HRI Catalytic Two-Stage Liquefaction (CTSL) Process Materials: Chemical Analysis and Biological Testing

**C. W. Wright
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December 1985

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**Pacific Northwest Laboratory
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by Battelle Memorial Institute**

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HRI CATALYTIC TWO-STAGE
LIQUEFACTION (CTSL) PROCESS
MATERIALS: CHEMICAL ANALYSIS
AND BIOLOGICAL TESTING

C. W. Wright
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FOREWORD

This report presents data from the chemical analysis and biological testing of coal liquefaction materials obtained from the Hydrocarbon Research, Incorporated (HRI) catalytic two-stage liquefaction (CTSL) process. Materials from both an experimental run and a 25-day demonstration run were analyzed. Chemical methods of analysis included adsorption column chromatography, high-resolution gas chromatography, gas chromatography/mass spectrometry, low-voltage probe-inlet mass spectrometry, and proton nuclear magnetic resonance spectroscopy. The biological activity was evaluated using the standard microbial mutagenicity assay and an initiation/promotion assay for mouse-skin tumorigenicity. Where applicable, the results obtained from the analyses of the CTSL materials have been compared to those obtained from the integrated and nonintegrated two-stage coal liquefaction processes.

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EXECUTIVE SUMMARY

The U.S. Department of Energy (DOE) supports an ongoing effort to chemically analyze and biologically test materials from various innovative coal liquefaction processes to evaluate these alternative energy sources from a health and environmental standpoint.

Data were compiled from the chemical analysis and biological testing of process materials from the directly coupled, catalytic-catalytic two-stage direct coal liquefaction (CTSL) process operated by Hydrocarbon Research, Incorporated. In the CTSL process, a catalyst is used in both the first- and second-stage reactors, with the first stage operated at relatively lower temperatures. These results were compared with those obtained from the analyses of other two-stage coal liquefaction process materials that had catalysts in the second-stage hydrogenation reactor but did not incorporate a catalyst in the first-stage thermal reactor; namely, the integrated and nonintegrated two-stage liquefaction processes (ITSL and NTSL, respectively).

Data were acquired on the pressure filter liquid (PFL; an internal post-second-stage process material) and the product distillate blend (PDB; more representative of a final product) from a 25-day demonstration run of the CTSL process. In addition, analyses were performed on both first- and second-stage materials from a previous experimental run of this coal liquefaction process. Samples were chemically analyzed by column adsorption chromatography, high-resolution gas chromatography (GC), GC/mass spectrometry (MS), low-voltage probe-inlet MS, and proton nuclear magnetic resonance. Biological testing was performed using the histidine reversion assay for microbial mutagenicity and the initiation/promotion assay for tumorigenicity in mouse skin.

PRESSURE FILTER LIQUIDS (PFL)

The following results were obtained from the analyses of PFL materials from selected days of the 25-day demonstration run. The major components were aliphatic hydrocarbons (AH), parent and alkylated polycyclic aromatic hydrocarbons (PAH), and parent and alkylated hydroaromatic PAH. There was an increase in heteroatomic, nitrogen-containing polycyclic aromatic compounds

(NPAC) and hydroxy-substituted PAH (hydroxy-PAH) content as the length of pilot plant operation time increased. The composition of the PFL material boiling above 975°F, as well as the concentration of heavy-molecular-weight PAH components (greater than four aromatic rings), also increased over the duration of the demonstration run. A concomitant decrease in AH and hydroaromatic content was noted in the PFL materials as the demonstration run progressed. Microbial mutagenicity of the PFL materials increased with pilot plant operation time, and there was also a tendency toward increased tumorigenic response in the PFL materials from later compared to those of earlier periods of the 25-day demonstration run. Although the most pronounced chemical composition changes occurred during the initial days of pilot-plant operation while temperatures were equilibrating, the overall changes indicated the deleterious effects of catalyst deactivation during the demonstration run.

PRODUCT DISTILLATE BLEND (POB)

Chemical components in the CTSL PDB were similar to those detected in the PFL, except that they were of a lower-molecular-weight range (an effect of the blended lower-boiling distillates used to make the PDB). The PDB gave a lower tumorigenic response than did the PFL; likewise, a lower mutagenic response was noted for the PDB as compared to the PFL materials from after about 10 days of pilot-plant operation. The PDB also displayed some degree of direct-acting mutagenesis.

FIRST- AND SECOND-STAGE MATERIALS

Results of chemical analyses were similar for both the first- and second-stage materials from the experimental CTSL run, with the exception that the first-stage material had more heavy-molecular-weight components. The tumorigenic response of the first-stage material tended to be slightly greater than that of the second-stage material. Both the tumorigenic response and the molecular-weight range of these materials were less than those of the 25-day demonstration run process materials.

Compared to the ITSL and NTSL processes, the CTSL materials, in general, had lower concentrations of AH, PAH and hydroaromatic PAH. The CTSL materials

had either the same degree of alkylation and hydrogenation as the ITSL and NTSL materials, or less. The CTSL PDB gave lower tumorigenic response than did the ITSL and NTSL materials; lower mutagenic response than the NTSL material; and slightly higher mutagenic response than the ITSL materials. The chemical composition of the CTSL PDB most closely resembled that of the NTSL material. Greater reductions in tumorigenicity were noted between first- and second-stage materials from the ITSL and NTSL processes than in the CTSL process, indicating that a catalyst in the first-stage reactor may reduce the tumorigenic potential of first-stage coal liquefaction products.

Chemical analysis and biological testing data on the CTSL process materials correlated with previous data showing that mutagenic potency was generally contained in NPAC fractions and that tumorigenic potential was generally a function of increased boiling point.

