri plate were counted electronically using a Biotran II automated colony counter. The specific mutagenic activities of the crudes and chemical class fractions isolated by alumina column chromatography are expressed as revertant colonies of *S. typhimurium*, TA98 per µg of test material (rev/µg), as estimated by linear regression analysis of dose-response data. The following criteria were used for selecting the best dose range for estimating a linear dose response: at least a four-point dose range; approximate doubling of response for doubled dose concentration; a correlation coefficient of 0.8 or greater; and an intercept on the response (ordinate) axis within 20% of the negative control for the day.

Initiation/Promotion Tumorigenicity Assay

The I/P mouse skin tumorigenicity assays were performed on the CCRITSL hydrotreater feed and heavy distillate product as described by Mahlum (1983) using female CD-1 mice (Charles River Laboratories, Portage, MI), approximately 6 to 8 weeks of age. The animals were housed five per cage on standard bedding material with food and water available *ad libitum* . Prior to administration of test materials, the animals were ear-tagged for unique identification, weighed, shaved, and assigned to a test group, 30 animals per group. One g of each test material was diluted to a total volume of 2.0 ml with methylene chloride, and 50 µl of the diluted material were applied to the shaved backs of the mice (approximately 25 mg dose per mouse). Two weeks after initiation, 5-µg doses of phorbol myristate acetate (0.1 mg/ml acetone) were applied to the initiated area, twice weekly for 24 weeks. The mice were shaved as necessary throughout the study, usually weekly. Animals were observed regularly for tumor growth, and the number of tumors per animal was counted biweekly. The data are expressed as the total number of tumors per group of 30 mice, the mean number of tumors per mouse ± standard deviation normalized to groups of 30 mice, and as the percent incidence.

Aquatic Toxicity

Aquatic toxicities of the water-soluble fractions (WSF) derived from the RITSL light and heavy distillate products (50378-098 and -101, respectively) were determined by conducting static bioassays with the freshwater invertebrate *D. magna*. All tests were conducted at 20°C with a 16:8-hour, light:dark cycle. The test consisted of placing five first-instar *D. magna* in each of four 100-ml-capacity glass jars at six treatment levels, plus a control (4 x 7 test matrix, 20 organisms per treatment level).

The WSF were generated by adding 100 ml of each of the light and heavy distillate products to ten L of well water (1:100 ratio) in a 15-L-capacity glass carboy. The mixture was stirred at 90 rpm with a teflon-coated rod for 4 hours. After a one hour settling period, approximately eight L of the WSF were siphoned from the center of the carboy, chemically analyzed, and used for bioassays. Exposure solutions for testing were made by diluting the WSF with well water.

Total carbon (TC) of the WSF was determined by direct aqueous injection into a Beckman 915B carbon analyzer. Detailed chemical analysis of the WSF by gas chromatography was conducted to determine phenol composition according to methodology outlined by Dauble *et al.* (1982, 1983). Total nitrogen base concentrations were determined by HRGC with a NPD (Thomas, 1984).

Paired tests were conducted one week apart using a WSF from each of the RITSL light and heavy distillate products. The 48 hour LC_{50} (lethal concentration for 50% of the organisms) values were determined by the graphical method (APHA 1980). Toxicity thresholds are expressed as percent WSF and as TC, based on dilution of measured stock solution.

RESULTS AND DISCUSSION

CHEMICAL ANALYSES

Proton Nuclear Magnetic Resonance Spectroscopy

Proton nmr spectra of the RITSL and CCRITSL heavy distillate products are shown in Figure 2. The percent hydrogen in five chemical shift regions are labeled in the figure. The general types of hydrogen characterized by the designated chemical shift regions are as follows: 0.5-1.0 ppm, paraffinic CH_3 or CH_3 γ or further from an aromatic ring; 1.0-1.5 ppm, paraffinic CH_2; 1.5-3.5 ppm, hydroaromatic; 6.5-7.5 ppm, aromatic; and 7.5-8.5 ppm, phenolic or hydrogen on aromatic nitrogen. The proton nmr spectra of the RITSL and CCRITSL heavy distillate products were similar to each other. Roughly 88% of both products contained aliphatic or hydroaromatic protons, with the other 12% represented by aromatic protons or hydrogens on polar molecules. The ITSL distillation column bottoms (comparable product of the ITSL process) gave similar nmr results as those shown in Figure 2. Aliphatic or hydroaromatic protons accounted for 89% of the ITSL product (0.5-1.0 ppm, 18.0%; 1.0-1.5 ppm, 33.2%; 1.5-3.5 ppm, 37.9%); aromatic protons (6.5-7.5 ppm, 9.0%) and hydrogens on polar molecules (7.5-8.5 ppm, 1.9%) accounted for 11% of the ITSL product.

Adsorption Column Chromatography

The results of the alumina column chromatographic separation of the RITSL, CCRITSL, and ITSL (Wyodak) first-stage coal-derived materials are given in Table 2. Low total recoveries of the naphtha or light fuel oil samples were due to the highly volatile nature of these materials. Better total recoveries (approximately 80-100%) were achieved for the other first-stage samples studied. Higher concentrations of AH were present in the lower boiling first-stage overhead product distillates and distillate process solvents as compared to the higher boiling hydrotreater unit feed and first-stage bottoms product; in addition, generally lower concentrations of NPAC and hydroxy-PAH were present in the former versus the latter products. These results were consistent with those of other coal liquids which showed decreased AH content and increased NPAC and hydroxy-PAH content corresponding to higher boiling range of the product (Wright *et al.* 1985; Later *et al.* 1982). The chemical compositions of the RITSL and CCRITSL first-stage products were generally comparable to each other, with the largest variations occurring in the first-stage overhead product distillates. Differences between the compositions of these two materials may also be a function of the highly volatile nature of these particular samples, since wide variations in total recoveries were noted.

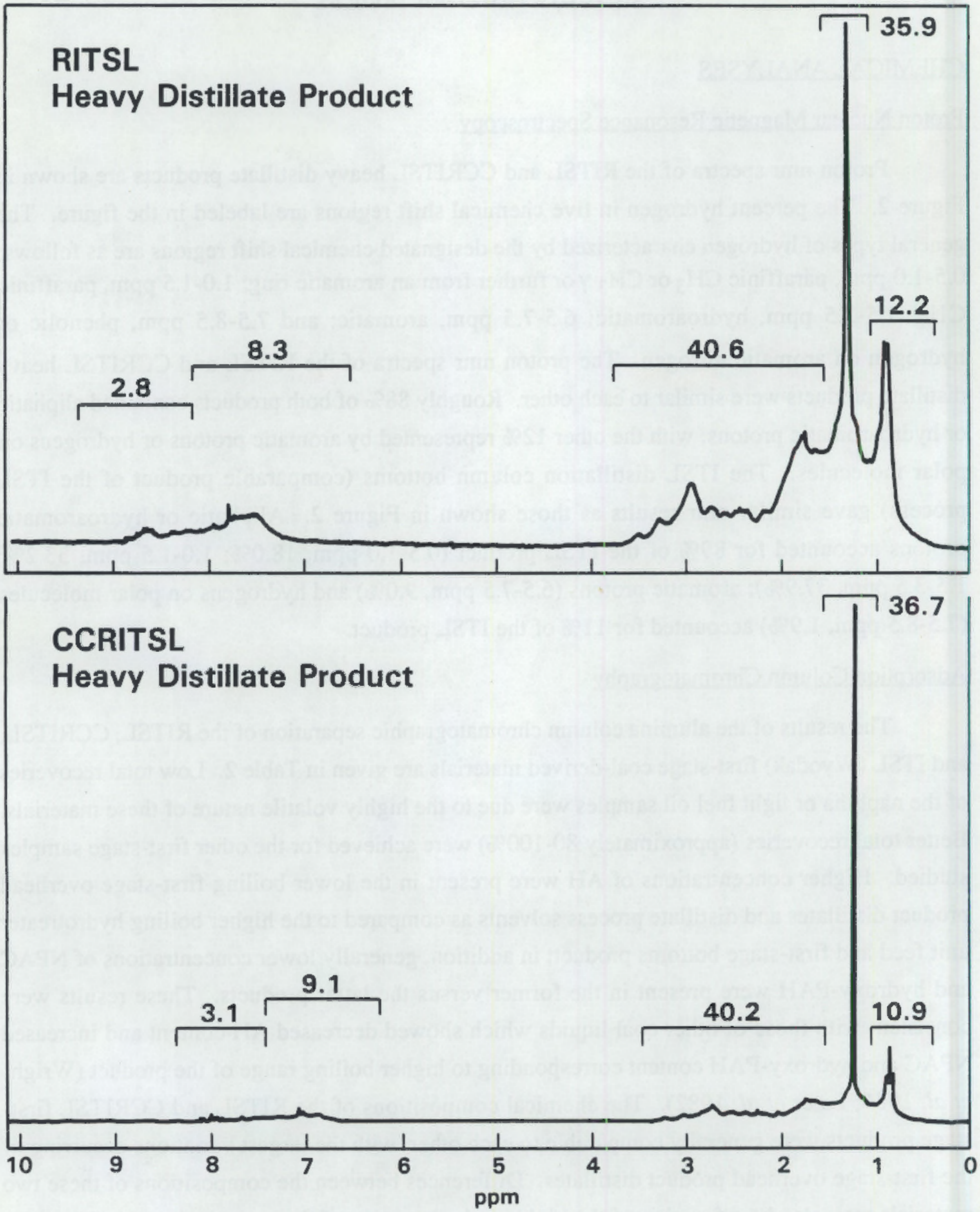

FIGURE 2. Proton Nuclear Magnetic Resonance Spectra of the Heavy Distillate Products from the Reconfigured, Integrated Two-Stage Liquefaction (RITSL; top) and the Close-Coupled RITSL (bottom) Processes. Percent Composition for Five Proton Regions are Given in Brackets. See Text for Explanation.

TABLE 2. Chemical Class Composition of Reconfigured, Integrated Two-Stage Liquefaction First-Stage Coal-Derived Products

			Chemical Class Fraction; Weight Percent[a]				
Sample Description	PNL Number	Process	AH	PAH	NPAC	Hydroxy-PAH	Total
Naphtha or Light Fuel Oil; T-104; Overheads	50378-093	RITSL	24	0.95	0.80	5.7	31
	50378-136	CCRITSL	19	1.0	0.35	2.0	22
First Stage Product Distillate; T-102; P-171; Overheads	50378-094	RITSL	57	8.8	4.7	18	88.5
	50378-135	CCRITSL	44	8.2	1.6	8.0	62
	50378-111	ITSL (Wyodak)	52	9.1	12.5	2.2	76
Thermal Liquefaction Unit Distillate Process Solvent; T-102; Tray 8	50378-095	RITSL	47	39	6.0	6.9	99
	50378-137	CCRITSL	42	34	3.9	7.4	87
Thermal Liquefaction Unit Product; T-102; Bottoms	50378-096	RITSL	4.9	30	29	15	79
	50378-142	CCRITSL	6.0	29	27	14	76
Hydrotreater Unit Feed; V-1064; Blend Tank	50378-097	RITSL	18	34	23	15	90
	50378-146	CCRITSL	22	33	16	12	83
	50378-112	ITSL (Wyodak)	27	45.5	19.5	8.3	100

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[a] Average of two determinations

The chemical class compositions of the second-stage RITSL, CCRITSL, and ITSL (Wyodak) samples are given in Table 3. The RITSL and CCRITSL products showed similar compositions to each other with the exception of the recycle pasting solvents. The recycle pasting solvent from the RITSL process had a decreased AH content and increased NPAC and hydroxy-PAH contents as compared to the same product from the CCRITSL process (see next paragraph for discussion). The light distillate products showed slightly increased AH and decreased NPAC content compared to the heavy distillate products. Hydroxy-PAH contents were the same for these two products. The vacuum flash bottoms had significantly lower AH and significantly higher NPAC and hydroxy-PAH content than did either the light or heavy distillate product, showing the familiar correlation of decreased AH content and increased heteroatom content with increased boiling temperature of the coal liquefaction product. Compared to the first-stage distillate products, the second-stage distillate products had generally increased concentrations of AH and slightly decreased concentrations of NPAC and hydroxy-PAH, indicating increased formation of saturates and hydroaromatic compounds as well as increased heteroatom removal in the second-stage hydrotreater compared to the first-stage thermal liquefaction unit.

The results of the chemical class fractionation on neutral alumina were different for the critical solvent deashing thermal resid products from the RITSL and CCRITSL processes (Table 4). The RITSL thermal resid product had significantly higher heteroatom-containing fraction compositions and lower AH composition than did the same CCRITSL product. This difference in the thermal resid products' compositions probably accounts for the different compositions noted above for the RITSL and CCRITSL recycle pasting solvents, since the latter was a blend of the former and heavy distillate product. This difference in RITSL and CCRITSL products gives slight evidence that some retrograde reactions may have occurred during the cooling down step after the first-stage thermal reactor in the RITSL process, which lead to less efficient heteroatom removal in the second-stage reactor (as compared to the CCRITSL process which had no intermediate cooling down step). More comparable fractionation results than those of the thermal resid products were achieved for the RISTL and CCRITSL critical solvent deashing ash concentrates, data also given in Table 4. AH composition was generally low, and heteroatom composition was generally high in the critical solvent deashing products compared to the first- and second-stage products.

Chemical class fractionation data for the following ITSL and NTSL products were reported by Later (1985): first-stage) overhead product distillate, distillate process solvent (ITSL only), and hydrotreater unit feed (which was deashed prior to the second-stage hydrotreater); second-stage) light fuel oil, distillation column bottoms, vacuum flash bottoms (NTSL only),

TABLE 3. Chemical Class Composition of Reconfigured, Integrated Two-Stage Liquefaction Second-Stage Coal-Derived Products

			Chemical Class Fraction; Weight Percent[a]				
Sample Description	PNL Number	Process	AH	PAH	NPAC	Hydroxy-PAH	Total
Hydrotreater Unit Light Distillate Product; V-1078; <500°F	50378-098	RITSL	67	6.2	1.6	2.7	78
	50378-148	CCRITSL	70	10	1.2	2.0	83
	50378-113	ITSL (Wyodak)	58	11	5.1	3.9	78
Hydrotreater Unit Heavy Distillate Product; V-1074; >500°F (Less Resids and Ash)	50378-100	RITSL	58	36	4.6	2.0	101
	50378-101	RITSL	57	39	4.4	2.4	103
	50378-139[b]	CCRITSL[b]	60	43	5.4	4.0	112
Hydrotreater Unit Vacuum Flash Bottoms (Resids and Ash); V-1082; Critical Solvent Deashing Feed	50378-099	RITSL	3.0	32.5	26	6.8	68
	50378-144	CCRITSL	3.6	37	28	7.9	76.5
Recycle Pasting Solvent ; V-131B	50378-103	RITSL	33	40	20	7.2	100
	50378-138	CCRITSL	41	44	11	1.6	98
	50378-114	ITSL (Wyodak)	27	44	23	6.4	100

---

[a] Average of two determinations

[b] V-1072

TABLE 4. Chemical Class Composition of Reconfigured, Integrated Two-Stage Liquefaction Critical Solvent Deashing Coal-Derived Products

Sample Description	PNL Number	Process	Chemical Class Fraction; Weight Percent[a]				
			AH	PAH	NPAC	Hydroxy-PAH	Total
Critical Solvent Deashing Thermal Resids[b]; KM: V-101-A	50378-102	RITSL	5.2	50	35	11	101
	50378-141	CCRITSL	25	25	8.8	5.4	64
Critical Solvent Deashing Ash Concentrate; KM: V-107	50378-104	RITSL	0.3	19	31	9.6	60
	50378-150	CCRITSL	1.6	35	30	9.0	76

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[a] Average of two determinations

[b] Blend of thermal and light thermal resids

and recycle solvent (ITSL only); and critical solvent deashing) ash concentrate. All the ITSL and NTSL samples had higher concentrations of hydroxy-PAH compared to their RITSL and CCRITSL counterparts. Most of the RITSL and CCRITSL had higher concentrations of AH compared to the ITSL and NTSL samples. Direct comparisons of ITSL, NTSL, RITSL, and CCRITSL materials are difficult to make since the nominal boiling ranges of the products of the ITSL and NTSL processes were not necessarily the same as those of the RITSL and CCRISTL products.

All four ITSL (Wyodak) coal liquefaction process materials (Tables 2 and 3) had higher concentrations of AH (indicative of the decreased aromatic character of sub-bituminous versus bituminous coals) and lower concentrations of hydroxy-PAH compared to their ITSL (Illinois No.6) counterparts (Later 1985). PAH and NPAC compositions were not consistently higher or lower for the Wyodak coal-derived samples versus the Illinois No. 6 coal-derived samples (see Later 1985). Previous analyses of EDS and H-Coal products derived from both bituminous and sub-bituminous coals indicated the bituminous coal-derived products had higher PAH, NPAC, and hydroxy-PAH content and lower AH content than did the sub-bituminous coal-derived products (Wright and Dauble 1986). The ITSL materials showed some of the same characteristics.