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LIST OF ABBREVIATIONS

AH	= Aliphatic hydrocarbon(s)
amino-PAH	= Amino-substituted polycyclic aromatic hydrocarbon(s)
amu	= Atomic mass unit
API	= American Petroleum Institute
BaP	= Benzo[a]pyrene
bp	= Boiling point
CAS	= Continuous atmospheric still
cm	= Centimeter(s)
CTSL	= Catalytic two-stage liquefaction
°C	= Degrees Celsius
°F	= Degrees Fahrenheit
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
HP	= Hewlett-Packard
HRGC	= High-resolution gas chromatography
HRI	= Hydrocarbon Research, Incorporated
HTR	= Hydrotreater
hydroxy-PAH	= Hydroxy-substituted polycyclic aromatic hydrocarbon(s)
IBP	= Initial boiling point
ID	= Inside diameter
I/P	= Initiation/promotion
ISTD	= Internal standard
ITSL	= Integrated two-stage liquefaction
LVMS	= Low-voltage probe-inlet mass spectrometry
m	= Meter(s)
MAF	= Moisture and ash free
mg	= Milligram(s)
µg	= Microgram(s)
ml	= Milliliter(s)
µl	= Microliter(s)
mm	= Millimeter(s)
µm	= Micrometer(s)
MS	= Mass spectrometry

ng	= Nanogram(s)
NMR	= Nuclear magnetic resonance
NPAC	= Nitrogen-containing polycyclic aromatic compound(s)
NTSL	= Nonintegrated two-stage liquefaction
PA ₁	= Aliphatic hydrocarbon(s) fraction
PA ₂	= Hydroaromatic compound(s) fraction
PA ₃	= Dihydro-PAH and less-than-three-aromatic-ringed PAH fraction
PA ₄	= Greater-than-three-aromatic-ringed PAH and some polar polycyclic aromatic compound(s) fraction
PAC	= Polycyclic aromatic compound(s)
PAH	= Polycyclic aromatic hydrocarbon(s)
PDB	= Product distillate blend
PDU	= Process development unit
PFL	= Pressure filter liquid(s)
PMA	= Phorbol myristate acetate
PNL	= Pacific Northwest Laboratory
ppm	= Parts per million
psig	= Pounds per square inch
S.	= <u>Salmonella</u>
S9	= Metabolic enzyme system used in microbial mutagenicity assay
sec	= Second(s)
SRC	= Solvent refined coal
TA98	= Designation for strain of <u>Salmonella typhimurium</u> used in microbial mutagenicity assay
TA100	= Designation for strain of <u>Salmonella typhimurium</u> used in microbial mutagenicity assay
THF	= Tetrahydrofuran
TIC	= Total ion current
TLP	= Total liquid product
TMS	= Trimethylsilane
V	= Volt(s)
Wt	= Weight
Wt %	= Weight percent
2-AA	= 2-Aminoanthracene
2-CA	= 2-Chloroanthracene

INTRODUCTION

The U.S. Department of Energy (DOE) is responsible for evaluating energy technologies to provide a broad range of future energy options that are acceptable from a health and environmental standpoint. Coal liquefaction is a means by which abundant U.S. supplies of coal can be utilized to produce petroleum substitutes, additives or extenders. Over the past few years, DOE has supported the chemical analysis and biological testing of materials from various innovative coal liquefaction processes as the technology has evolved. The purpose of this report is to present data from the biological and chemical analyses of coal liquefaction materials from the advanced catalytic two-stage liquefaction (CTSL) coal conversion process operated by Hydrocarbon Research, Incorporated (HRI) under contract to DOE.

During July of 1984, HRI performed a 25-day demonstration run of their CTSL coal conversion process at Lawrenceville, NJ. An objective of this CTSL process was to take advantage of catalytic reactions in converting coal to a liquid; both the first-stage solvation and hydrogenation and second-stage hydroconversion reactors incorporated catalysts with no distillation or solids separation occurring until after the second stage. Samples of the pressure filter liquid (PFL; the solids-free portion of the recycle slurry oil) were taken each day of the demonstration run. The pressure filter is a postconversion treatment step that follows the second-stage catalytic reactor in the CTSL process; the PFL samples represent an internal process stream material. Differences observed in the chemical composition and biological activity of the PFL samples during the course of the demonstration run are probably attributable to catalyst aging effects. A product distillate blend (PDB), more representative of the actual net product from the CTSL process, was also supplied by HRI. No first-stage samples were supplied from the 25-day demonstration run.

Preliminary results of the chemical composition and biological testing of sample materials from both the first and second stages of experimental runs of the CTSL process unit have been previously reported by Later and Wilson (1985). This report will present data from the analysis of PFL samples from selected days of the 25-day CTSL demonstration run. The PFL from Days 1, 5,

10, 15, 19, 24 and a composite (or intermediate) PFL material were chemically analyzed and biologically tested. In addition, data are presented from the detailed chemical analysis and biological testing of a PDB and two previously reported materials (a first- and a second-stage) from an experimental CTSL run.

Chemical analyses were performed on fractions isolated from the PFL, PDB and experimental run materials by adsorption column chromatography. Chemical class fractions of aliphatic hydrocarbons (AH), polycyclic aromatic hydrocarbons (PAH), nitrogen-containing polycyclic aromatic compounds (NPAC) and hydroxy-substituted PAH (hydroxy-PAH) were produced using neutral alumina as an adsorbant. Due to the high concentration of hydrogenated and partially hydrogenated components present in these samples, the hydroaromatic compounds found in the samples were isolated using picric-acid-coated alumina as an adsorbant. Selected chemical fractions isolated from the PFL, PDB, and first- and second-stage sample materials were then analyzed by high-resolution gas chromatography (HRGC), gas chromatography/mass spectrometry (GC/MS), low-voltage probe-inlet mass spectrometry (LVMS) and proton nuclear magnetic resonance (NMR). Individual components were quantified in the PAH and NPAC fractions since these chemical class fractions were previously shown to be the most tumorigenic and mutagenic fractions, respectively, isolated from coal-derived materials, as determined by laboratory bioassays (Later et al., 1982, 1983; Wilson et al., 1984; Mahlum et al., 1983, 1984).

The biological activity of the CTSL materials was measured using two bioassays. The mutagenic response of all crude samples and selected chemical class fractions were measured using the histidine reversion microbial mutagenicity test with Salmonella typhimurium, TA98 and TA100. Selected crudes were tested for carcinogenic potential using the initiation/promotion (I/P) assay for tumorigenicity in mouse skin.

Where applicable, the data from the analyses of the CTSL materials are compared to the results obtained from the chemical analysis and biological testing of materials from other two-stage coal liquefaction processes. The comparative processes include the integrated two-stage liquefaction (ITSL) and the nonintegrated two-stage liquefaction (NTSL) processes.

ENGINEERING

Two-stage liquefaction bench-scale experiments have been performed at HRI since the early 1970s. Initial experiments used Wyodak coal, with and without catalysts, in the first-stage reactor. In the 1980s, experiments were run using Illinois No. 6 coal; a short contact time, thermal (high temperature, $>800^{\circ}\text{F}$), first-stage reactor was closely coupled to an ebullated-bed, catalytic, second-stage reactor that was operated at a milder temperature. Two other configurations of this two-stage process were also investigated: 1) a back-mixed, high residence time, first-stage thermal reactor was followed by a catalytic second stage; and 2) both stages were operated using catalytic ebullated beds at equivalent high temperatures (Comolli, 1984).

Improvements in selectivity were noted: each of the thermal-catalytic systems gave lower gas make, higher distillate yields, and better hydrogen efficiency albeit at two to four times the reactor residence of the original single-stage H-Coal process. Micro-autoclave and bench-unit experiments conducted in 1982 with two catalytic stages indicated that significant improvements in conversion and hydrogenation over existing technology were feasible (Comolli, 1984). These findings resulted in the present 2-year, DOE-sponsored program at HRI to investigate the directly coupled, catalytic-catalytic two-stage direct coal liquefaction process, CTSL, using low operating temperatures in the first stage.

A schematic flow diagram of the CTSL process is shown in Figure 1. Coal is slurried with process-derived heavy recycle oils, pressurized, mixed with hydrogen, and fed to the first catalytic ebullated-bed reactor. Operation of the first stage is controlled at low temperatures (less than 800°F) to promote hydrogenation that weakens the coal matrix. In addition, the low first-stage reactor temperature assists in maintaining the donor potential of the process solvent and in minimizing cracking, dehydrogenation and polymerization reactions.

The total first-stage product, including reacted and unreacted coal, is next passed directly to the second ebullated-bed catalytic reactor without any

FIGURE 1. CTSL Process Schematic

intermediate distillation or separation steps. In the second stage, high-temperature hydrotreatment results in liquefaction and heteroatom removal of the feed material. The severity of this stage can be selectively regulated to control distillate and product composition. Both stages are conventional ebullated-bed reactors, utilizing 1/16-in. extrudate catalysts that allow fluidized catalyst operation over a wide range of viscosity and density.

Following the second stage, the product is separated via hot and cold separators and distilled using a continuous atmospheric still (CAS). The CAS bottoms are then pressure-filtered and vacuum-distilled (see Figure 1). The recycle solvent used to slurry the feed coal is an oil composed of CAS bottoms and/or pressure-filtered bottoms liquid. The solids and residual oil composition in the recycle stream can be varied for optimum process performance.

The objective of run #227-20, from which the samples were taken, was to demonstrate the new CTSL process technology while processing Illinois No. 6 coal over a 25-day period under optimized, lined-out conditions. Operating conditions and a set of normalized yields for Period 15 are given in Table 1. The plant was operated under constant conditions except for Days 1 through 3, when equilibrated operating temperatures were established gradually.

TABLE 1. Operating Conditions and Yield Results, Run #227-20/Period 15, Illinois No. 6 Demonstration Run (from Comolli, 1984)

Operating Conditions		Yields, Weight % (Wt %) Moisture and Ash Free (MAF) Coal	
<u>First Stage</u>		C ₁ -C ₃	6.6
Temperature (°F)	750	C ₄ -390°F	18.2
Catalyst	Amocat 1C	390-500°F	13.7
		500-650°F	19.1
		650-850°F	12.5
<u>Second Stage</u>		850-975°F	4.1
		975°F+	12.1
Temperature (°F)	825	Unconverted coal	5.2
Catalyst	Amocat 1A	H ₂ O + CO + CO ₂	10.4
		NH ₃	1.2
Pressure, total psig	2500	H ₂ S	3.0
Space velocity/stage, pounds of dry coal/hour/ft ³ catalyst	68	Total	106.1
Performance Parameters Wt % MAF Coal		Liquid Product Quality	
Coal conversion	94.8	°API gravity	23.7
975°F+ conversion	82.8	Sulfur (Wt %)	0.036
Hydrogen efficiency	11.1	Nitrogen (Wt %)	0.32
C ₄ -975°F	67.6		

SAMPLE MATERIALS

Materials sampled from 25-day demonstration run #227-20 of the HRI CTSL process unit in Lawrenceville, NJ, are listed in Table 2. These samples were shipped to the Pacific Northwest Laboratory (PNL) for chemical analysis and biological testing. Samples are listed with a brief description, a PNL repository number, and an HRI identification number. Also included in Table 2 are samples of first- and second-stage internal process materials from a previous experimental run of the CTSL process with distillate recycle. Preliminary analyses of these two materials have been reported by Later and Wilson (1985); additional information will be supplied in this report. All samples listed in Table 2 were tested for microbial mutagenicity. Only a limited number of the samples were both chemically analyzed and biologically tested for tumorigenic potential; these samples are indicated in Table 2.