The hydroaromatic compositions (as determined by picric-acid-doped alumina column chromatography) of selected RITSL and CCRITSL process materials are given in Table 5. For those RITSL and CCRITSL products studied, nearly comparable fractionation results were achieved. Both hydrotreater heavy distillate products had significantly higher concentrations of aliphatic hydrocarbons (fraction PA_1) and hydroaromatic compounds (fraction PA_2) compared to their respective hydrotreater feeds. The recycle pasting solvents had PA_1 and PA_2 compositions intermediate to both the hydrotreater feed andthe heavy distillate products. The RITSL recycle pasting solvent had lower PA_1 and PA_2 compositions than did the same CCRITSL product, a results that was consistent with the alumina column fractionation results of Table 3. Both the hydrotreater feeds and heavy distillate products from the RITSL and CCRITSL processes had comparable PA_1 and PA_2 compositions to their respective ITSL counterparts (see Later 1985). The RITSL and CCRITSL materials had significantly higher PA_1 and PA_2 compositions compared to NTSL process materials, however, as was the case with the ITSL materials.

HRGC and GC/MS

A representative high resolution gas chromatogram of an AH fraction isolated from a CCRITSL coal liquefaction material is shown in Figure 3. The major components of this fraction for all the RITSL, CCRITSL, and ITSL (Wyodak) were the straight-chained aliphatic hydrocarbons, as labeled in the figure with the number of carbon atoms. Different ranges of

TABLE 5. Hydroaromatic Composition of Selected Reconfigured, Integrated Two-Stage Coal Liquefaction Process Materials

			Picric Acid Fraction; Weight Percent[a]				
Sample Description	PNL Number	Process	PA$_1$[b]	PA$_2$[c]	PA$_3$[d]	PA$_4$[e]	Total
Hydrotreater Unit Feed; V-1064; Blend Tank	50378-097	RITSL	13	9.4	9.6	15	47
	50378-146	CCRITSL	19	13	8.1	16	56
Hydrotreater Unit Heavy Distillate Product; V-1074; >500°F (Less Resids and Ash)	50378-100	RITSL	43	31	12	7.0	93
	50378-101	RITSL	45	32.5	13	12	102.5
	50378-139[f]	CCRITSL[f]	48.5	34	12	9.6	104
Recycle Pasting Solvent ; V-131B	50378-103	RITSL	22.5	18	12	17	69.5
	50378-138	CCRITSL	29	29	11	21	90

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[a] Average of two determinations

[b] Aliphatic hydrocarbons

[c] Hydroaromatic compounds

[d] Dihydro-PAH and <three-aromatic-ringed PAH

[e] >Three-aromatic-ringed PAH and some polar PAC

[f] V-1072

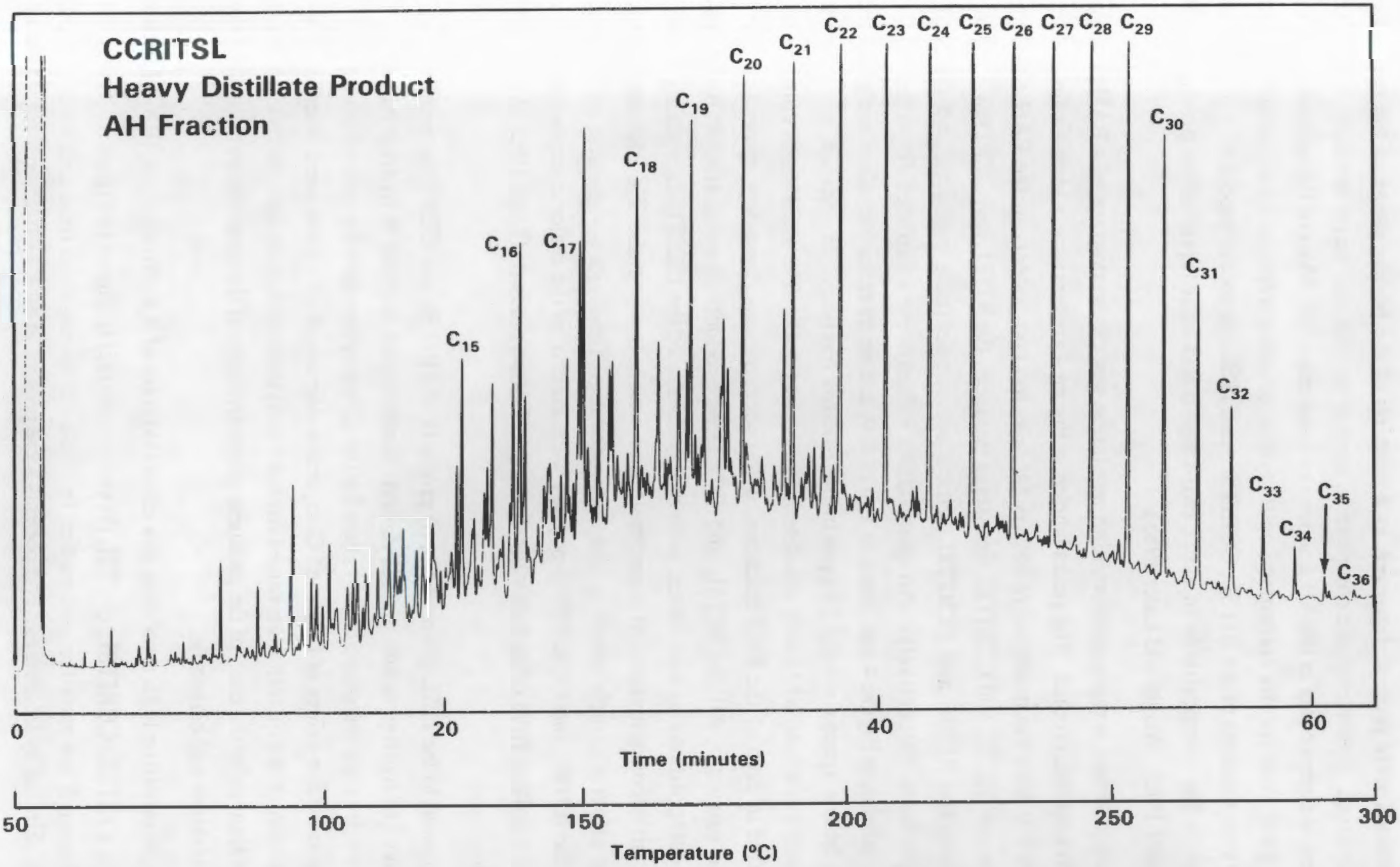

FIGURE 3. High Resolution Gas Chromatogram of the Aliphatic Hydrocarbon Fraction Isolated from the Close-Coupled, Reconfigured, Integrated Two-Stage Liquefaction Heavy Distillate Product. Straight-Chained Hydrocarbons are Labeled with Their Number of Carbon Atoms. See Text for Conditions.

these compounds were present, however, as a function of the boiling range of the particular product of interest. Hydroaromatic compounds, such as tetralin and methyltetralins, were also present as major components in the AH fractions of these materials. Most of the unlabeled peaks of Figure 3 gave mass spectra corresponding to hydroaromatic compounds such as those listed above. The compositions of the RITSL, CCRITSL, and ITSL (Wyodak) products' AH fractions were similar to the compositions of other two-stage direct coal liquefaction products' AH fractions (Later 1985; Wright and Later 1985).

Figure 4 shows a representative high resolution gas chromatogram of a PAH fraction isolated from a RITSL product. The peaks labeled in Figure 4 are tentatively identified in Tables 6-9. Tables 6-9 give the quantitative results for selected components in the PAH fractions isolated from the RITSL and CCRITSL first-stage products, the RITSL and CCRITSL second-stage products, the RITSL and CCRITSL critical solvent deashing products, and the ITSL (Wyodak) products, respectively. No quantitative values were calculated for some of the components labeled in Figure 4 and listed in Tables 6-9, and no quantitative values are given for components below approximately 25 ppm in the isolated fractions. In addition, no standard deviations were calculated when only one determination was made. The same major components were identified in each of the PAH fractions, with concentrations dependent upon the boiling range of the product. All the RITSL and CCRITSL products showed similar individual component compositions to each other, with the exception of the CCRITSL products having increased relative concentrations of lower molecular weight compounds. This difference may have been an effect of sample handling, and not processing. The major components of the PAH fraction of the RITSL and CCRITSL processes were similar to the major components of the PAH fractions isolated from other two-stage direct liquefaction products (Later 1985; Wright and Later 1985).

Compared to the ITSL (Illinois No. 6) products, the RITSL and CCRITSL products had similar degrees of hydrogenation and alkylation. Comparable degrees of hydrogenation were determined by dividing the quantitative values for the dihydrophenalene by each of the products' respective quantitative values of fluorene. Comparable degrees of alkylation were determined by dividing the sum of the quantitative values for the methylphenanthrenes and methylcarbazoles (data not yet shown) by the each of the products' respective sum of the quantitative values for the parent phenanthrene and carbazole.

A representative high resolution gas chromatogram of a hydroaromatic (PA_2) fraction isolated from a RITSL, CCRITSL, or ITSL (Wyodak) product is shown in Figure 5. The peaks labeled in Figure 5 are tentatively identified in Table 10 by retention time and mass spectral information. Similar hydroaromatic components were present in all PA_2 fractions, regardless of

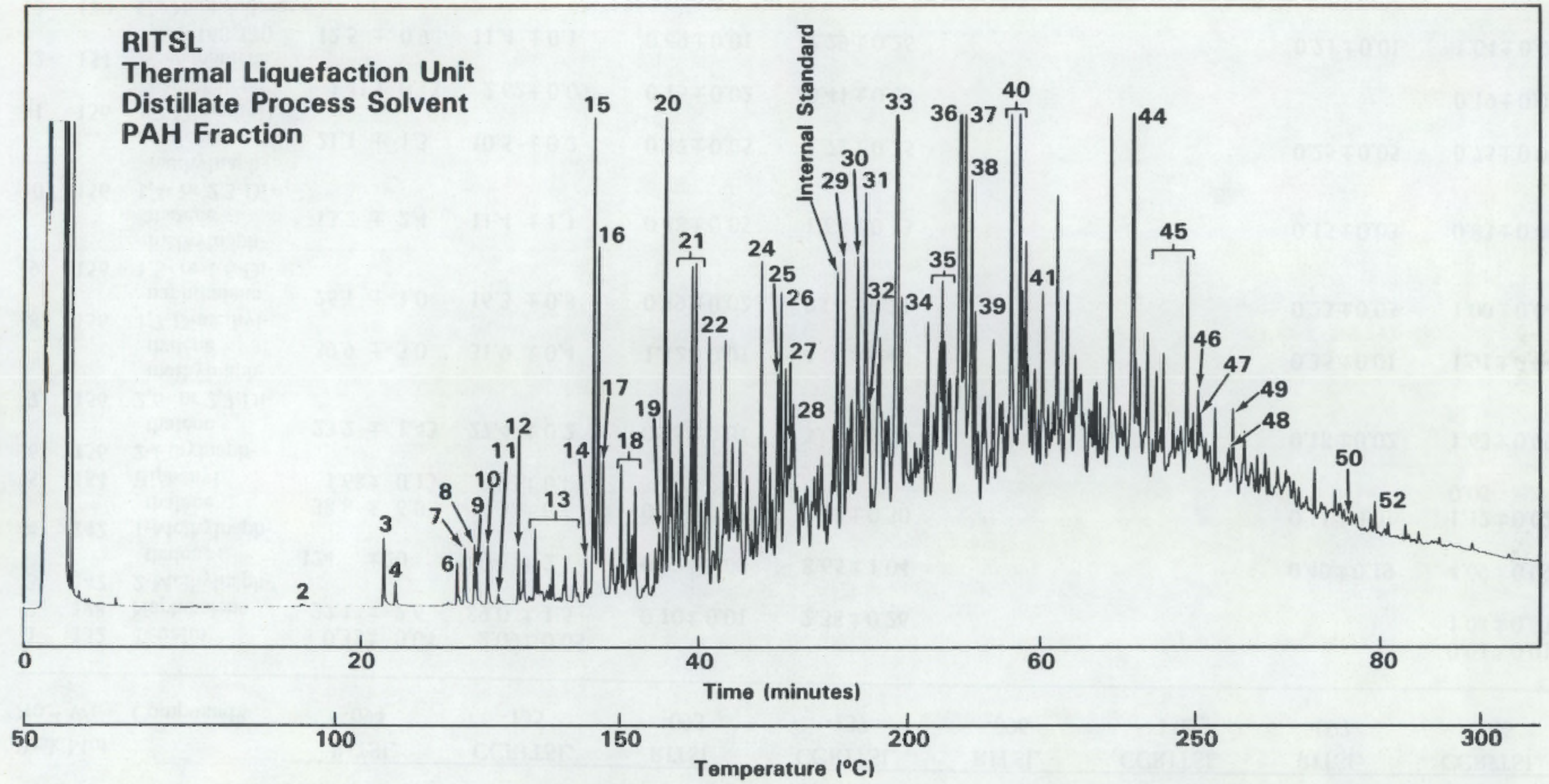

FIGURE 4. High Resolution Gas Chromatogram of the Polycyclic Aromatic Hydrocarbon Fraction Isolated from the Reconfigured, Integrated Two-Stage Liquefaction Thermal Liquefaction Unit Distillate Process Solvent. Numbered Peaks Refer to Identifications Given in Tables 6-9. See Text for Conditions.

TABLE 6. Quantitative Results for Selected Components in the Polycyclic Aromatic Hydrocarbon Fractions Isolated from the Reconfigured, Integrated Two-Stage Coal Liquefaction First-Stage Materials

			Quantitative Results, Parts per Thousand PAH Fraction; Sample Description; Process; and PNL 50378- Number							
			Overhead Distillate Product		Distillate Process Solvent		Bottoms Product		Hydrotreater Feed	
Peak No.[a]	Mol. Wt.	Compound[b]	RITSL -094	CCRITSL -135	RITSL -095	CCRITSL -137	RITSL -096	CCRITSL -142	RITSL -097	CCRITSL -146
1	132	Tetralin	0.33 ± 0.04	2.09 ± 0.05						0.03 ± 0.01
2	128	Naphthalene	27.1 ± 2.6	89.0 ± 1.5	0.10 ± 0.01	2.38 ± 0.26				1.08 ± 0.03
3	142	2-Methylnaphthalene	124 ± 20	140 ± 2	0.99 ± 0.08	8.65 ± 1.04			0.40 ± 0.19	4.09 ± 0.09
4	142	1-Methylnaphthalene	38.8 ± 6.0	34.3 ± 0.6	0.38 ± 0.03	2.32 ± 0.30			0.11 ± 0.01	1.12 ± 0.02
5	154	Biphenyl	1.68 ± 0.13	0.93 ± 0.03						0.05
6	156	2-Ethylnaphthalene	23.2 ± 1.43	27.4 ± 0.2	0.55 ± 0.01	3.03 ± 0.39			0.18 ± 0.02	1.63 ± 0.09
7	156	2,6- or 2,7 Dimethylnaphthalene	39.9 ± 3.0	31.9 ± 0.4	1.12 ± 0.01	4.03 ± 0.49			0.35 ± 0.01	1.91 ± 0.04
8	156	1,7-Dimethylnaphthalene	26.1 ± 1.0	16.3 ± 0.8	0.79 ± 0.02	2.04 ± 0.31			0.23 ± 0.03	1.00 ± 0.04
9	156	1,3- or 1,6-Dimethylnaphthalene	13.2 ± 2.4	11.4 ± 1.1	0.48 ± 0.05	1.66 ± 0.13			0.15 ± 0.03	0.83 ± 0.08
10	156	1,4- or 2,3-Dimethylnaphthalene	21.1 ± 1.3	10.5 ± 0.2	0.87 ± 0.05	1.72 ± 0.25			0.25 ± 0.05	0.75 ± 0.09
11	156	1,2-Dimethylnaphthalene	1.41 ± 0.15	2.62 ± 0.09	0.15 ± 0.02	0.41 ± 0.05				0.19 ± 0.01
12	154	Acenaphthene, m/z 168,170	12.5 ± 0.9	11.4 ± 0.1	0.69 ± 0.01	2.29 ± 0.26			0.21 ± 0.01	1.04 ± 0.02
13	170	C_3-Naphthalenes								

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[a] Refers to peaks labeled in Figure 4

[b] Tentative identifications based on retention time and mass spectral information

TABLE 6. Continued

Quantitative Results, Parts per Thousand PAH Fraction; Sample Description; Process; and PNL 50378- Number