Forty-gram samples of the PFL were obtained on each day of the demonstration run. The PFL represents a post-second-stage internal stream material with a nominal boiling point (bp) >500°F; approximately 35% (by weight) of the PFL was resid material. Table 3 provides distillation and elemental analyses data for selected PFL samples at approximately 5-day intervals. Changes in PFL composition that were observed during the course of the demonstration run included a general decrease in the carbon content of the material and an increase in the heteroatom content (sulfur and nitrogen) with catalyst age and duration of the run. Furthermore, the °API gravity decreased and 975°F+ fraction weight increased during the course of demonstration run #227-20. These trends will be correlated with other observed changes in PFL chemical composition and biological activity later in this report.

In addition to the 40-g daily samples, 500 g of PFL from an intermediate run period (hereafter referred to as the PFL composite) and 500 g of a PDB from the same run period were supplied by HRI. The PFL is more representative of an internal process stream material; the PDB is a representative net product from the CTSL process. Distillation and blending data for the PDB sample are given in Table 4. In general, the PDB is a <850°F blend of second-stage separator, atmospheric, and vacuum still overheads. First-stage products from

TABLE 2. HRI CTSL Samples from Run #227-20^a

PNL Number	HRI Number	Description	Day
50378-064 ^b	L0-3969	PFL	1
50378-065	L0-3970	PFL	2
50378-066	L0-3971	PFL	3
50378-067	L0-3972	PFL	4
50378-068 ^{b,c}	L0-3973	PFL	5
50378-069	L0-3974	PFL	6
50378-070	L0-3975	PFL	7
50378-071	L0-3976	PFL	8
50378-072	L0-3977	PFL	9
50378-073 ^b	L0-3978	PFL	10
50378-074	L0-3979	PFL	11
50378-075	L0-3980	PFL	12
50378-076	L0-3981	PFL	13
50378-077	L0-3982	PFL	14
50378-078 ^{b,c}	L0-3983	PFL	15
50378-079	L0-3984	PFL	16
50378-080	L0-3985	PFL	17
50378-081	L0-3986	PFL	18
50378-082	L0-3987	PFL	19
50378-083	L0-3988	PFL	20
50378-084	L0-3989	PFL	21
50378-085	L0-3990	PFL	22
50378-086	L0-3991	PFL	23
50378-087 ^{b,c}	L0-3992	PFL	24
50378-088 ^{b,c}	L0-3993	PFL	25
50378-089 ^{b,c}	L0-3996	PFL composite	
50378-090 ^{b,c}	L0-3997	POB	
50378-040 ^{b,c}	L0-3936	First-stage tetrahydrofuran (THF) extracted filtrate	
50378-041 ^{b,c}	L0-3940	Second-stage pressure filtered topped separator bottoms	

^aExcept for samples 50378-040 and -041, which were taken from run #227-18

^bSamples chemically analyzed

^cSamples tested in the I/P assay for mouse-skin tumorigenicity

TABLE 3. Distillation and Elemental Analysis Data for Selected PFL Sample Materials from Run #227-20

	Period (Days) ^a				
	5	10	15	19	24
°API Gravity	3.1	-0.5	-3.2	-4.3	-9.0
Wt % Distribution					
IBP-650°F ^b	28.1	21.0	18.9	14.9	13.1
650-850°F	33.4	32.7	30.9	31.8	30.9
850-975°F	11.4	12.7	13.8	8.7	6.8
975°F+	27.1	33.6	36.4	44.6	49.2
Wt % Elemental Analysis					
Carbon	89.38	88.43	88.40	88.57	84.35
Hydrogen	9.13	8.19	7.94	7.61	7.69
Sulfur	0.046	0.102	0.137	0.146	0.186
Nitrogen	0.61	0.72	0.86	0.96	0.99
^a Samples from other periods not analyzed in detail; trends are probable continuous					
^b IBP = Initial boiling point					

the 25-day demonstration run #227-20 were not provided by HRI for these studies.

Similarly, Table 5 shows distillation and elemental analyses data for the first- and second-stage products from CTSL experimental run #227-18, which were also analyzed in this work.

Comparative samples from the ITSL and NTSL coal liquefaction processes have been previously reported by Wilson et al. (1983) and Later (1985). The ITSL materials studied were from both the Wilsonville, AL pilot plant and the Lummus Process Development Unit (PDU) in New Brunswick, NJ. The NTSL samples were from the Wilsonville, AL pilot plant.

TABLE 4. PDB Compositional Data

Blending Fractions (Wt %)

Separator overhead	26.1
Atmospheric still overhead	33.7
850°F- Vacuum still overhead	<u>40.2</u>
	100

Estimated Distillate Cuts (Wt %)

390-°F	22.7
390-500°F	23.2
500-650°F	32.2
650-850°F	21.9
850°F+	<u>0</u>
	100

TABLE 5. Elemental Analysis and Distillation Data for First- and Second-Stage Experimental Run CTSL Sample Materials

	Period 3/Run #277-18	
	First Stage	Second Stage
°API Gravity	13.5	14.2
Wt % Distribution		
IBP-650°F	56.9	61.9
650-850°F	22.7	11.6
850°F+	20.4	26.5
Wt % Elemental Analysis		
Carbon	84.62	87.68
Hydrogen	10.30	10.30
Sulfur	0.17	0.04
Nitrogen	0.31	0.26
Hydrogen:Carbon Ratio	1.46	1.41
% CHX Insolubles	7.93	3.19
% Toluene Insolubles	3.11	0.39

METHODS

CHEMICAL ANALYSIS

The CTSI sample materials indicated in Table 2 were chemically analyzed and prepared for biological testing using an initial fractionation by adsorption column chromatography, followed by HRGC, GC/MS, LVMS and proton NMR analyses of selected fractions. Details of the methods employed are outlined below.

Adsorption Column Chromatography

The sample materials were fractionated using alumina and picric-acid-coated alumina adsorption column chromatographic procedures. Details of these separations follow.

Alumina. Samples were fractionated by chemical class according to the method described by Later et al. (1981) and Later and Lee (1983). Samples were sequentially eluted from standardized alumina (1.5% H₂O) with 20 ml hexane, 50 ml benzene, 70 ml chloroform:ethanol (99:1), 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.

Picric-Acid-Coated Alumina. The hydroaromatic compounds were isolated from the CTSI samples using a method developed and described by Wozniak and Hites (1983). A layered adsorption column of 15% picric-acid-coated alumina over alumina was sequentially eluted with 10 ml hexane, 40 ml methylene chloride:hexane (3:97), 30 ml methylene chloride:hexane (3:17), and 25 ml benzene. The following fractions were obtained with this separation procedure: AH (PA₁), hydroaromatic compounds (PA₂), dihydro-PAH and less-than-three-aromatic-ringed PAH (PA₃), and greater-than-three-aromatic-ringed PAH and some polar polycyclic aromatic compounds (PAC; PA₄). Again, the weight percent contribution of each fraction was determined gravimetrically.

High-Resolution Gas Chromatography (HRGC)

The PAH, NPAC and selected AH and PA₂ fractions were analyzed by HRGC using a Hewlett-Packard (HP) 5880A gas chromatograph equipped with a 15-m x 0.25-mm-ID fused-silica capillary column coated with 0.25- μ m film thickness DB-5 (J & W Scientific). The oven temperature was isothermal at 50°C for 2 minutes, followed by temperature-programming to 300°C at 3°C/minute. The oven temperature was then held at 300°C for 5 minutes. Helium was used as the carrier gas, with a linear velocity of 50 cm/second. Samples were introduced to the column using the splitless injection technique. 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 GC/MS data.

Selected components of the PAH and NPAC fractions were quantified according to the internal standard (ISTD) calibration method outlined by Wilson et al. (1984). 2-Chloroanthracene (2-CA) was added as an ISTD at a final concentration of 50 ng/ μ l. Response factors (amount/area) were calculated from standard PAC 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. Fractions isolated from the PFL and PDB materials were analyzed at three concentration levels: 10.0, 5.00 and 2.50 mg/ml. Averaged results, with standard deviations of the mean, are reported in parts per million (ppm), or μ g/g, for each particular fraction. Fractions isolated from the experimental run first- and second-stage materials were analyzed at 5.00 mg/ml, in duplicate; average results are given in ppm.

Gas Chromatography/Mass Spectrometry (GC/MS)

Retention index and absolute retention time identifications were supplemented with coupled GC/MS determinations. The GC/MS analyses were performed on an HP-5982A quadrupole mass spectrometer interfaced with an HP-5710 GC equipped with a 15-m x 0.30-mm-ID DB-5 fused-silica capillary column (J & W Scientific). The GC transfer line was modified so that the fused silica could be inserted to within 5 to 10 mm of the ionizing electron beam within the ion

source. Gas chromatographic conditions were similar to those previously described for GC analyses, except that the oven was temperature-programmed at 8°C/ minute. The quadrupole MS was operated in the electron impact mode at 70 eV, and scan rates were typically 100 atomic mass units per second (amu/sec). Spectra of the capillary GC peaks were acquired and processed on an HP-5934A data system.

Low-Voltage Probe-Inlet Mass Spectrometry (LVMS)

LVMS was used as an additional means of identifying compounds present in the chemical class fractions of the CTSL sample materials. A VG ZAB 2-F double-focusing mass spectrometer was operated in the electron impact mode, with an accelerating voltage of 6000 or 7000 V, a magnet scan rate of 2 to 3 seconds/mass decade, a source temperature of 250°C, and a dynamic resolving power (as determined by the VG 2035 data system) of 1:2000. Each sample (10 to 20 µg) was loaded into a glass capillary tube, which was 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, slowly desorbing the sample from the capillary tube in what amounted to fractional distillation. The mass spectrometer was scanned repeatedly throughout this desorption period, and data were collected across the entire desorption profile. By using the data system to sum the intensities of each mass across the entire profile, an average spectrum was generated that was representative of the entire sample.

Averaged spectra were obtained using ionizing electron energies of 10-12 eV; these spectra were composed primarily of signals representing molecular ions rather than fragments or doubly charged ions. The resulting profile, therefore, more accurately represented the molecular weight distribution and composition of the sample than would a 70-eV spectrum, although fragment ions of alkanes were still produced at the lower voltage.

Proton Nuclear Magnetic Resonance (NMR)

Proton NMR was obtained on a Varian FT-80 instrument for the crude PDB CTSL material as well as for the chemical class fractions derived from the crude. Aliquots of the crude and of each chemical fraction were dissolved in

about 20 μ l of acetone- d_6 (Aldrich Chemical Co.) and sealed in 1.7-mm capillary tubes. Satisfactory spectra were obtained in less than 50 acquisitions. Chemical shifts are reported in ppm with respect to trimethylsilane (TMS).

BIOLOGICAL ASSAYS

The biological activity of the CTSL materials was evaluated using two different assays. The mutagenic potencies for all crude CTSL materials and selected chemical class fractions were estimated using the standard plate incorporation microsomal assay. The tumorigenic potencies of selected crude CTSL samples were evaluated by the I/P assay for mouse-skin tumorigenicity. The specific details of these bioassays are outlined below.

Standard Microbial Mutagenicity Test

Standard agar-plate mutagenicity assays were performed as described by Ames et al. (1975) using S. typhimurium, TA98 and TA100 microbial tester strains. Dimethylsulfoxide (DMSO) was used as a solvent, and samples were tested with and without Aroclor-induced rat liver (S9) homogenate metabolic activation. Optimum levels for S9 were established and monitored daily during the course of the experiments. Negative controls included the Salmonella test strains, with and without microsomal enzymes (S9), and appropriate solvent controls. Control responses were consistent with historical values of 48 ± 16 and 53 ± 19 revertants/plate for less than 100 μ l S9 (354 values) and 100 μ l S9 added (120 values), respectively. In addition to the mutagens used to check the phenotypes of Salmonella strains, fixed concentrations of the following were tested as positive controls: 2-aminoanthracene (2-AA), benzo[a]pyrene (BaP), 1-nitropyrene, a nitrosoguanidine and the NPAC fraction from solvent refined coal (SRC)-II 850°F+ bp cut. Revertant colonies per petri plate were counted electronically using a Biotran II automated colony counter. Raw, untransformed mutagenicity data for the samples analyzed are given in Appendix A.