			Overhead Distillate Product		Distillate Process Solvent		Bottoms Product		Hydrotreater Feed	
Peak No.[a]	Mol. Wt.	Compound[b]	RITSL -094	CCRITSL -135	RITSL -095	CCRITSL -137	RITSL -096	CCRITSL -142	RITSL -097	CCRITSL -146
14	166	Fluorene	3.35± 0.35	5.68± 0.25	0.48± 0.01	1.71± 0.22			0.15 ±0.02	0.76±0.12
15	168	1,2-Dihydrophenalene, m/z 184	38.4 ±4.9	38.0 ±0.6	5.71±0.13	13.6 ±1.8			1.80±0.18	6.15±0.97
16	168	Dihydrofluorene	27.3 ±6.3	28.1 ±1.7	5.08±0.22	11.6 ±2.3			1.52±0.04	4.93±1.78
17	168	Dihydrofluorene								
18	182	C_1-168								
19	180	Methylfluorene	1.92± 0.15	2.55±0.15	0.57±0.15	0.92± 0.03			0.11±0.03	0.44±0.09
20	182	C_1-168	16.4 ±1.7	22.9 ±0.5	6.68±0.06	13.0 ±1.4	0.01	0.10±0.01	2.22±0.37	6.03±0.81
21	196	C_2-168								
22	178	Phenanthrene	4.07±0.44	14.5 ±1.1	3.37±1.18	10.4 ±1.8	0.04	0.17±0.01	1.33±0.12	4.99±0.27
23	178	Anthracene	0.84±0.02	1.80±0.46	0.74±0.23	1.35±0.04		0.05	0.24±0.10	0.59±0.08
24	210	C_3-168								
25	192	3-Methylphenanthrene	1.86±0.04	5.53±0.22	2.99±0.36	5.66±0.62	0.02	0.12±0.06	0.73±0.07	2.88±0.28
26	192	2-Methylphenanthrene	2.57±0.107	6.49±0.41	3.67±0.29	6.68±0.11	0.08	0.19±0.09	1.14±0.09	3.00±0.82
27	192	9- or 4-Methylphenanthrene	0.85±0.05	2.40±0.05	1.50±0.10	1.90±1.50		0.01	0.26±0.15	1.39±0.40
28	192	1-Methylphenanthrene	1.94±0.14	3.74±0.04	3.56±0.75	3.23±0.72		0.04±0.01	0.69±0.18	1.80±0.28
29	208	Hexahydro-202								
30	208	Hexahydro-202								
31	204	Dihydrofluoranthene	1.77±0.02	2.14±0.08	6.44±0.91	1.49±0.52	0.21± 0.04	0.17±0.09	1.91±0.18	1.85±0.53
32	202	Fluoranthene	0.47	0.66±0.09	1.42±0.15	0.49±0.26	0.04		0.42±0.05	0.43±0.39

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[a] Refers to peaks labeled in Figure 4

[b] Tentative identifications based on retention time and mass spectral information

TABLE 6. Continued

Peak No.[a]	Mol. Wt.	Compound[b]	Quantitative Results, Parts per Thousand PAH Fraction; Sample Description; Process; and PNL 50378- Number							
			Overhead Distillate Product		Distillate Process Solvent		Bottoms Product		Hydrotreater Feed	
			RITSL -094	CCRITSL -135	RITSL -095	CCRITSL -137	RITSL -096	CCRITSL -142	RITSL -097	CCRITSL -146
33	202	Pyrene	2.50 ± 0.10	9.12 ± 0.26	17.4 ± 1.9	24.8 ± 1.0	2.44 ± 0.56	3.41 ± 0.02	6.30 ± 0.34	12.3 ± 0.6
34	204	Dihydropyrene	0.51 ± 0.11	1.28 ± 0.02	2.57 ± 0.46	3.39 ± 0.63	0.11 ±	0.22 ± 0.02	0.92 ± 0.02	1.40 ± 0.17
35	222	C_1-Hexahydro-202								
36	216	Benzo[b]fluorene	1.04 ± 0.09	4.95 ± 0.04	18.5 ± 1.4	22.2 ± 0.9	3.07 ± 0.17	4.30 ± 0.09	6.82 ± 0.16	12.5 ± 0.64
37	218	C_1-204	0.59 ± 0.27	2.26 ± 0.42	7.39 ± 0.33	11.8 ± 0.4	0.83 ± 0.16	1.69 ± 0.08	3.01 ± 0.09	5.94 ± 0.52
38	216	C_1-Pyrene								
39	216	1-Methylpyrene		0.52 ± 0.18	2.82 ± 0.05	2.92 ± 0.21	0.33 ± 0.03	0.24 ± 0.16	0.92 ± 0.09	1.08 ± 0.36
40	230	C_2-Pyrene								
41	232	C_2-204								
42	228	Benz[a]anthracene			0.48 ± 0.39	0.49 ± 0.42	0.06 ± 0.01	0.02	0.17 ± 0.05	0.09 ± 0.03
43	228	Chrysene			0.52 ± 0.41	1.27 ± 0.56	0.35 ± 0.02	0.22 ± 0.09	0.46 ± 0.06	0.43 ± 0.32
44	242	6- or 4-Methylchrysene			9.00 ± 0.64	6.60 ± 0.72	5.85 ± 0.18	4.44 ± 0.55	5.47 ± 0.37	5.35 ± 0.54
45	256	C_2-Chrysene								
46	252	Benzo[j or b]fluoranthene			0.85 ± 0.43	0.55 ± 0.05	1.17 ± 0.17	1.02 ± 0.47	0.82 ± 0.02	0.87 ± 0.32
47	252	Benzo[k]fluoranthene			0.96 ± 0.29	0.61 ±	0.92 ± 0.28		0.68 ± 0.08	0.86
48	252	Benzo[e]pyrene			0.44 ± 0.25	0.71 ± 0.04	0.97 ± 0.07	1.36 ± 0.84	0.55 ± 0.01	0.82 ± 0.22
49	252	Benzo[a]pyrene			1.19 ± 0.47	1.37 ± 0.01	2.30 ± 0.59	2.05 ± 0.51	1.26 ± 0.05	1.96 ± 0.47
50	276	Indeno[1,2,3-cd]-pyrene					0.38 ± 0.17	0.90 ± 0.04	0.26 ± 0.05	0.59 ± 0.01
51	278	Dibenzanthracene								
52	276	Benzo[ghi]perylene			0.48 ± 0.04	0.62 ± 0.03	4.41 ± 1.83	4.17 ± 1.09	1.76 ± 0.42	3.03 ± 0.16

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[a] Refers to peaks labeled in Figure 4

[b] Tentative identifications based on retention time and mass spectral information

TABLE 7. Quantitative Results for Selected Components in the Polycyclic Aromatic Hydrocarbon Fractions Isolated from the Reconfigured, Integrated Two-Stage Coal Liquefaction Second-Stage Materials.

Quantitative Results, Parts per Thousand PAH Fraction; Sample Description; Process; and PNL 50378- Number

			Light Distillate Product		Heavy Distillate Product			Recycle Pasting Solvent		Vacuum Flash Bottoms	
Peak No.[a]	Mol. Wt.	Compound[b]	RITSL -098	CCRITSL -148	RITSL -100	RITSL -101	CCRITSL -139	RITSL -103	CCRITSL -138	RITSL -099	CCRITSL -144
1	132	Tetralin	0.68±0.10	2.04±0.47			0.07±0.01		0.04±0.01		
2	128	Naphthalene	0.25±0.02	2.07±0.48			0.11±0.02		0.08±0.03		
3	142	2-Methylnaphthalene	3.52±0.53	11.3 ±2.4	0.15±0.01	0.14±0.03	0.67±0.12	0.06	0.54±0.13		
4	142	1-Methylnaphthalene	0.61±0.08	2.42±0.57			0.17±0.02		0.13±0.04		
5	154	Biphenyl	0.43±0.07	0.46±0.08			0.10±0.01	0.03			
6	156	2-Ethylnaphthalene	1.89±0.31	4.50±0.89	0.09	0.11±0.02	0.28±0.11		0.21±0.10		
7	156	2,6- or 2,7 Dimethylnaphthalene	1.72±0.27	4.35±0.86			0.36±0.08		0.32±0.07		
8	156	1,7-Dimethylnaphthalene	1.04±0.13	2.82±0.88	0.04±0.01	0.04±0.02	0.19±0.04	0.02	0.15±0.07		
9	156	1,3- or 1,6-Dimethylnaphthalene	0.96±0.15	2.62±0.28	0.02		0.18±0.06		0.12±0.06		
10	156	1,4- or 2,3-Dimethylnaphthalene	1.14±0.18	1.94±0.32		0.02	0.13±0.07	0.02	0.08±0.02		
11	156	1,2-Dimethylnaphthalene	0.59±0.10	0.63±0.33							
12	154	Acenaphthene, m/z 168,170	0.97±0.18	1.34±0.58		0.03					
13	170	C_3-Naphthalenes									

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[a] Refers to peaks labeled in Figure 4

[b] Tentative identifications based on retention time and mass spectral information

TABLE 7. Continued

			Quantitative Results, Parts per Thousand PAH Fraction; Sample Description; Process; and PNL 50378- Number								
			Light Distillate Product		Heavy Distillate Product			Recycle Pasting Solvent		Vacuum Flash Bottoms	
Peak No.[a]	Mol. Wt.	Compound[b]	RITSL -098	CCRITSL -148	RITSL -100	RITSL -101	CCRITSL -139	RITSL -103	CCRITSL -138	RITSL -099	CCRITSL -144
14	166	Fluorene	1.67 ± 0.05	3.93 ± 0.84	0.15 ± 0.07	0.18 ± 0.03	0.69 ± 0.16	0.07 ± 0.01	0.51 ± 0.11		
15	168	1,2-Dihydrophenalene, m/z 184	8.79 ± 0.89	14.9 ± 2.96	1.02 ± 0.11	1.07 ± 0.02	2.65 ± 0.63	0.44 ± 0.01	2.16 ± 0.51		
16	168	Dihydrofluorene	4.09 ± 0.50	7.96 ± 3.12	0.38 ± 0.10	0.44 ± 0.01	1.23 ± 0.48	0.13 ± 0.03	0.93 ± 0.52		
17	168	Dihydrofluorene									
18	182	C_1-168									
19	180	Methylfluorene	0.82 ± 0.14	1.23 ± 0.14							
20	182	C_1-168	9.81 ± 1.28	17.6 ± 3.0	1.51 ± 0.11	1.66 ± 0.18	4.06 ± 0.68	0.72 ± 0.03	3.31 ± 0.73		
21	196	C_2-168									
22	178	Phenanthrene	4.57 ± 0.31	7.15 ± 0.81	0.68 ± 0.07	0.83 ± 0.10	1.99 ± 0.25	0.31 ± 0.04	1.42 ± 0.14		
23	178	Anthracene	1.04 ± 0.14	0.41 ± 0.10	0.13 ± 0.01	0.14 ± 0.08	0.07 ± 0.02	0.08 ± 0.05			
24	210	C_3-168									
25	192	3-Methylphenanthrene	1.48 ± 0.34	3.07 ± 0.43	0.38 ± 0.01	0.35 ± 0.04	1.38 ± 0.18	0.20 ± 0.02	1.03 ± 0.14		
26	192	2-Methylphenanthrene	3.76 ± 0.21	4.31 ± 0.86	1.25 ± 0.04	1.20 ± 0.06	1.90 ± 0.06	0.54 ± 0.09	1.39 ± 0.03		
27	192	9- or 4-Methylphenanthrene	0.67 ± 0.15	2.15 ± 0.04	0.15	0.16	0.35 ± 0.31	0.01	0.11 ± 0.04		
28	192	1-Methylphenanthrene	1.28 ± 0.16	2.99 ± 0.22	0.46 ± 0.32	0.39 ± 0.13	0.95 ± 0.40	0.29 ± 0.21	0.50 ± 0.12		
29	208	Hexahydro-202									
30	208	Hexahydro-202									
31	204	Dihydrofluoranthene	4.63 ± 0.23	7.78 ± 0.65	2.68 ± 0.21	2.25 ± 0.54	5.25 ± 0.81	1.42 ± 0.05	3.75 ± 1.02	0.02	
32	202	Fluoranthene	1.03 ± 0.21	0.82 ± 0.03	0.40	0.39 ± 0.17	0.23 ± 0.12	0.21 ± 0.03	0.07 ± 0.01		

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[a] Refers to peaks labeled in Figure 4

[b] Tentative identifications based on retention time and mass spectral information

TABLE 7. Continued

Quantitative Results, Parts per Thousand PAH Fraction; Sample Description; Process; and PNL 50378- Number

Peak No.[a]	Mol. Wt.	Compound[b]	Light Distillate Product		Heavy Distillate Product			Recycle Pasting Solvent		Vacuum Flash Bottoms	
			RITSL -098	CCRITSL -148	RITSL -100	RITSL -101	CCRITSL -139	RITSL -103	CCRITSL -138	RITSL -099	CCRITSL -144
33	202	Pyrene	4.44 ± 0.47	7.65 ± 0.78	5.09 ± 0.75	5.13 ± 0.11	7.23 ± 0.09	2.73 ± 0.10	5.31 ± 0.45	0.11 ± 0.01	0.06 ± 0.01
34	204	Dihydropyrene	1.42 ± 0.37	1.30 ± 0.06	0.84 ± 0.50	0.87 ± 0.05	0.83 ± 0.20	0.38 ± 0.18	0.60 ± 0.11		
35	222	C_1-Hexahydro-202									
36	216	Benzo[b]fluorene	2.73 ± 0.32	3.82 ± 1.10	5.91 ± 0.19	5.70 ± 0.30	6.02 ± 0.22	3.65 ± 0.11	4.26 ± 0.92	0.20 ± 0.01	0.09 ± 0.01
37	218	C_1-204	1.27 ± 0.22	2.15 ± 0.78	2.02 ± 0.15	1.98 ± 0.12	3.55 ± 0.29	1.16 ± 0.05	1.71 ± 0.69	0.03 ± 0.01	
38	216	C_1-Pyrene									
39	216	1-Methylpyrene	0.87 ± 0.16	1.13 ± 0.44	1.38 ± 0.05	1.34 ± 0.04	0.78 ± 0.03	0.78 ± 0.03	0.13		
40	230	C_2-Pyrene									
41	232	C_2-204									
42	228	Benz[a]anthracene	0.06 ± 0.08		0.09 ± 0.03	0.35 ± 0.19	1.12	0.10 ± 0.13			
43	228	Chrysene	0.36 ± 0.42	0.35 ± 0.27	0.32 ± 0.26	0.56 ± 0.53	0.26 ± 0.03	0.39 ± 0.23	0.23 ± 0.10	0.08 ± 0.02	
44	242	6- or 4-Methylchrysene	0.61 ± 0.08	1.63 ± 0.10	6.99 ± 0.10	7.04 ± 0.56	5.06 ± 0.09	4.88 ± 0.34	4.04 ± 0.34	1.21 ± 0.13	0.39 ± 0.01
45	256	C_2-Chrysene									
46	252	Benzo[j or b]fluoranthene			0.74 ± 0.15	0.72 ± 0.14	0.59 ± 0.29	0.32 ± 0.10	0.22 ± 0.08	0.19 ± 0.07	
47	252	Benzo[k]fluoranthene			0.71 ± 0.24	0.78 ± 0.34	0.45 ± 0.17	0.36 ± 0.22		0.14 ± 0.09	
48	252	Benzo[e]pyrene			0.48 ± 0.39	0.34 ± 0.11	0.38 ± 0.06	0.34 ± 0.19	0.34	0.14 ± 0.02	0.08 ± 0.01
49	252	Benzo[a]pyrene	0.05	0.14	0.70 ± 0.30	0.51 ± 0.05	0.23 ± 0.24	0.54 ± 0.20	0.24	0.19 ± 0.13	0.01 ±
50	276	Indeno[1,2,3-cd]-pyrene			0.98 ± 0.36	0.82 ± 0.14	0.79 ± 0.01	0.85 ± 0.25	0.89 ± 0.04	0.70 ± 0.18	0.55 ± 0.04
51	278	Dibenzanthracene									
52	276	Benzo[ghi]perylene			1.17 ± 0.47	0.85 ± 0.17	1.56 ± 0.06	1.22 ± 0.54	1.96 ± 0.11	1.50 ± 0.77	1.71 ± 0.55

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[a] Refers to peaks labeled in Figure 4

[b] Tentative identifications based on retention time and mass spectral information

TABLE 8. Quantitative Results for Selected Compounds in the Polycyclic Aromatic Hydrocarbon Fractions Isolated from the Reconfigured, Integrated Two-Stage Coal Liquefaction Critical Solvent Deashing Materials

			Quantitative Results, Parts per Thousand PAH Fraction; Sample Description; Process; and PNL 50378- Number			
			Thermal Resids		Ash Concentrate	
Peak No.[a]	Mol. Wt.	Compound[b]	RITSL -102	CCRITSL -141	RITSL -104	CCRITSL -150
1	132	Tetralin		0.02		
2	128	Naphthalene		0.02		
3	142	2-Methylnaphthalene		0.28 ± 0.06		
4	142	1-Methylnaphthalene		0.07 ± 0.02		
5	154	Biphenyl		0.01		
6	156	2-Ethylnaphthalene		0.16 ± 0.07		
7	156	2,6- or 2,7-Dimethylnaphthalene		0.21 ± 0.05		
8	156	1,7-Dimethylnaphthalene		0.10 ± 0.05		
9	156	1,3- or 1,6-Dimethylnaphthalene		0.09 ± 0.06		
10	156	1,4- or 2,3-Dimethylnaphthalene		0.09 ± 0.03		
11	156	1,2-Dimethylnaphthalene				
12	154	Acenaphthene, m/z 168,170				
13	170	C_3-Naphthalenes				
14	166	Fluorene		0.42 ± 0.07		
15	168	1,2-Dihydrophenalene, m/z 184		2.04 ± 0.37		
16	168	Dihydrofluorene		0.94 ± 0.27		
17	168	Dihydrofluorene				
18	182	C_1-168				
19	180	Methylfluorene				
20	182	C_1-168		3.24 ± 0.73		0.02
21	196	C_2-168				
22	178	Phenanthrene		1.42 ± 0.10	0.04	
23	178	Anthracene				
24	210	C_3-168				
25	192	3-Methylphenanthrene		1.06 ± 0.16		
26	192	2-Methylphenanthrene		1.44 ± 0.11	0.04	
27	192	9- or 4-Methylphenanthrene		0.32 ± 0.44		
28	192	1-Methylphenanthrene		0.60 ± 0.42		
29	208	Hexahydrofluoranthene/pyrene				
30	208	Hexahydrofluoranthene/pyrene				
31	204	Dihydrofluoranthene	0.03	4.26 ± 1.11	0.05 ± 0.01	0.03
32	202	Fluoranthene		0.26 ± 0.16		
33	202	Pyrene	0.09 ± 0.02	5.53 ± 0.65	0.39 ± 0.08	0.14 ± 0.01
34	204	Dihydropyrene		0.78 ± 0.05		
35	222	C_1-Hexahydrofluoranthene/pyrene				
36	216	Benzo[b]fluorene	0.17 ± 0.01	3.12 ± 1.67	0.50 ± 0.07	0.16 ± 0.02
37	218	C_1-Dihydrofluoranthene/pyrene	0.02	1.84 ± 0.49	0.07 ± 0.01	0.05
38	216	C_1-Pyrene				
39	216	1-Methylpyrene	0.02	0.14	0.06 ± 0.01	
40	230	C_2-Pyrene				

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[a] Refers to peaks labeled in Figure 4

[b] Tentative identifications based on retention time and mass spectral information

TABLE 8. Continued.

Peak No.[a]	Mol. Wt.	Compound[b]	Quantitative Results, Parts per Thousand PAH Fraction; Sample Description; Process; and PNL 50378- Number			
			Thermal Resids		Ash Concentrate	
			RITSL -102	CCRITSL -141	RITSL -104	CCRITSL -150
41	232	C_2-Dihydrofluoranthene/pyrene				
42	228	Benz[a]anthracene	0.02		0.01	
43	228	Chrysene	0.06 ± 0.01	0.28	0.08 ± 0.01	0.03
44	242	6- or 4-Methylchrysene	1.03 ± 0.18	3.87 ± 0.05	1.79 ± 0.14	0.68 ± 0.03
45	256	C_2-Chrysene				
46	252	Benzo[j or b]fluoranthene	0.11 ± 0.01	0.25 ± 0.26	0.25 ± 0.55	0.09
47	252	Benzo[k]fluoranthene	0.07 ± 0.01	0.44	0.17 ± 0.07	0.11 ± 0.05
48	252	Benzo[e]pyrene	0.07 ± 0.03	0.29	0.14 ± 0.07	0.23 ± 0.03
49	252	Benzo[a]pyrene	0.15 ± 0.06	0.07	0.30 ± 0.07	0.22 ± 0.03
50	276	Indeno[1,2,3-cd]pyrene	0.71 ± 0.07	0.91 ± 0.10	1.09 ± 0.44	0.78 ± 0.15
51	278	Dibenzanthracene				
52	276	Benzo[ghi]perylene	1.66 ± 0.37	1.90 ± 0.10	4.90 ± 2.28	3.34 ± 0.57

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[a] Refers to peaks labeled in Figure 4

[b] Tentative identifications based on retention time and mass spectral information

TABLE 9. Quantitative Results for Selected Components in the Polycyclic Aromatic Hydrocarbon Fractions Isolated from the Integrated Two-Stage Coal Liquefaction (Wyodak) Process Materials

Peak No.[a]	Mol. Wt.	Compound[b]	Quantitative Results, Parts per Thousand PAH Fraction; Sample Description; and PNL 50378- Number			
			First-Stage Overhead Distillate Product; -111	Hydrotreater Unit Feed -112	Hydrotreater Light Distillate Product; -113	Recycle Pasting Solvent -114
1	132	Tetralin	0.32 ± 0.23			
2	128	Naphthalene	47.5 ± 1.1	0.25 ± 0.07	1.23 ± 0.06	0.07 ± 0.01
3	142	2-Methylnaphthalene	138 ± 3	1.79 ± 0.16	10.4 ± 0.5	0.68 ± 0.16
4	142	1-Methylnaphthalene	33.4 ± 1.1	0.48 ± 0.05	2.64 ± 0.15	0.19 ± 0.05
5	154	Biphenyl	3.21 ± 0.05	0.08 ± 0.01	0.77 ± 0.04	0.43 ± 0.10
6	156	2-Ethylnaphthalene	30.6 ± 0.6	0.82 ± 0.06	4.78 ± 0.24	0.44 ± 0.13
7	156	2,6- or 2,7-Dimethylnaphthalene	54.5 ± 3.7	1.55 ± 0.22	8.55 ± 0.44	0.75 ± 0.18
8	156	1,7-Dimethylnaphthalene	25.6 ± 0.6	0.84 ± 0.07	4.62 ± 0.34	0.42 ± 0.10
9	156	1,3- or 1,6-Dimethylnaphthalene	13.6 ± 0.3	0.63 ± 0.06	2.83 ± 0.20	0.32 ± 0.09
10	156	1,4- or 2,3-Dimethylnaphthalene	19.1 ± 0.3	0.95 ± 0.09	3.26 ± 0.18	0.32 ± 0.08
11	156	1,2-Dimethylnaphthalene				
12	154	Acenaphthene, m/z 168,170	18.8 ± 0.4	1.08 ± 0.30	1.97 ± 0.12	0.25 ± 0.05
13	170	C_3-Naphthalenes				

---

[a] Refers to peaks labeled in Figure 4

[b] Tentative identifications based on retention time and mass spectral information

TABLE 9. Continued.

			Quantitative Results, Parts per Thousand PAH Fraction; Sample Description; Process; and PNL 50378- Number			
Peak No.[a]	Mol. Wt.	Compound[b]	First-Stage Overhead Distillate Product; -111	Hydrotreater Unit Feed -112	Hydrotreater Light Distilllate Product; -113	Recycle Pasting Solvent -114
14	166	Fluorene	6.02 ± 0.38	1.24 ± 0.13	4.73 ± 0.32	0.79 ± 0.19
15	168	1,2-Dihydrophenalene, m/z 184	42.1 ± 0.8	6.67 ± 0.53	17.7 ± 0.8	3.52 ± 0.73
16	168	Dihydrofluorene	17.8 ± 0.8	3.17 ± 0.16	6.30 ± 0.33	1.25 ± 0.27
17	168	Dihydrofluorene				
18	182	C_1-168				
19	180	Methylfluorene	3.25 ± 1.11	2.54 ± 0.29	6.91 ± 0.44	1.89 ± 0.39
20	182	C_1-168	20.7 ± 2.3	9.67 ± 0.63	24.4 ± 1.6	7.68 ± 1.50
21	196	C_2-168				
22	178	Phenanthrene	14.0 ± 0.3	11.9 ± 0.68	13.6 ± 0.7	4.33 ± 0.44
23	178	Anthracene	1.53 ± 0.04	1.16 ± 0.05	1.39 ± 0.14	0.41 ± 0.06
24	210	C_3-168				
25	192	3-Methylphenanthrene	4.26 ± 0.11	7.05 ± 0.22	6.49 ± 0.37	2.51 ± 0.18
26	192	2-Methylphenanthrene	5.00 ± 0.34	9.28 ± 0.84	11.6 ± 0.5	3.97 ± 0.31
27	192	9- or 4-Methylphenanthrene	1.63 ± 0.82	2.91 ± 0.25	3.12 ± 1.33	1.08 ± 0.63
28	192	1-Methylphenanthrene	2.12 ± 0.64	5.22 ± 0.20	3.66 ± 0.84	2.37 ± 0.20
29	208	Hexahydrofluoranthene/pyrene				
30	208	Hexahydrofluoranthene/pyrene				
31	204	Dihydrofluoranthene	1.14 ± 0.12	4.30 ± 0.12	14.4 ± 0.9	8.90 ± 0.63
32	202	Fluoranthene	0.93 ± 0.08	1.76 ± 0.06	1.25 ± 0.20	0.83 ± 0.08
33	202	Pyrene	3.74 ± 0.05	19.3 ± 2.1	7.64 ± 0.66	5.40 ± 0.66
34	204	Dihydropyrene	0.45 ± 0.18	3.70 ± 0.46	2.17 ± 0.86	0.68 ± 0.16
35	222	C_1-Hexahydrofluoranthene/pyrene				
36	216	Benzo[b]fluorene	2.30 ± 0.06	19.9 ± 1.7	6.89 ± 1.08	5.05 ± 1.53
37	218	C_1-Dihydrofluoranthene/pyrene	1.29 ± 0.03	13.8 ± 0.8	7.66 ± 1.95	5.73 ± 1.26
38	216	C_1-Pyrene				
39	216	1-Methylpyrene	0.19 ± 0.04	2.65 ± 0.23	0.97 ± 0.33	0.74 ± 0.40
40	230	C_2-Pyrene				
41	232	C_2-Dihydrofluoranthene/pyrene				
42	228	Benz[a]anthracene	0.07	0.82 ± 0.04	0.37 ± 0.20	0.77 ± 0.12
43	228	Chrysene	0.11 ± 0.02	0.62 ± 0.11	0.39 ± 0.16	0.66 ± 0.08
44	242	6- or 4-Methylchrysene	0.24 ± 0.12	4.75 ± 0.93	0.61 ± 0.07	2.48 ± 0.71
45	256	C_2-Chrysene				
46	252	Benzo[j or b]fluoranthene		0.95 ± 0.20	0.07 ± 0.04	0.69 ± 0.23
47	252	Benzo[k]fluoranthene		0.24 ± 0.02		0.63 ± 0.51
48	252	Benzo[e]pyrene		0.97 ± 0.20		0.26 ± 0.03
49	252	Benzo[a]pyrene		1.15 ± 0.29		0.15 ± 0.05
50	276	Indeno[1,2,3-cd]pyrene		0.39 ± 0.11		0.31 ± 0.09
51	278	Dibenzanthracene		0.15		0.09 ± 0.03
52	276	Benzo[ghi]perylene		1.27 ± 0.34		0.57 ± 0.15

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[a] Refers to peaks labeled in Figure 4

[b] Tentative identifications based on retention time and mass spectral information

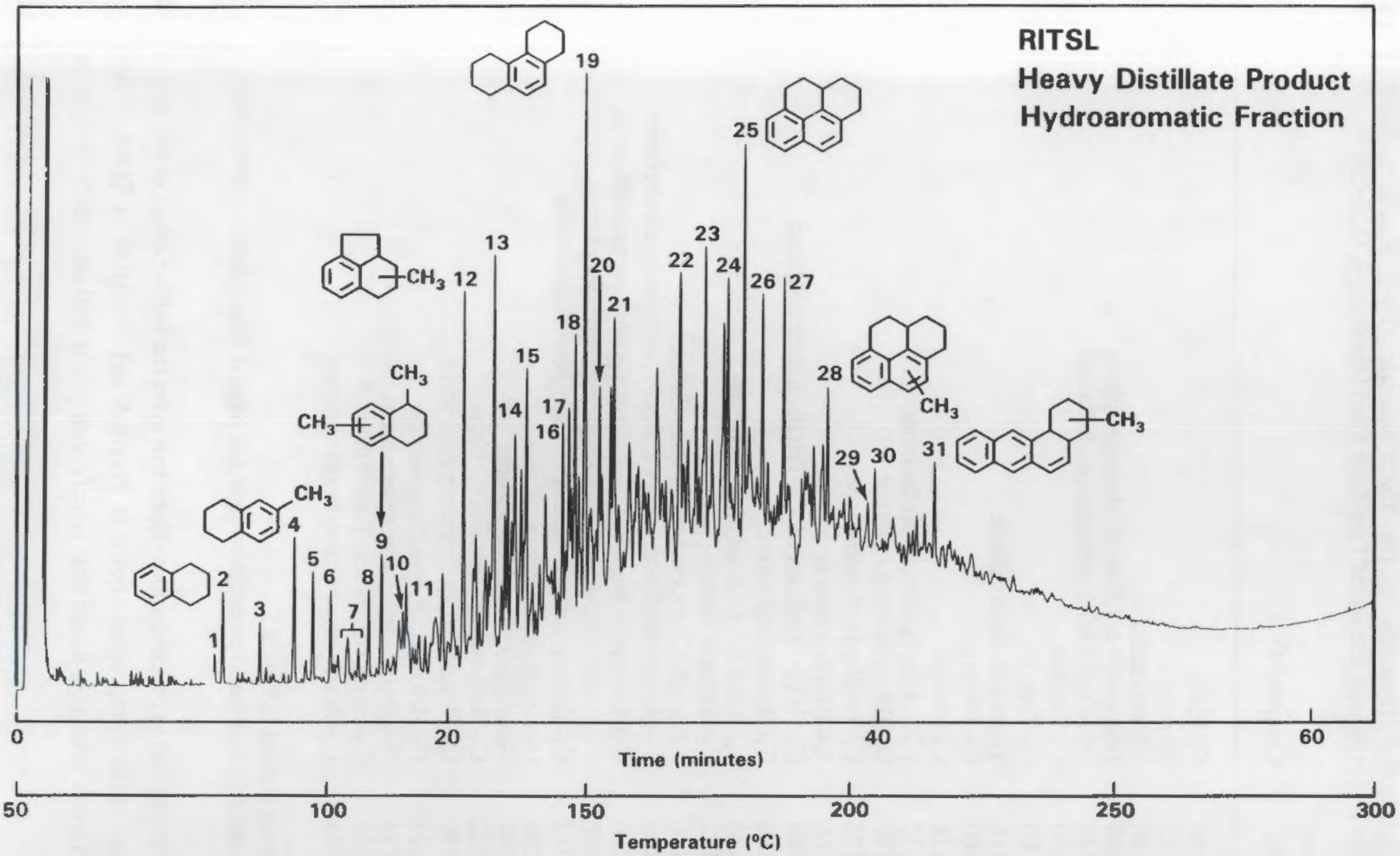

FIGURE 5. High Resolution Gas Chromatogram of the Hydroaromatic (PA_2) Fraction Isolated from the Reconfigured, Integrated Two-Stage Liquefaction Heavy Distillate Product. Numbered Peaks Refer to Identifications Given in Table 10. See Text for Conditions.

TABLE 10. Selected Compounds in the Hydroaromatic (PA_2) Fractions Isolated from the Reconfigured, Integrated Two-Stage Coal Liquefaction Materials

Peak No.[a]	Mol. Wt.	Compound[b]
1	132	C_1-Indan
2	132	Tetralin
3	146	2-Methyltetralin
4	146	2-Methyl-5,6,7,8-tetrahydronaphthalene
5	146	1-Methyl-5,6,7,8-tetrahydronaphthalene
6	160	C_2-Tetralin
7	160	C_2-Tetralin
8	158	Tetrahydroacenaphthene
9	160	C_2-Tetralin
10	174	C_3-Tetralin
11	172	1,2,3,4,4a,9a-Hexahydrofluorene
12	172	C_1-Tetrahydroacenaphthene
13	172	C_1-Tetrahydroacenaphthene
14	168	1,4-Dihydrofluorene
15	186	C_1-Hexahydrofluorene, C_2-Tetrahydroacenaphthene
16	186	C_1-Hexahydrofluorene
17	186	1,2,3,4,5,6,7,8-Octahydroanthracene
18	182	C_1-Dihydrofluorene
19	186	1,2,3,4,5,6,7,8-Octahydrophenanthrene
20	200	C_2-Hexahydrofluorene, C_1-Octahydrophenanthrene/anthracene
21	200	C_2-Hexahydrofluorene, C_1-Octahydrophenanthrene/anthracene
22	212	C_3-Tetrahydrofluorene, Decahydropyrene/fluoranthene
23	212	C_3-Tetrahydrofluorene, Decahydropyrene/fluoranthene
24	208	Hexahydropyrene/fluoranthene
25	208	Hexahydropyrene/fluoranthene
26	222	C_1-Hexahydropyrene/fluoranthene
27	226	C_3-Hexahydrophenanthrene/anthracene
28	222	C_1-Hexahydropyrene/fluoranthene
29	234	Hexahydrochrysene/benzanthracene
30	236	C_2-Hexahydropyrene/fluoranthene
31	248	C_1-Hexahydrochrysene/benzanthracene

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[a] Refers to peaks labeled in Figure 5

[b] Tentative identifications based on retention time and limited mass spectral information

the process origin, but in concentrations dependent upon the boiling range of the product. The same hydroaromatic components shown in Figure 5 and identified in Table 10 have been identified in other two-stage direct coal liquefaction products (Later 1985; Wright and Later 1985).