The specific mutagenic activity of all the crude CTSL samples and the chemical class fractions of the samples indicated in Table 2 are expressed as revertant colonies of S. typhimurium, TA98 or TA100 per μ g of test material,

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. Mutagenicity experiments were usually replicated several times to obtain an average value for the slope of the regression line, or mutagenic potency, in revertants/ μ g. Maximum responses (given in revertants/plate) are also given.

I/P Assay for Mouse Skin Tumorigenicity

The I/P mouse skin tumor assays were performed as described by Mahlum (1983b). Female CD-1 mice (Charles River Laboratories, Portage, MI), approximately 6 to 8 weeks of age, were housed five per cage on standard bedding material (Sani-Cel, Paxton Processing Co., Paxton, IL), 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. Each test material was diluted 1:1 with acetone or methylene chloride, and 50 μ l of the diluted material was applied to the shaved backs of the mice. The resulting dose was approximately 25 mg per mouse. Positive controls consisted of 50 μ g of BaP (Sigma Chemical Company); negative controls received 50 μ l of the appropriate solvents. Two weeks after initiation, 5- μ g doses of phorbol myristate acetate (PMA; 0.1 mg/ml of acetone) were applied to the initiated area, twice weekly for 25 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. For comparison, the data are expressed as the total number of tumors per group of 30 mice, as the percent incidence and as mean number of tumors per mouse.

The following selected crude HRI CTSL samples were analyzed in the I/P assay: first-stage 50378-040; second-stage 50378-041; PFL, Day 5 (50378-068), Day 15 (50378-078), Day 24 (50378-087) and composite (50378-089); and PDB (50378-090).

RESULTS AND DISCUSSION

CHEMICAL ANALYSES

Results from the chemical analyses of the CTSL materials are given in the following manner. Chemical composition data (as determined by adsorption column chromatographic methods) are given first. The analyses of selected fractions thus isolated from the PFL, PDB, and first- and second-stage materials follow. HRGC, GC/MS, LVMS and NMR data are presented together when a particular sample and/or fraction is discussed. Comparisons are made to ITSL and NTSL process materials data from Later (1985) and Wilson et al. (1983).

Chemical Class Composition

Table 6 presents the chemical class composition data as determined by adsorption column chromatography on alumina for the CTSL samples studied. Recoveries for the PFL samples were high. As the 25-day demonstration run progressed, the PFL material exhibited a significantly decreased (by more than a factor of two) AH content. A concomitant increase in NPAC and hydroxy-PAH content was also noted. The PAH content remained essentially constant. The combined AH and PAH content of all the PFL samples (which represented the solids-free portion of the recycle slurry oil) was greater than 55%, with a maximum of 79%.

The combined AH and PAH content of the CTSL PDB was 66%, roughly comparable to the PFL composite; however, the PDB contained a significantly higher AH composition than did the PFL. PAH, NPAC and hydroxy-PAH content was significantly less in the PDB than in the PFL samples. Samples representative of product materials from the ITSL and NTSL processes contained a higher proportion of material eluting into the AH and PAH fractions than did the CTSL PDB; 79, 89 and 73% of the Wilsonville NTSL and ITSL hydrotreater (HTR) distillation column bottoms (>450°F bp) and the ITSL total liquid product (TLP) from the Lummus PDU (400-850°F+ bp), respectively, eluted in the combined AH and PAH fractions. Similar weight percent compositions eluted in the NPAC and

TABLE 6. Chemical Class Composition of CTSL Process Materials

Sample	Weight Percent Distribution in Fractions ^a				Total
	AH	PAH	NPAC	Hydroxy-PAH	
50378-064 PFL Day 1	36	42	17	14	109
50378-068 PFL Day 5	30	49	20	13	112
50378-073 PFL Day 10	25	48	23	16	112
50378-078 PFL Day 15	20	46	27	17	110
50378-082 PFL Day 19	17	44	29	18	108
50378-087 PFL Day 24	16	40	31	20	107
50378-089 PFL Composite	22	43	27	17	109
50378-090 ^b PDB	43	23	5.2	6.7	78
50378-040 ^c First-stage THF extracted filtrate	53	22	7.5	13	96
50378-041 ^c Second-stage pressure-filtered topped separator bottoms	68	24	6.5	11	110

^aAverage of two determinations, unless otherwise noted^bAverage of five determinations^cSamples generated using all distillate recycle

hydroxy-PAH chemical class fractions for the ITSL HTR distillation column bottoms and the CTSL PDB.

The first- and second-stage products from an experimental run of the CTSL process had significantly higher AH content than did the PFL materials from the demonstration run. In addition, these CTSL first- and second-stage materials had higher AH content than their counterparts from the previously studied two-stage liquefaction process.

Hydrogenated and partially hydrogenated PAH compounds were detected in both the AH and PAH fractions isolated from the samples by the alumina column chromatography chemical class fractionation. Because of the high hydroaromatic compound composition of the CTSL materials and the inadequate class separation of PAH and hydroaromatics on alumina, a second adsorption column chromatographic separation was performed on these samples, as described in the Methods section. The hydroaromatic composition of the CTSL process materials (as determined by picric-acid-coated alumina column chromatography) is given in Table 7. Both the PA₁ and PA₂ fraction content of the PFL samples decreased with time during the 25-day demonstration run; the PA₁ fraction by a factor of three, and the PA₂ fraction by a factor of two. These results were similar to the decrease in the AH fraction content previously described for the PFL samples. The PA₃ fraction content remained essentially constant over time. These results indicated that a loss in efficiency of hydrogen incorporation and heteroatom removal occurred during the course of operation over an extended period at lined-out conditions.

The PDB had a slightly higher PA₁ fraction content than did the PFL. In addition, the combined PA₁ and PA₂ fraction contents of the ITSL (81%) and NTSL (77%) HTR distillation column bottoms product materials were significantly higher than that of the PDB (61%). The sum of PA₁ and PA₂ fractions from the second-stage CTSL material was 77%, which was comparable to the NTSL HTR distillation column bottoms. However, the PA₁ and PA₂ combined content of the first-stage CTSL material (64%) was significantly higher than that of first-stage products from the ITSL (24%) and NTSL (18%) processes.

TABLE 7. Hydroaromatic Composition of CTSL Process Materials

Sample	Weight Percent Distribution in Fractions ^a				Total
	PA ₁ ^b	PA ₂ ^c	PA ₃ ^d	PA ₄ ^e	
50378-064 PFL Day 1	27	30	10	18	85
50378-068 PFL Day 5	19	27	14	17	77
50378-073 PFL Day 10 ^f	19	21	14	14	68
50378-078 PFL Day 15	23	20	13	16	72
50378-082 PFL Day 19 ^f	12	18	12	48	90
50378-087 PFL Day 24 ^f	9.1	16	12	29	66
50378-089 PFL Composite ^f	16	19	13	21	69
50378-090 PD8 ^f	38	23	6.8	3.0	71
50378-040 First-stage THF extracted filtrate ^g	38	26	5.5	4.5	74
50378-041 Second-stage pressure-filtered topped separator bottoms ^g	45	32	7.0	6.1	90

^aAverage of two determinations, unless otherwise noted^bAH^cHydroaromatic compounds^dDihydro-PAH and <three-ringed PAH^e>Three-ringed PAH and some lower molecular weight, slightly polar compounds (e.g., alkylated indoles and azaarenes)^fOne determination only^gSamples generated using all distillate recycle

The results of both adsorption column chromatographic fractionation methods indicated that the PFL internal stream process material changed, with time, as an effect of catalyst aging; the AH and hydroaromatic content decreased significantly. The PDB from the CTSL process contained less AH and less hydroaromatic content than similar product materials from the ITSL and NTSL processes. However, the CTSL first-stage product material had a higher AH and hydroaromatic content than did similar products from the ITSL and NTSL processes.

Pressure Filter Liquids (PFL)

Chemical analysis data of the PFL materials from the 25-day demonstration run of the HRI CTSL process are presented for the chemical class fractions obtained by alumina column adsorption chromatography in the following order: 1) AH, 2) PAH, 3) NPAC, and 4) hydroxy-PAH. Selected HRGC and LVMS data are given. Comparisons to the ITSL recycle solvent data of Later (1985) are made when possible.

AH. Figure 2 shows the gas chromatograms obtained from the HRGC analysis of the AH fractions isolated from PFL Day 1 and Day 10, and from the composite by alumina column chromatography. The even-numbered and selected odd-numbered straight-chain alkane compounds were labeled from GC retention time and GC/MS data. The unlabeled components in the AH fractions that do not correspond to the alkane series were identified, based on GC/MS data, as various parent and alkylated hydroaromatic species of indane, tetralin, dihydronaphthalene, dihydroacenaphthene and dihydrophenalene. Although chromatograms were also obtained from the analysis of AH fractions isolated from Days 5, 15 and 24, the selected PFL materials shown in Figure 2 indicated the general trends of change versus time of pilot plant operation. The straight-chain alkanes were the major species present in the Day 1 PFL AH fraction. A decrease of the alkane compounds, with a corresponding increase of hydroaromatic species, was noted in the PFL AH fractions from the subsequent days of operation. These HRGC data were in agreement with the column adsorption chromatography fractionation data presented above, where the trend of decreased AH content was noted with increased pilot-plant operating time. In addition, it was apparent from the chromatograms that increased concentrations of higher-molecular-

FIGURE 2. Gas Chromatograms of Selected AH Fractions Isolated from PFL Materials from the HRI CTSL 25-Day Demonstration Run. See text for conditions. Top: Day 1; Middle: Day 10; Bottom: Composite

weight components were present in the PFL AH fractions as the length of operating time increased, indicating lower efficiency of carbon:carbon bond cleavage.

The shift to an increased concentration of high-molecular-weight components with increased pilot-plant operating time is shown graphically in Figure 3. The LVMS results from the analyses of the AH fractions isolated from the Day 1 and composite PFL materials are shown. The components of highest concentration in the Day 1 material were of mass 242, whereas the components of mass 268 were highest in concentration in the PFL composite AH fraction. The LVMS response at 111 and 125 amu represented the fragment ions from the alkane species present in the AH fractions; conditions of 10 to 12 eV produced these fragment ions when standard straight-chain alkanes were analyzed. A decrease in AH concentration was again noted when comparing the LVMS results from the AH fractions of Day 1 and of composite PFL materials. Highly alkylated hydroaromatic compounds were shown to be major components of the alumina column chromatographic AH fractions from the PFL materials; alkyl-series from parent compounds, such as indane, tetralin, dihydronaphthalene, dihydroacenaphthene, dihydrophenalene or dihydrofluorene, were also present.

PAH. The HRGC analyses of the PAH fractions isolated from the Day 1, Day 10 and composite PFL materials are shown in Figure 4. The quantitative and qualitative data for the components identified in these fractions are given in Table 8. Also included in Table 8 are the quantitative results from the HRGC analyses of the PAH fractions isolated from the Day 5, 15, 19 and 24 PFL materials. The major species present in these fractions were alkylated and parent PAH ranging from two to seven rings. Hydroaromatic components were also present, notably the 1,2-dihydrophenalene (identified by GC/MS data and absolute GC retention time of the synthesized standard compound). The quantitative results of the PAH fractions isolated from the PFL materials from the 25-day demonstration run were similar, with two exceptions: 1) there was a general trend of decreasing concentration of lower-molecular-weight species with increasing length of pilot plant operation time; and 2) there was a corresponding significantly increased concentration of higher-molecular-weight species with increased operating time. For example, the combined concentration of the 2-methyl- and 2-ethylnaphthalenes decreased from 1647 to 516 ppm,

FIGURE 3. LVMS Results for Selected AH Fractions Isolated from PFL Materials from the HRI CTSL 25-Day Demonstration Run. Top: Day 1; Bottom: Composite

FIGURE 4. Gas Chromatograms of Selected PAH Fractions Isolated from PFL Materials from the HRI CTSL 25-Day Demonstration Run. Top: Day 1; Middle: Day 10; Bottom: Composite. See text for conditions. Peaks are identified in Table 8.