Carbazole and the methylcarbazoles were the major components of the gas chromatographable portions of the RITSL, CCRITSL, and ITSL (Wyodak) products' NPAC fractions. A representative high resolution gas chromatogram of an NPAC fraction is shown in Figure 6. The peaks labeled in Figure 6 are identified in Tables 11-13 for the first-stage RITSL and CCRITSL products, the second-stage RITSL and CCRITSL products, and the ITSL (Wyodak) products, respectively. The majority of the chromatographable compounds in the NPAC fractions were not identified, but were nitrogen-containing based on the simultaneous response of the nitrogen-specific NPD and the universal FID when analyzed by HRGC. Quantitative results for the compounds identified are also given in Tables 11-13. None of the compounds listed in Tables 11-13 were present above 25 ppm in the RITSL and CCRITSL critical solvent deashing products' NPAC fractions with the exception of that fraction isolated from the CCRITSL critical solvent deashing thermal resids (50378-141). The following compounds were present in that fraction in the following concentrations (parts per thousand ± standard deviation): carbazole, 0.08 ± 0.03; 1-methylcarbazole, 0.19 ± 0.06, 3-methylcarbazole, 0.11 ± 0.01; 2-methylcarbazole, 0.16 ± 0.04; 4-methylcarbazole, 0.05 ± 0.01; 1- or 4-azapyrene, 0.11 ± 0.01; benzo[a]carbazole, 0.03; and benzo[c]carbazole, 0.21 ± 0.11. In all cases, the CCRITSL products gave higher quantitative values for the selected NPAC components that were quantified than did the corresponding RITSL products. The quantitative values for the ITSL and NTSL products were generally within the same ranges as those given for the RITSL and CCRITSL products.

Low-Voltage Probe-Inlet Mass Spectrometry

Spectra acquired by LVMS of the PAH (top), NPAC (middle), and hydroxy-PAH (bottom) fractions isolated from the CCRITSL first-stage distillate process solvent are shown in Figure 7. For keys to mass identifications of the PAH, NPAC, and hydroxy-PAH fractions, see Tables A-1, A-2, and A-3, respectively, in the appendix. The major components of the CCRITSL first-stage distillate process solvent's PAH fraction were pyrene (or other PAH compounds of 202 amu), benzofluorene (or others isomers of 216 amu), and alkylated derivatives of the aforementioned (add 14 amu for each methyl group). Other high intensity components included the alkyl series of 218 amu (perhaps dihydromethylpyrenes/fluoranthenes) and 242 amu (methylchrysenes or isomers). Alkylated pyridines (series including 107 amu), carbazole and its alkylated derivatives (series including 167 amu), and benzocarbazoles and their alkylated derivatives (series including 217 amu) were the major nitrogen-containing compounds present in the isolated NPAC fraction. The series including 221 amu (tetrahydrobenzocarbazoles) was also present, but found in lower concentrations than the previously mentioned compounds of the NPAC fraction. The major components of the

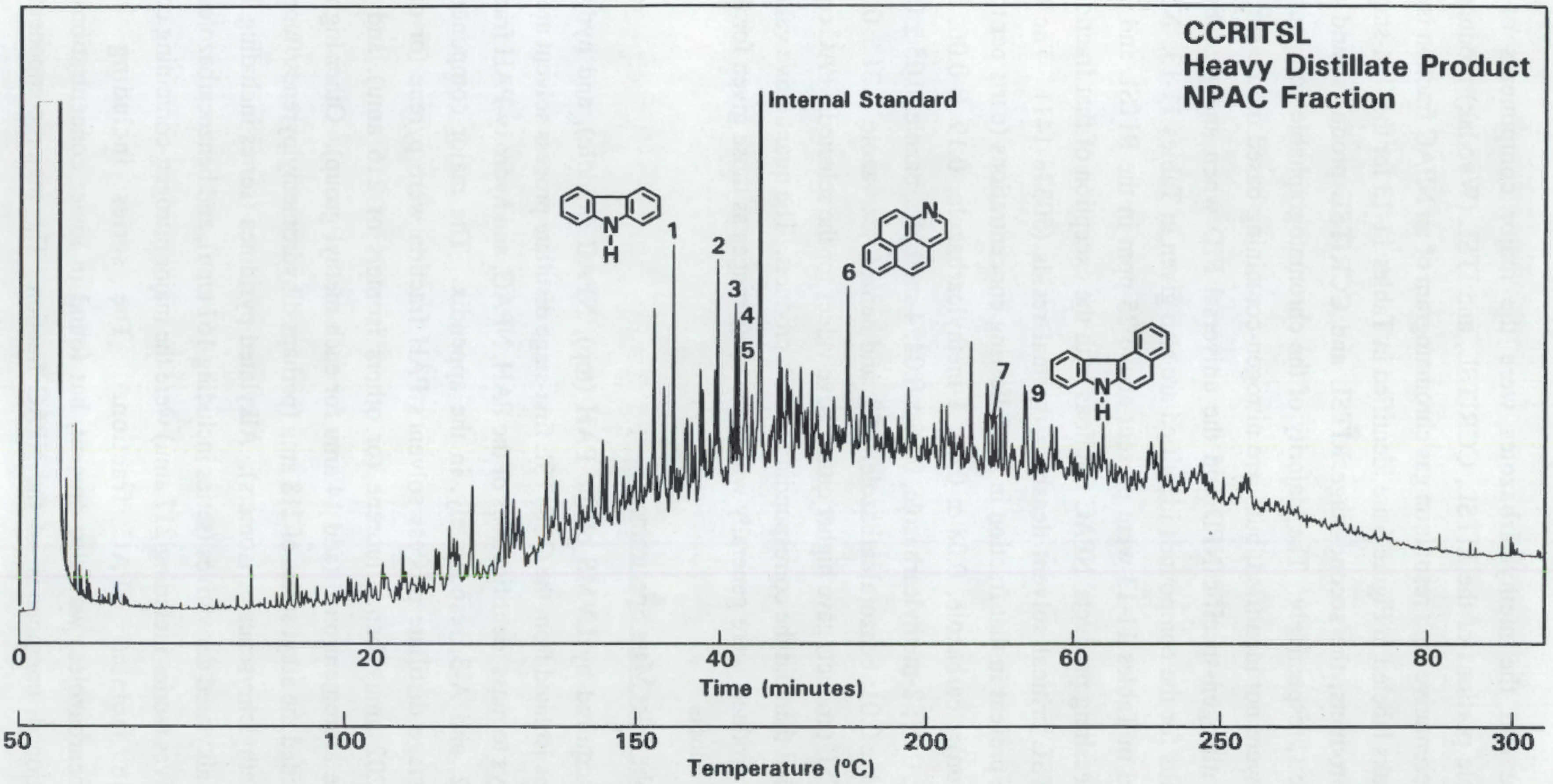

FIGURE 6. High Resolution Gas Chromatogram of the Nitrogen-Containing Polycyclic Aromatic Compound Fraction Isolated from the Close-Coupled, Reconfigured, Integrated Two-Stage Liquefaction Heavy Distillate Product. Numbered Peaks Refer to Identifications Given in Tables 11-13. See Text for Conditions.

TABLE 11. Quantitative Results for Selected Components in the Nitrogen-Containing Polycyclic Aromatic Compound Fractions Isolated from the Reconfigured, Integrated Two-Stage Coal Liquefaction First-Stage Materials

Quantitative Results, Parts per Thousand NPAC Fraction; Sample Description; Process; and PNL 50378- Number

Peak No.[a]	Mol. Wt.	Compound[b]	Overhead Distillate Product		Distillate Process Solvent		Bottoms Product		Hydrotreater Feed	
			RITSL -094	CCRITSL -135	RITSL -095	CCRITSL -137	RITSL -096	CCRITSL -142	RITSL -097	CCRITSL -146
1	167	Carbazole	0.56 ± 0.13	2.39 ± 0.43	1.48 ± 0.45	4.66 ± 0.47			0.16 ± 0.04	0.50 ± 0.08
2	181	1-Methylcarbazole	0.27 ± 0.04	1.73 ± 0.04	2.20 ± 0.29	5.14 ± 0.48			0.17 ± 0.05	0.46 ± 0.08
3	181	3-Methylcarbazole	0.13 ± 0.08	1.43 ± 0.07	2.18 ± 0.79	4.47 ± 0.14			0.23 ± 0.04	0.45 ± 0.04
4	181	2-Methylcarbazole	0.08 ± 0.04	0.88 ± 0.09	1.01 ± 0.08	2.56 ± 0.16			0.09 ± 0.01	0.25 ± 0.02
5	181	4-Methylcarbazole	0.08 ± 0.03	0.94 ± 0.54	0.63 ± 0.07	1.58 ± 0.33			0.02 ± 0.01	0.11 ± 0.06
6	203	1- or 4-Azapyrene		0.33 ± 0.24	1.37 ± 0.77	1.94 ± 0.94		0.04	0.09 ± 0.01	0.12 ± 0.04
7	217	Benzo[a]carbazole			0.81 ± 0.34	1.83 ± 0.34		0.04		0.23 ± 0.02
8	217	Benzo[b]carbazole			0.32 ± 0.11	0.89 ± 0.01				0.04
9	217	Benzo[c]carbazole			0.94 ± 0.51	3.04 ± 0.21		0.07		0.56 ± 0.12

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[a] Refers to peaks labeled in Figure 6

[b] Tentative identifications based on retention time and mass spectral information

TABLE 12. Quantitative Results for Selected Components in the Nitrogen-Containing Polycyclic Aromatic Compound Fractions Isolated from the Reconfigured, Integrated Two-Stage Coal Liquefaction Second-Stage Materials

			Quantitative Results, Parts per Thousand NPAC Fraction; Sample Description; Process; and PNL 50378- Number								
			Light Distillate Product		Heavy Distillate Product			Recycle Pasting Solvent		Vacuum Flash Bottoms	
Peak No.[a]	Mol. Wt.	Compound[b]	RITSL -098	CCRITSL -148	RITSL -100	RITSL -101	CCRITSL -139	RITSL -103	CCRITSL -138	RITSL -099	CCRITSL -144
1	167	Carbazole	1.87 ± 0.89	5.17 ± 1.08	0.09 ± 0.02	1.07 ± 0.34	1.32 ± 0.15	0.09 ± 0.07	0.40 ± 0.05		
2	181	1-Methylcarbazole	1.34	3.04 ± 0.24	0.03 ± 0.01	0.34 ± 0.10	1.14 ± 0.02	0.04 ± 0.04	0.37 ± 0.08		
3	181	3-Methylcarbazole	0.38 ± 0.03	1.79 ± 0.09	0.02 ± 0.01	0.29 ± 0.01	0.77 ± 0.15	0.05	0.24 ± 0.05		
4	181	2-Methylcarbazole	0.25 ± 0.21	1.89 ± 0.23	0.02 ± 0.01	0.18 ± 0.02	0.69 ± 0.15	0.03 ± 0.01	0.18 ± 0.03		
5	181	4-Methylcarbazole	0.33 ± 0.03	1.54 ± 0.77	0.02 ± 0.01	0.14 ± 0.03	0.55 ± 0.46		0.28 ± 0.04		
6	203	1- or 4-Azapyrene	0.52 ± 0.02	3.07 ± 0.59	0.10 ± 0.03	1.38 ± 0.36	1.52 ± 0.58	0.15 ± 0.01	0.45 ± 0.09		
7	217	Benzo[a]carbazole		0.23 ± 0.04	0.01	0.33 ± 0.02	0.50 ± 0.09		0.16 ± 0.03		
8	217	Benzo[b]carbazole		0.17		0.16	0.33 ± 0.23				
9	217	Benzo[c]carbazole		0.57 ± 0.15	0.03 ± 0.01	0.34	0.79 ± 0.30	0.04	0.33 ± 0.25		

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[a] Refers to peaks labeled in Figure 6

[b] Tentative identifications based on retention time and mass spectral information

TABLE 13. Quantitative Results for Selected Components in the Nitrogen-Containing Polycyclic Aromatic Compound Fractions Isolated from the Integrated Two-Stage Coal Liquefaction (Wyodak) Process Materials.

			Quantitative Results, Parts per Thousand NPAC Fraction; Sample Description; and PNL 50378- Number			
Peak No.[a]	Mol. Wt.	Compound[b]	First-Stage Overhead Distillate Product; -111	Hydrotreater Unit Feed -112	Hydrotreater Light Distillate Product; -113	Recycle Pasting Solvent -114
1	167	Carbazole	0.26 ± 0.11	1.86 ± 0.05	4.27	0.78 ± 0.02
2	181	1-Methylcarbazole	0.19 ± 0.05	1.17 ± 0.13	3.43 ± 0.06	0.74 ± 0.08
3	181	3-Methylcarbazole	0.11 ± 0.03	1.69 ± 0.18	2.22 ± 0.5	0.64 ± 0.01
4	181	2-Methylcarbazole	0.12 ± 0.04	1.03 ± 0.06	1.76 ± 0.15	0.52 ± 0.02
5	181	4-Methylcarbazole	0.12	0.41 ± 0.11	0.77 ± 0.04	0.35 ± 0.24
6	203	1- or 4-Azapyrene		0.45 ± 0.19	0.42 ± 0.24	0.30 ± 0.06
7	217	Benzo[a]carbazole		1.02 ± 0.18		0.19 ± 0.16
8	217	Benzo[b]carbazole		0.62		0.09
9	217	Benzo[c]carbazole		1.05 ± 0.13		0.60 ± 0.10

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[a] Refers to peaks labeled in Figure 6

[b] Tentative identifications based on retention time and mass spectral information

CCRITSL first-stage distillate process solvent hydroxy-PAH fraction had masses corresponding to parent and alkylated phenols, indanols, hydroxyfluorenes, and hydroxybiphenyls.

The components of the CCRITSL hydrotreater unit feed's PAH, NPAC, and hydroxy-PAH fractions were similar to those of the first-stage distillate process solvent, except they were of a higher molecular weight range (Figure 8). The most notable difference between the former versus the latter was found in the molecular weight range of the isolated NPAC fractions. The average molecular weight of the first-stage distillate process solvent's NPAC fraction was 220 amu; the average molecular weight of the hydrotreater feed's NPAC fraction was 375 amu.

The spectra from the LVMS analyses of the CCRITSL heavy distillate product's PAH (top), NPAC (middle), and hydroxy-PAH (bottom) fractions are shown in Figure 9. Although many of the same components were present in the second-stage distillate compared to the first-stage products (shown in Figures 7 and 8), the masses indicative of hydrogenated components for both the PAH and NPAC fractions were more intense in the second-stage versus the first-

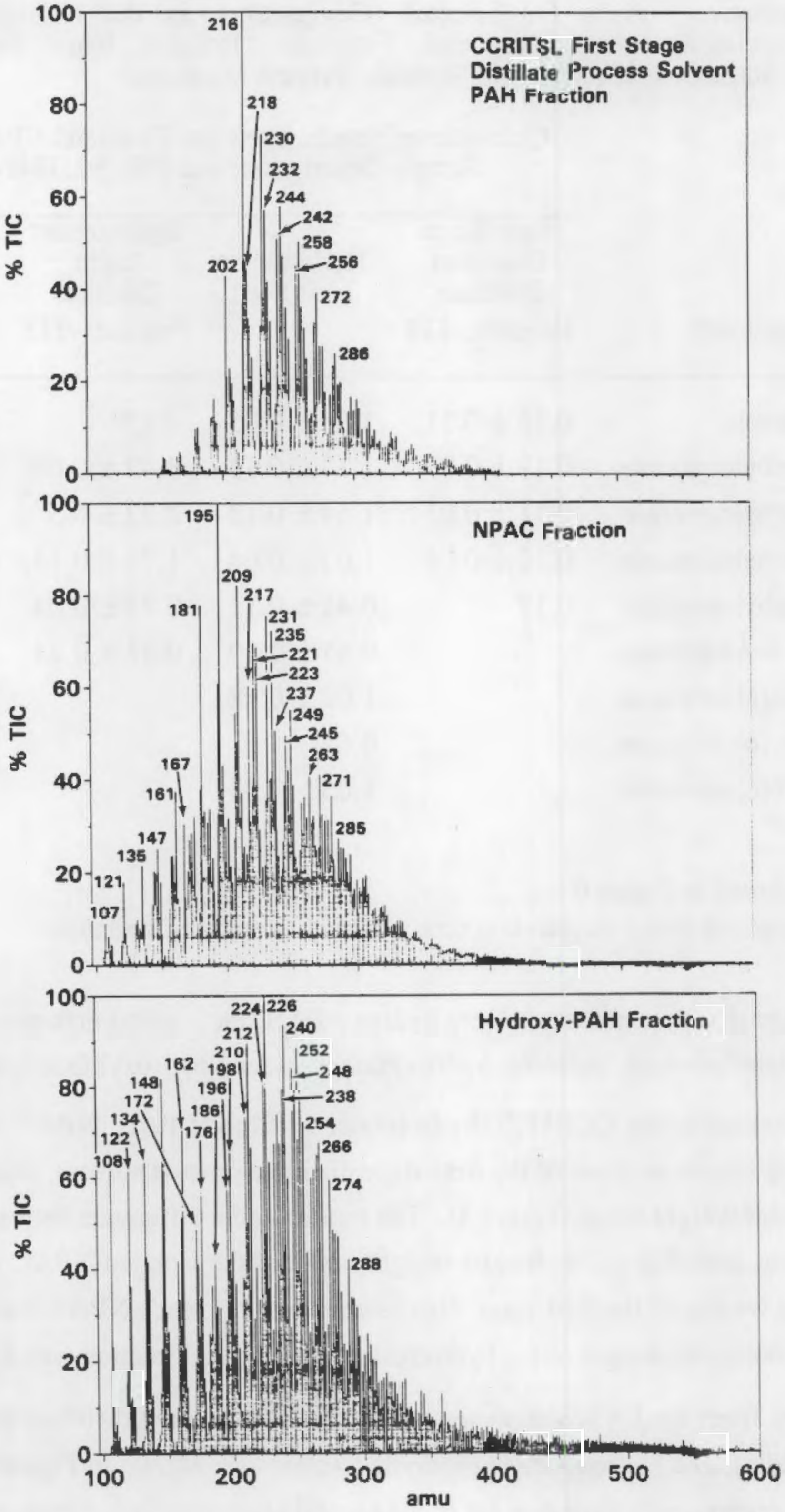

FIGURE 7. Low-Voltage Probe-Inlet Mass Spectra of the PAH (top), NPAC (middle), and Hydroxy-PAH (bottom) Fractions Isolated from the Close-Coupled, Reconfigured, Integrated Two-Stage Liquefaction First-Stage Distillate Process Solvent. For a Key to Mass Identifications, See Tables A-1, A-2, and A-3 in the Appendix.

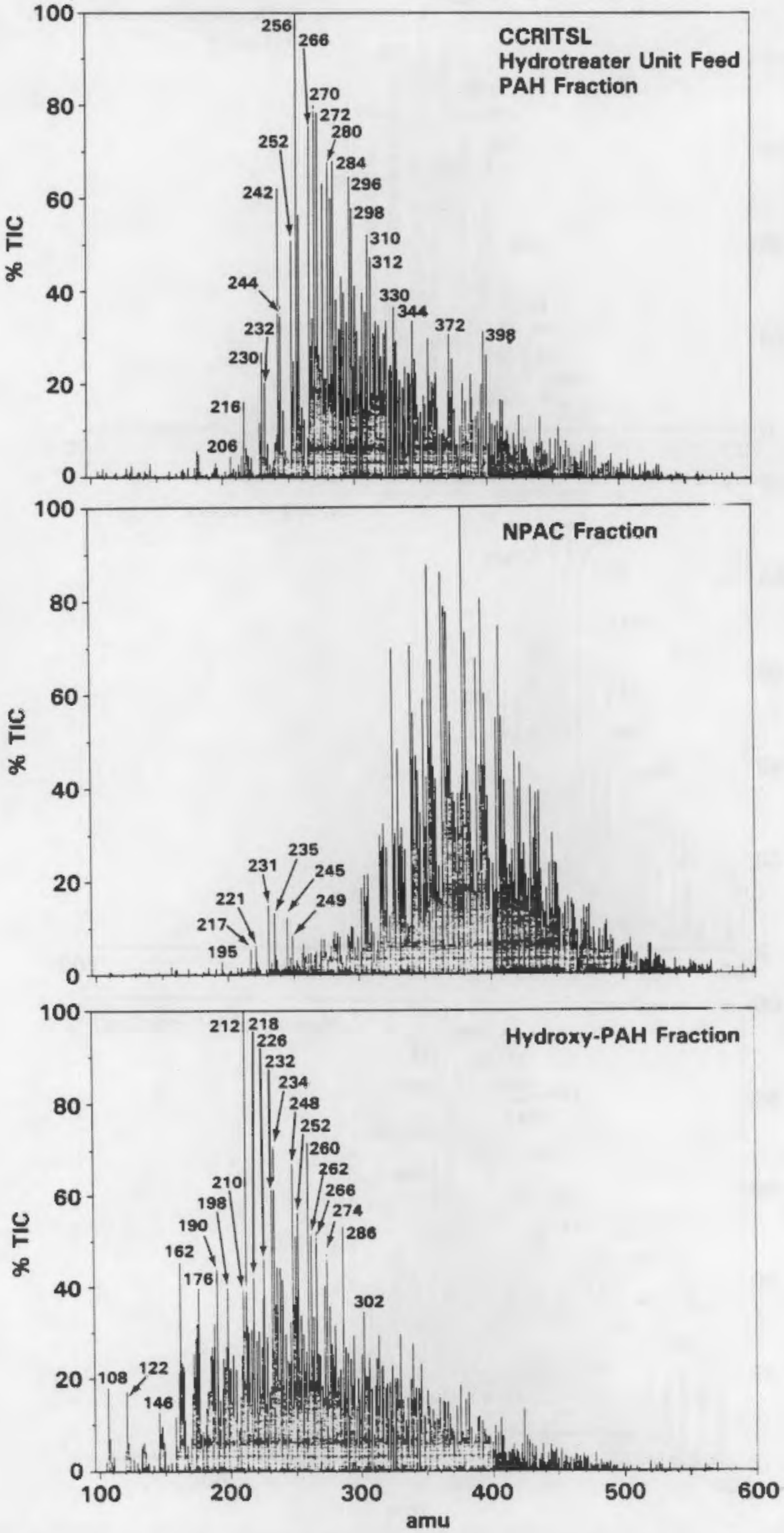

FIGURE 8. Low-Voltage Probe-Inlet Mass Spectra of the PAH (top), NPAC (middle), and Hydroxy-PAH (bottom) Fractions Isolated from the Close-Coupled, Reconfigured, Integrated Two-Stage Liquefaction Hydrotreater Unit Feed. For a Key to Mass Identifications, See Tables A-1, A-2, and A-3 in the Appendix.

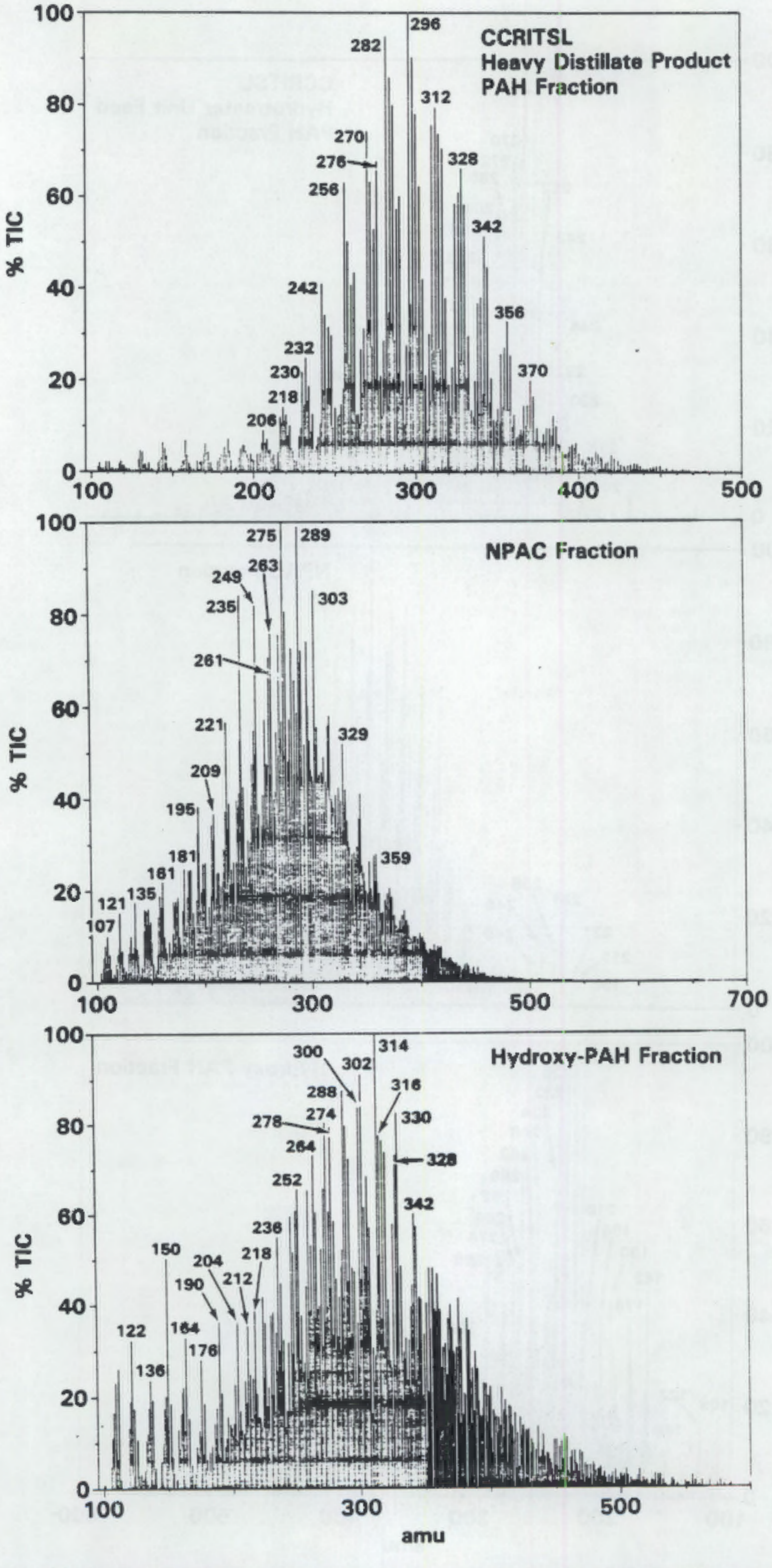

FIGURE 9. Low-Voltage Probe-Inlet Mass Spectra of the PAH (top), NPAC (middle), and Hydroxy-PAH (bottom) Fractions Isolated from the Close-Coupled, Reconfigured, Integrated Two-Stage Liquefaction Heavy Distillate Product. For a Key to Mass Identifications, See Tables A-1, A-2, and A-3 in the Appendix.

stage products. The masses indicative of the hydroxybiphenyls were found in significantly lower concentrations in the second-stage distillate versus the first-stage distillate hydroxy-PAH fraction. The heavy distillate product had a higher molecular weight range than did the first-stage distillate. The PAH and hydroxy-PAH fractions isolated from the heavy distillate product were also of a higher molecular weight range than were the same fractions isolated from the hydrotreater unit feed. The opposite was true for the isolated NPAC fractions. (See Tables A-1 through A-3 in the appendix for keys to mass identifications of PAH, NPAC, and hydroxy-PAH fractions).

The LVMS spectra of the PAH, NPAC, and hydroxy-PAH fractions isolated from the CCRITSL recycle pasting solvent showed that the major components were of the same masses or alkyl series as were present in the heavy distillate product (Figure 10). The recycle pasting solvent's fractions were, however, more complex (had more masses represented at high intensities) and were composed of higher molecular weight components compared to the heavy distillate's isolated fractions.

Similar general results as those described above were achieved when comparisons of LVMS spectra from the other first-stage and second-stage CCRITSL materials listed in Table 1 were made (data not shown). Analyses of isolated RITSL fractions by LVMS showed these materials were generally comparable to the CCRITSL materials when analyzed by this method (data not shown).

Figures 11 and 12 show the LVMS results for the analyses of the PAH (top), NPAC (middle), and hydroxy-PAH (bottoms) fractions isolated from the ITSL (Wyodak) hydrotreater unit feed and recycle pasting solvent, respectively. Many of the components in these isolated fractions had masses similar to the components in the corresponding isolated fractions from the CCRITSL process. The ITSL (Wyodak) first-stage product also showed increased responses for the masses corresponding to parent and alkylated PAH compounds versus partially hydrogenated PAH than did the ITSL (Wyodak) second-stage product, as did the CCRITSL materials (see Tables A-1 through A-3 in the appendix for keys to LVMS mass identifications). The ITSL (Wyodak) hydrotreater unit feed and recycle pasting solvent were of a lower molecular weight range than were the comparable CCRITSL or ITSL products derived from Illinois No. 6 coal (see Later 1985). Coal liquefaction products from the same process derived from sub-bituminous coals have been noted to be of lower molecular weight ranges than products derived from bituminous coals by Wright and Dauble (1986).

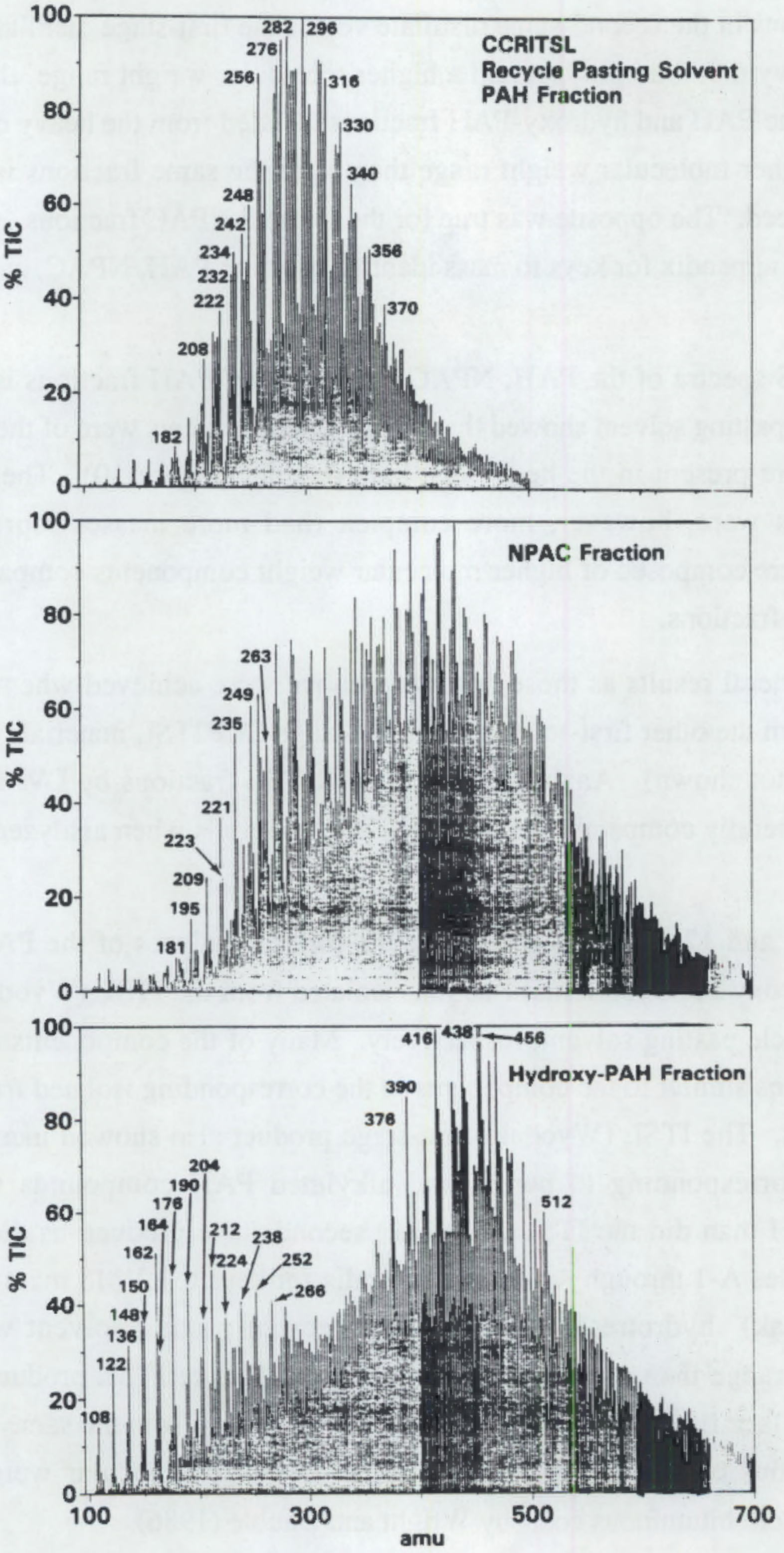

FIGURE 10. Low-Voltage Probe-Inlet Mass Spectra of the PAH (top), NPAC (middle), and Hydroxy-PAH (bottom) Fractions Isolated from the Close-Coupled, Reconfigured, Integrated Two-Stage Liquefaction Recycle Pasting Solvent. For a Key to Mass Identifications, See Tables A-1, A-2, and A-3 in the Appendix.

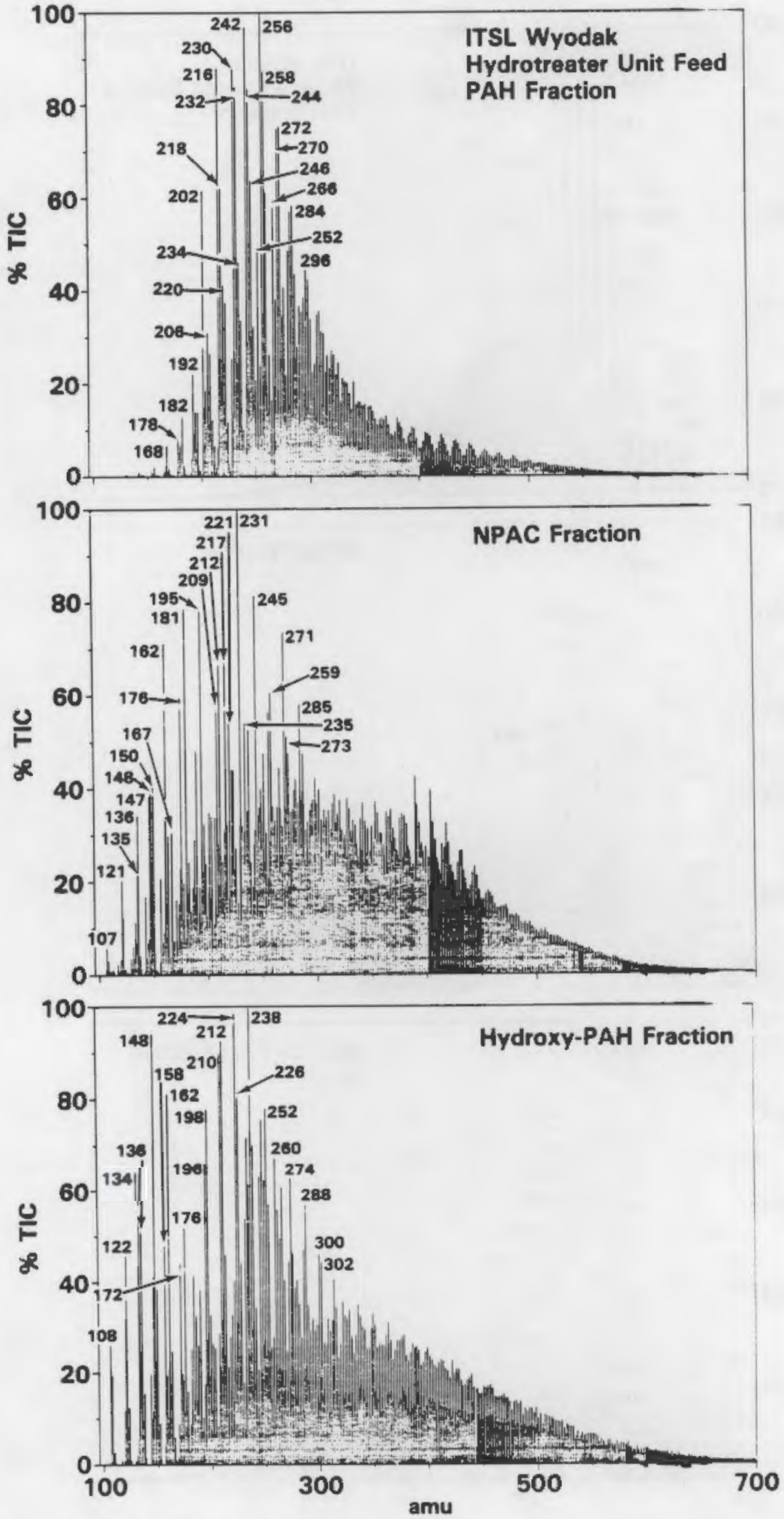

FIGURE 11. Low-Voltage Probe-Inlet Mass Spectra of the PAH (top), NPAC (middle), and Hydroxy-PAH (bottom) Fractions Isolated from the Integrated Two-Stage Liquefaction (Wyodak) Hydrotreater Unit Feed. See Text for Conditions. For a Key to Mass Identifications, See Tables A-1, A-2, and A-3 in the Appendix.

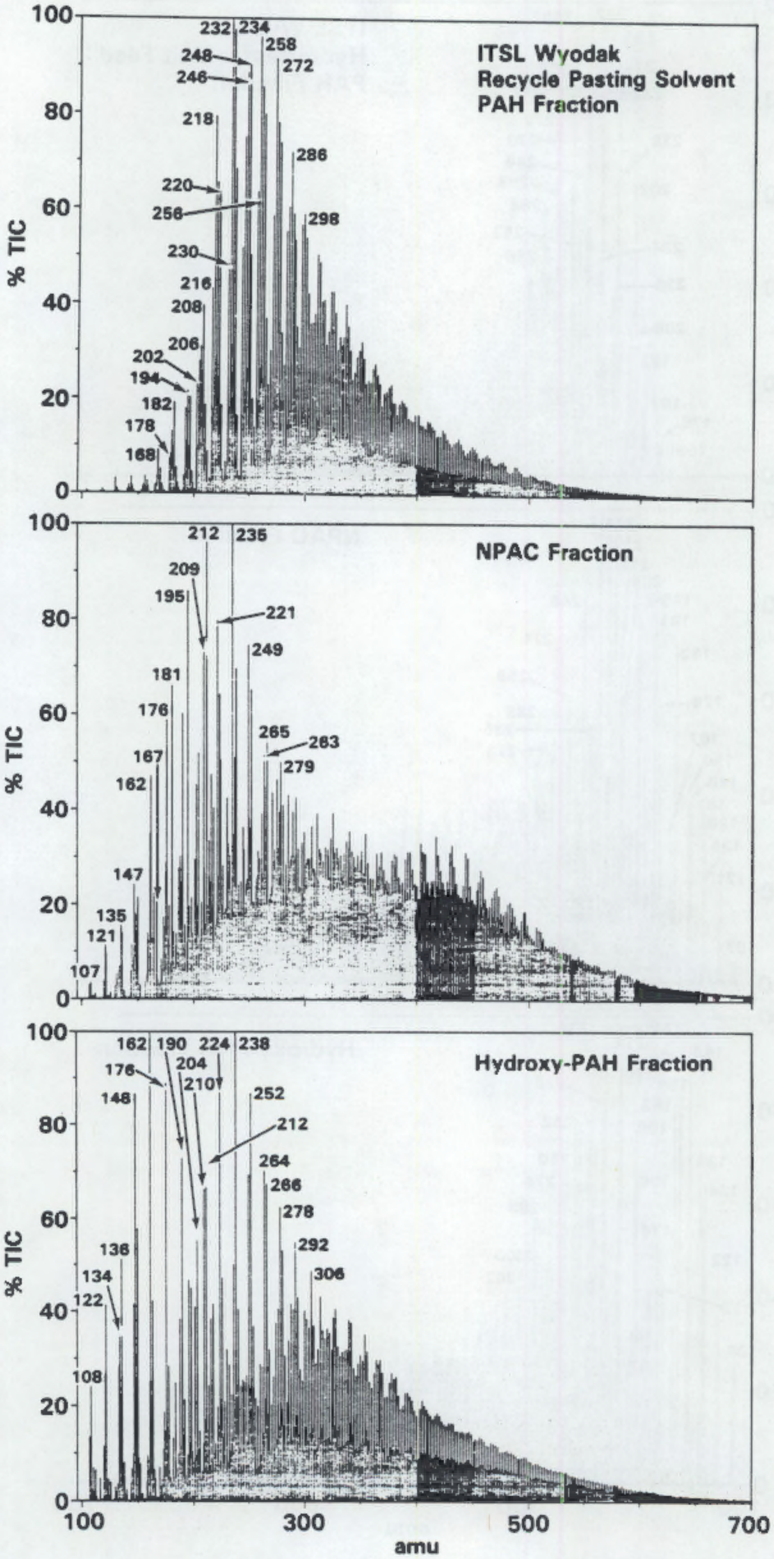

FIGURE 12. Low-Voltage Probe-Inlet Mass Spectra of the PAH (top), NPAC (middle), and Hydroxy-PAH (bottom) Fractions Isolated from the Integrated Two-Stage Liquefaction (Wyodak) Recycle Pasting Solvent. See Text for Conditions. For a Key to Mass Identifications, See Tables A-1, A-2, and A-3 in the Appendix.

Summary

Chemical analyses of the RITSL and CCRITSL product and internal process stream samples indicated there were little differences between the products based on a close-coupled to non-close-coupled pilot plant configuration. There was slight evidence, however, for the occurrence of retrograde reactions during the cooling down step of the RITSL process compared to the CCRITSL process, due to increased heteroatom-containing compositions in the thermal resids and recycle pasting sovent of the former versus the latter. The first-stage products of both processes had higher heteroatom (NPAC and hydroxy-PAH fractions) content and lower AH and hydroaromatic composition than did the second-stage products. Materials of higher boiling ranges (particularly the bottoms products) had increased NPAC and hydroxy-PAH contents with corresponding decreased AH contents. The RITSL, CCRITSL, and ITSL (Wyodak) process materials all had the same individual components present as have been identified in other two-stage direct coal liquefaction products. The RITSL and CCRITSL products had the same degree of alkylation and hydrogenation as the ITSL products, and were more alkylated and hydrogenated than the NTSL products. The major ions of the RITSL and CCRITSL chemical class fractions from the second-stage products tended to be more hydrogenated than the first-stage products, as were the with ITSL process materials. Compared to the ITSL (Illinois No. 6) products, the ITSL (Wyodak) products were of a generally lower molecular weight range and had increased AH content and decreased hydroxy-PAH content.

TOXICOLOGICAL TESTING

Microbial Mutagenicity

Microbial mutagenic activities for the RITSL, CCRITSL, and ITSL (Wyodak) process materials are given in Tables 14-16 for the first-stage, second-stage, and critical solvent deashing products, respectively. All RITSL and CCRITSL materials taken from the same sampling points gave reasonably comparable mutagenicity results. No significant mutagenicity was detected in the first-stage naphtha or overhead distillate product samples. Little to no mutagenic response was noted for any of the isolated AH or PAH chemical class fractions, in agreement with mutagenicity results for all direct coal liquefaction products studied to date. When microbial mutagenicity was detected in the first-stage or second-stage crude product materials, the majority of the microbial mutagenic response was expressed by the isolated NPAC fractions (with the exception of the hydrotreater vacuum flash bottoms). Microbial mutagenic response of coal liquefaction materials has historically been related to the NPAC compounds, particularly the amino-substituted PAH (Later *et al.* 1982; Later 1985; Wright *et al.* 1985; Wright and Later 1985; Wilson, Pelroy, and Cresto 1980). Some of the isolated hydroxy-PAH fractions

TABLE 14. Microbial Mutagenicity Results of Reconfigured, Integrated Two-Stage Liquefaction First-Stage Coal-Derived Products

			Microbial Mutagenicity (rev/µg); Chemical Class Fraction				
Sample Description	PNL Number	Process	AH	PAH	NPAC	Hydroxy-PAH	Crude
Naphtha or Light Fuel Oil; T-104; Overheads	50378-093	RITSL	0	0	0	0	0
	50378-136	CCRITSL	0	0	0	0	0
First-Stage Product Distillate; T-102; P-171; Overheads	50378-094	RITSL	0	0	<1	0	0
	50378-135	CCRITSL	0	0	0	0	0
	50378-111	ITSL (Wyodak)	0	0	0	0	0
Thermal Liquefaction Unit Distillate Process Solvent; T-102; Tray 8	50378-095	RITSL	0	0	71	0[a]	6
	50378-137	CCRITSL	0	0	38	0	3
Thermal Liquefaction Unit Product; T-102; Bottoms	50378-096	RITSL	0	0	20	14	11
	50378-142	CCRITSL	0	1	5	7	12
Hydrotreater Unit Feed; V-1064; Blend Tank	50378-097	RITSL	0	<1	6	2	7
	50378-146	CCRITSL	0	<1	12	4	7
	50378-112	ITSL (Wyodak)	0	0	13	0	3

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[a] Some activity present, but no correlation of 0.80 or greater

TABLE 15. Microbial Mutagenicity Results of Reconfigured, Integrated Two-Stage Liquefaction Second-Stage Coal-Derived Products

Sample Description	PNL Number	Process	Microbial Mutagenicity (rev/µg); Chemical Class Fraction				
			AH	PAH	NPAC	Hydroxy-PAH	Crude
Hydrotreater Unit Light Distillate Product; V-1078; <500°F	50378-098	RITSL	0	0	6	0	0
	50378-148	CCRITSL	0	0	23	0	<1
	50378-113	ITSL (Wyodak)	0	0	2	0	0
Hydrotreater Unit Heavy Distillate Product; V-1074; >500°F (Less Resids and Ash)	50378-100	RITSL	0	0	36	0[b]	3
	50378-101	RITSL	0	0	58	0[b]	7
	50378-139[a]	CCRITSL[a]	0	0	31	3	3
Hydrotreater Unit Vacuum Flash Bottoms (Resids and Ash); V-1082; Critical Solvent Deashing Feed	50378-099	RITSL	0	0	1	5	2
	50378-144	CCRITSL	0	0	1	3	<1
Recycle Pasting Solvent ; V-131B	50378-103	RITSL	0	0	1	4	1
	50378-138	CCRITSL	0	0	3	2	2
	50378-114	ITSL (Wyodak)	0	0	0[b]	0	0[b]

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[a] V-1072

[b] Some activity present, but no correlation of 0.80 or greater

TABLE 16. Microbial Mutagenicity Results of Reconfigured, Integrated Two-Stage Liquefaction Critical Solvent Deashing Coal-Derived Products

			Microbial Mutagenicity (rev/µg); Chemical Class Fraction				
Sample Description	PNL Number	Process	AH	PAH	NPAC	Hydroxy-PAH	Crude
Critical Solvent Deashing Thermal Resids[a]; KM: V-101-A	50378-102	RITSL	0	0	1	4	2
	50378-141	CCRITSL	0	<1	2	1	0[b]
Critical Solvent Deashing Ash Concentrate; KM: V-107	50378-104	RITSL	0	0	1	5	<1
	50378-150	CCRITSL	0	0	2	3	2

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[a] Blend of thermal and light thermal resids

[b] Some activity present, but no correlation greater than 0.80

expressed significant levels of mutagenic activity, although these levels were generally much less than the isolated NPAC fractions. The hydroxy-PAH fractions isolated from the critical solvent deashing feed, thermal resids, and ash concentrate did, however, show slightly increased mutagenic response compared to their respective NPAC fractions. The exact compounds responsible for the mutagenic response of the hydroxy-PAH fractions have not been identified. For those crudes exhibiting mutagenic activity, slightly higher responses were noted to be associated with the first-stage products versus the second-stage or critical solvent deashing products.

Microbial mutagenic responses of ITSL and NTSL products which correspond to many of the RITSL, CCRITSL, and ITSL (Wyodak) products have been reported by Later (1985). Compared to the ITSL and NTSL process materials, the results reported for the RITSL and CCRITSL products in Tables 14-16 gave no consistently higher or lower mutagenic responses. Comparable mutagenic activities of crudes and chemical class fractions were noted for the following NTSL products and their corresponding RITSL and CCRITSL products: naphtha, first-stage overhead distillate product, hydrotreater unit feed, hydrotreater vacuum flash bottoms, and critical solvent deashing ash concentrate. Comparable mutagenic activities of crudes and chemical class fractions were noted for the following ITSL products and their corresponding RITSL and CCRITSL products: first-stage distillate process solvent and critical solvent deashing ash concentrate. A slightly higher mutagenic response was noted for the NTSL distillation column bottoms crude and NPAC fraction compared to its RITSL and CCRITSL heavy distillate product counterparts. Slightly higher mutagenic responses were noted for the NPAC fractions isolated from the ITSL naphtha and first-stage distillate overhead products compared to their RITSL and CCRITSL NPAC counterparts. Slightly lower mutagenic responses were noted for all the ITSL NPAC fractions and crude materials corresponding to the RITSL and CCRITSL hydrotreater feed, light and heavy distillate products, and recycle pasting solvent, as well as for the NPAC fraction isolated from the NTSL product corresponding to the RITSL and CCRITSL hydrotreater unit light distillate product.

Comparable mutagenic activities were noted between the ITSL (Wyodak) recycle pasting solvent and hydrotreater light distillate product and their ITSL counterparts derived from the higher rank Illinois No. 6 coal reported by Later (1985). Slightly lower and higher mutagenicities were noted for the ITSL (Wyodak) first-stage overhead distillate product and the hydrotreater unit feed, respectively, when compared to their ITSL (Illinois No. 6) counterparts. These results were not consistent with previously reported results from the testing of H-Coal products derived from different ranks of coal. Lower levels of mutagenic activity were noted to be associated with the products derived from sub-bituminous coal compared to the products derived from a bituminous coal by Wright and Dauble (1986). This inconsistency may be related to the overall low levels of mutagenic activity expressed by ITSL products compared to the H-Coal products.

Initiation/Promotion Tumorigenicity Assay

Results of the I/P assay to determine the tumor initiation activities of the CCRITSL heavy distillate product and hydrotreater unit feed are shown in Figure 13 with methylene chloride solvent control data. The percent incidence is graphed on the top, while the total number of tumors normalized to groups of 30 mice is graphed on the bottom. The highest percent incidence was expressed by the hydrotreater unit feed giving a reponse of 90% compared to the heavy distillate product and solvent control at 73 and 21%, respectively. The hydrotreater unit feed elicited 113 total number of tumors compared to 39 total number of tumors from the same dose of heavy distillate product and 7 total number of tumors from the solvent control. The mean number of tumors per mouse ± standard deviation of the mean was 0.24 ± 0.37 for the solvent control, 1.3 ± 1.2 for the heavy distillate product (significantly higher response than the solvent control at a 95% confidence limit, α=0.05), and 3.77 ± 2.29 for the hydrotreater unit feed (significantly higher response than the heavy distillate product at α=0.05). The increased tumor initiation activity of the hydrotreater unit feed compared to the heavy distillate product corresponded to higher concentrations of parent PAH (such as benzo[a]pyrene) in the feed versus the product, and increased concentrations of aliphatic hydrocarbons and hydroaromatic compounds in the product versus the feed. Tumorigenic responses of coal liquefaction materials have historically been related to their PAH content, with AH and hydroaromatic compounds generally exhibiting little to no significant activity (Mahlum *et al.* 1984).

The mean number of tumors per mouse data from the CCRITSL heavy distillate product were comparable to the I/P results reported for the ITSL and NTSL distillation column bottoms reported by Later (1985). The ITSL and NTSL distillation column bottoms elicited 1.1 ± 1.4 and 1.3 ± 1.2 mean numbers of tumors per mouse responses which were not significantly different from the CCRITSL heavy distillate product at α=0.05. Significantly higher mean numbers of tumors per mouse were expressed by both the ITSL and NTSL hydrotreater feeds (3.2 and 2.2, respectively) compared to their hydrotreated heavy distillate products. Similar results were found for the CCRITSL hydrotreater feed and heavy distillate product.

Aquatic Toxicity

Acute toxic responses of *D. magna* to WSF derived from the light and heavy distillate products from the RITSL process are given in Table 17. Differences in acute toxic response of *D. magna* to WSF derived from the two distillate products can be related to their solubility in

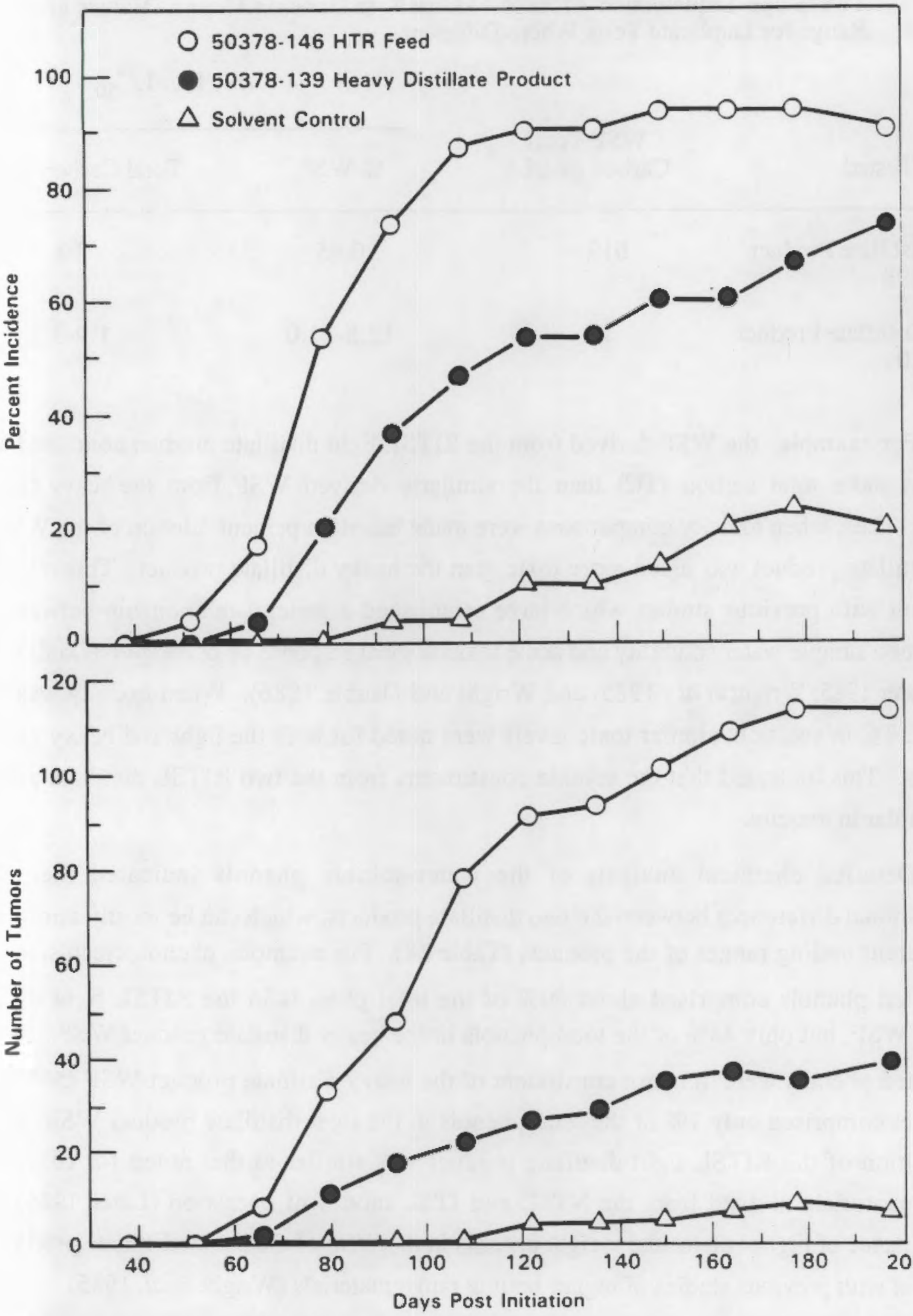

FIGURE 13. Initiation/Promotion Mouse Skin Tumorigenicity Results for the Close-Coupled, Reconfigured, Integrated Two-Stage Liquefaction Hydrotreater Unit Feed and Heavy Distillate Product. Top: Percent Incidence. Bottom: Total Number of Tumors per Mouse Data Normalized to Groups of 30 Mice.

TABLE 17. Acute Toxicity of Water-Soluble Fractions Derived from Reconfigured, Integrated Two-Stage Liquefaction Process Materials to *Daphnia Magna*. Values given as a Range for Duplicate Tests Where Different.

Sample Tested	WSF Total Carbon (mg/L)	48 Hour LC_{50} % WSF	48 Hour LC_{50} Total Carbon (mg/L)
Light Distillate Product 50378-098	619	0.45	2.8
Heavy Distillate Product 50378-101	15	12.5-21.0	1.9-3.2

water. For example, the WSF derived from the RITSL light distillate product contained about 40 times more total carbon (TC) than the similarly derived WSF from the heavy distillate product. Thus, when toxicity comparisons were made based on percent dilution of the WSF, the light distillate product was much more toxic than the heavy distillate product. This result was consistent with previous studies which have established a general relationship between coal liquefaction sample water solubility and acute toxicological response of *D. magna* (Dauble *et al.* 1983; Later 1985; Wright *et al*. 1985; and Wright and Dauble 1986). When toxicity was based on mg/L TC in solution, similar toxic levels were noted for both the light and heavy distillate products. This indicated that the soluble constituents from the two RITSL distillate products were similar in toxicity.

Detailed chemical analysis of the water-soluble phenols indicated there were compositional differences between the two distillate products, which can be mostly attributed to the different boiling ranges of the products (Table 18). For example, phenol, cresols, and C_2-substituted phenols comprised about 80% of the total phenols in the RITSL light distillate product WSF, but only 44% of the total phenols in the heavy distillate product WSF. The C_5-substituted phenols were a major constituent of the heavy distillate product WSF (50% of the total), yet comprised only 1% of the total phenols in the light distillate product WSF. Phenol composition of the RITSL light distillate product was similar to that noted for comparable process materials derived from the NTSL and ITSL modes of operation (Later 1985). The predominance of higher molecular weight phenols in the WSF of the heavy distillate product was consistent with previous studies of higher boiling range materials (Wright *et al.* 1985).

Total nitrogen bases were 110 mg/L and 0.9 mg/L for the WSF from the light and heavy distillate products, respectively. There was little difference in the amount of water-soluble nitrogen bases relative to the total phenols in solution.

TABLE 18. Phenol Concentrations in Water-Soluble Fractions Derived from Reconfigured, Integrated Two-Stage Liquefaction Process Materials. Concentrations (mg/L) Expressed as Means of Duplicate Determinations.

Compound	Light Distillate Product 50378-098	Heavy Distillate Product 50378-101
Phenol	122.5	0.7
Cresols	198.6	0.5
C_2-Phenols	100.9	0.3
C_3-Phenols	42.1	0.1
C_4-Phenols	8.7	<0.1
C_5-Phenols, and greater	4.7	1.7
Indanols	31.2	<0.1
C_1-Indanols	11.3	<0.1
C_2-Indanols	2.5	<0.1
Total	522.5	3.4

Based on the presence of equal amounts of toxic constituents in solution, the second-stage hydrotreater overheads product from the NTSL process was slightly more toxic to daphnids than was the RITSL light distillate product. The 48 hr LC_{50} reported by Later (1985) for the NTSL product was 1.5 mg/L TC. Using the same criteria, the ITSL second-stage hydrotreater overhead product (48 hr LC_{50}=6.4 mg/L TC) was slightly less toxic than was the RITSL light distillate product.

Summary

The location of the critical solvent deashing unit did not appear to change the tumorigenic potency of the heavy distillate product derived from the CCRITSL process compared to the ITSL process. Similar decreases in tumor initiation activities between the hydrotreater feeds and heavy distillate products were noted for the CCRITSL process as were noted for the ITSL and NTSL processes. The microbial mutagenic responses of the RITSL, CCRITSL, and ITSL (Wyodak) materials were low, consistent with the low microbial mutagenic responses of the comparable NTSL and ITSL materials. The second-stage process materials exhibited lower mutagenic responses than did the first-stage process materials, in general. The RITSL hydrotreater distillate products showed a toxic response to daphnids intermediate to the responses of the ITSL and NTSL hydrotreater overhead products based on the same total carbon dosage.

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APPENDIX

KEY TO MASS IDENTIFICATIONS OF LOW-VOLTAGE PROBE-INLET MASS SPECTRA

TABLE A-1. Key to Low-Voltage Mass Spectra of Polycyclic Aromatic Hydrocarbon Fractions. Nominal Masses for Alkylated Homologous Series.

Compound[a]	C_0	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}
Benzene	78	92	106	120	134	148	162	176	190	204	218	232
Indene	116	130	144	158	172	186	200	214	228	242	256	270
Indane	118	132	146	160	174	188	202	216	230	244	258	272
Naphthalene	128	142	156	170	184	198	212	226	240	254	268	282
Acenaphthalene	152	166	180	194	208	222	236	250	264	278	292	306
Biphenyl/ Acenaphthene	154	168	182	196	210	224	238	252	266	280	294	308
Fluorene/Phenalene	166	180	194	208	222	236	250	264	278	292	306	320
Phenanthrene	178	192	206	220	234	248	262	276	290	304	318	332
Cyclopenta[def]-phenanthrene	190	204	218	232	246	260	274	288	302	316	330	344
Pyrene/Fluoranthene	202	216	230	244	258	272	286	300	314	328	342	356
Phenylnaphthalene	204	218	232	246	260	274	288	302	316	330	344	358
Benzofluorene	216	230	244	258	272	286	300	314	328	342	356	370
Cyclopenta[cd]-pyrene/Benzo-[ghi]fluoranthene	226	240	254	268	282	296	310	324	338	352	366	380
Chrysene/Benzo-[a]anthracene	228	242	256	270	284	298	312	326	340	354	368	382
Cyclopentachrysenes/Benzo[a]-anthracenes	240	254	268	282	296	310	324	338	352	366	380	394
Phenylfluorene	242	256	270	284	298	312	326	340	354	368	382	396
Benzopyrenes/ Benzofluoranthenes	252	266	280	294	308	322	336	350	364	378	392	406
Binaphthyls	254	268	282	296	310	324	338	352	366	380	394	408
Cyclopentabenzopyrenes	264	278	292	306	320	334	348	362	376	390	404	418
Dibenzofluorenes	266	280	294	308	322	336	350	364	378	392	406	420
Indenopyrenes/ Cyclopentachrysenes	276	290	304	318	332	346	360	374	388	402	416	430
Dibenzanthracenes/Phenanthrenes	278	292	306	320	334	348	362	376	390	404	418	432

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[a] In most cases, only selected isomers are given. The MS data merely provide assistance in determining isomer groups, rather than identifying precise molecular structures. Furthermore, several of the mass assignments can be attributed directly to hydroaromatic species of the PAH. Increments of two mass units for dihydro-PAH species, four mass units for tetrahydro-PAH species, etc. can be used to provide a key for the hydroaromatic compounds.

TABLE A-2. Key to Low-Voltage Mass Spectra of Nitrogen-Containing Polycyclic Aromatic Compound Fractions. Nominal Masses for Alkylated Homologous Series.

Compound[a]	C_0	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}
Pyridine	79	93	107	121	135	149	163	177	191	205	219	233
Indole	117	131	145	159	173	187	201	215	229	243	257	271
Quinoline/Isoquinoline	129	143	157	171	185	199	213	227	241	255	269	283
Azaacenaphthalene	153	167	181	195	209	223	237	251	265	279	293	307
Azaacenaphthene/ Azabiphenyls	155	169	183	197	211	225	239	253	267	281	295	309
Carbazole	167	181	195	209	223	237	251	265	279	293	307	321
Benzoquinolines	179	193	207	221	235	249	263	277	291	305	319	333
Benzo[def]carbazole	191	205	219	233	247	261	275	289	303	317	331	345
Azapyrene/Azafluoranthene	203	217	231	245	259	273	287	301	315	329	343	357
Azaphenylnaphthalene	205	219	233	247	261	275	289	303	317	331	345	359
Benzocarbazoles	217	231	245	259	273	287	301	315	329	343	357	371
Azabenzo[ghi]-fluoranthene/ Azacyclopentapyrene	227	241	255	269	283	297	311	325	339	353	367	381
Azachrysenes/Azabenzanthracenes	229	243	257	271	285	299	313	327	341	355	369	383
Azacyclopentachrysene	241	255	269	283	297	311	325	339	353	367	381	395
Azabenzopyrenes/ Azabenzofluoranthenes	253	267	281	295	309	323	337	351	365	379	393	407
Azabinaphthyls	255	269	283	297	311	325	339	353	367	381	395	409
Azacyclopentabenzopyrenes	265	279	293	307	321	335	349	363	377	391	405	419
Dibenzocarbazoles	267	281	295	309	323	337	351	365	379	395	407	421
Azaindenopyrenes	277	291	305	319	333	347	361	375	389	403	417	431

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[a] In most cases, only selected isomers are given. The MS data merely provide assistance in determining isomer groups, rather than identifying precise molecular structures. Only pyrrolic and pyridinic NPAC have been considered. Hydro-substituted NPAC were also present in most A_3 fractions and appropriate masses can be determined by addition of two mass units to the parent PAH molecular weight for dihydro-substitution, four mass units for tetrahydro-substitution, etc.

TABLE A-3. Key to Low-Voltage Mass Spectra of Hydroxy-Substituted Polycyclic Aromatic Hydrocarbon Fractions. Nominal Masses for Alkylated Homologous Series.

Compound[a]	C_0	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}
Phenol	94	108	122	136	150	164	178	192	206	220	234	248
Indenols	132	146	160	174	188	202	216	230	244	258	272	286
Indanols	134	148	162	176	190	204	218	232	246	260	274	288
Naphthols	144	158	172	186	200	214	228	242	256	270	284	298
Acenaphthylenols	168	182	196	210	224	238	252	266	280	294	308	322
Hydroxybiphenyls/ Acenaphthenols	170	184	198	212	226	240	254	268	282	296	310	324
Hydroxyfluorenes	182	196	210	224	238	252	266	280	294	308	322	336
Hydroxyphenanthrenes/Anthracenes	194	208	222	236	250	264	278	292	306	320	334	348
Hydroxycyclopentaphenanthrenes	206	220	234	248	262	276	290	304	318	332	346	360
Hydroxypyrenes/ Fluoranthenes	218	232	246	260	274	288	302	316	330	344	358	372
Hydroxyphenylnaphthalenes	220	234	248	262	276	290	304	318	332	346	360	374
Hydroxybenzofluorenes	232	246	260	274	288	302	316	330	344	358	372	386
Hydroxyindenopyrenes	242	256	270	284	298	312	326	340	354	368	382	396
Hydroxychrysenes/ Benzanthracenes	244	258	272	286	300	314	328	342	356	370	384	398
Hydroxycyclopentachrysenes	256	270	284	298	312	326	340	354	368	382	396	410
Hydroxyphenylfluorenes	258	272	286	300	314	328	342	356	370	384	398	412
Hydroxybenzopyrenes/Benzofluoranthenes	268	282	296	310	324	338	352	366	380	394	408	422
Hydroxybinaphthyls	270	284	298	312	326	340	354	368	382	396	410	424
Hydroxycyclopentabenzopyrenes	280	294	308	322	336	350	364	378	392	406	420	434
Hydroxydibenzofluorenes	282	296	310	324	338	352	366	380	394	408	422	436
Hydroxyindenopyrenes	292	306	320	334	348	362	376	390	404	418	432	446
Hydroxybenzochrysenes	294	308	322	336	350	364	378	392	406	420	434	448

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[a] In most cases, only selected isomers are given. The MS data merely provide assistance in determining isomer groups, rather than identifying precise molecular structures.

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