TABLE 8. Concentrations of Selected Components in PAH Fractions of HRI CTSL PFL from the 25-Day Demonstration Run

Peak Number ^a	Compound ^b	Molecular Weight	Concentration (µg/g)							Composite
			Day							
			1	5	10	15	19	24		
1	Tetralin	132	-- ^c	--	--	--	--	--	--	
2	Naphthalene	128	--	--	--	--	--	--	--	
3	2-Methylnaphthalene	142	965 ± 126 ^d	601 ± 35	446 ± 28	478 ± 59	432 ± 8	370 ± 26	488 ± 62	
4	1-Methylnaphthalene	142	155 ^e	137	108	--	--	--	127	
5	1,2,2a,3,4,5-Hexahydro-acenaphthylene	158	1280 ± 150	241 ± 18	--	200	--	--	--	
6	Biphenyl	154	516 ± 44	--	--	--	--	--	--	
7	2-Ethyl-naphthalene	156	682 ± 190	244 ± 27	188	243	175	146	226	
8	2,6- or 2,7-Dimethyl-naphthalene	156	1170 ± 130	--	--	--	--	--	--	
9	1,7-Dimethylnaphthalene	156	198 ± 67	180	147	124	121	112	167	
10	C ₂ -Naphthalenes	156	--	--	--	--	--	--	--	
11	C ₃ -Naphthalenes	170	--	--	--	--	--	--	--	
12	C ₁ -Hexahydroacenaphthylene	172	4520 ± 600	770 ± 42	282 ± 8	587 ± 8	204	--	231	
13	C ₃ -Naphthalenes	170	--	--	--	--	--	--	--	
14	C ₁ -Hexahydroacenaphthylene	172	2360 ± 310	558 ± 17	--	507 ± 71	148	--	148	
15	Fluorene	166	3850 ± 410	661 ± 28	522 ± 102	516 ± 42	534 ± 10	504 ± 55	631 ± 48	

^aRefers to peaks labeled in Figure 4^bIdentifications based on GC retention times and mass spectral data^cNone detected (below approximately 75 ppm), or no data collected^dAverage of three determinations; mean $\pm$ standard deviation^eOne determination only

TABLE 8. (Continued)

Peak Number ^a	Compound ^b	Molecular Weight	Concentration (µg/g)						
			Day						Composite
			1	5	10	15	19	24	
16	1,2-Dihydrophenalene	168	5960 ± 890	3000 ± 130	2920 ± 350	2850 ± 140	3060 ± 410	2490 ± 280	3620 ± 580
17	1,4-Dihydrofluorene, C ₄ -naphthalene	168,184	--	--	--	--	--	--	--
18	C ₁ -Dihydrophenalene/fluorene	182	--	--	--	--	--	--	--
19	2-Methylfluorene	180	1670 ± 240	334 ± 204	232 ± 29	482	366 ± 149	354 ± 119	517
20	1-Methylfluorene	180	1570 ± 190	300 ± 140	131 ± 13	405	211 ± 137	264	353
21	C ₁ -Dihydrophenalene/fluorene	182	5330 ± 560	2740 ± 390	2870 ± 410	2700 ± 240	2920 ± 550	2640 ± 310	3520 ± 630
22	Octahydrophenanthrene	186	2020 ± 290	557 ± 23	338 ± 11	523 ± 70	328 ± 55	244	299
23	Tetrahydrophenanthrene	182	977 ± 110	696 ± 75	701 ± 46	755 ± 31	823 ± 102	825 ± 65	846 ± 35
24	1,2,3,4-Tetrahydrophenanthrene	182	2010 ± 280	980 ± 89	994 ± 90	957 ± 59	1130 ± 190	1080 ± 100	1220 ± 150
25	Phenanthrene	178	3180 ± 450	958 ± 20	950 ± 93	904 ± 19	1220 ± 120	1270 ± 130	1070 ± 170
26	C ₂ -Fluorenes, C ₂ -dihydrophenalene/fluorene	194,196	--	--	--	--	--	--	--
27	3-Methylphenanthrene	192	1330 ± 140	588 ± 198	574 ± 266	594 ± 236	768 ± 266	710 ± 212	669 ± 191

^aRefers to peaks labeled in Figure 4

^bIdentifications based on GC retention times and mass spectral data

^cNone detected (below approximately 75 ppm), or no data collected

^dAverage of three determinations; mean ± standard deviation

^eOne determination only

TABLE 8. (Continued)

Peak Number ^a	Compound ^b	Molecular Weight	Concentration (µg/g)						
			Day						
			1	5	10	15	19	24	Composite
28	2-Methylphenanthrene	192	1860 ± 60	1030 ± 20	1060 ± 60	1090 ± 10	1215 ± 10	1310 ± 100	1270 ± 130
29	9- or 4-Methylphenanthrene	192	630	96	74	97	124	54	--
30	1-Methylphenanthrene	192	338 ± 250	82 ± 14	89	99	111	77	81
31	Hexahdropyrene/ fluoranthene	208	--	--	--	--	--	--	--
32	2-Chloroanthracene, ISTD	212	--	--	--	--	--	--	--
33	Hexahdropyrene/ fluoranthene	208	--	--	--	--	--	--	--
34	Dihdropyrene/fluoranthene	204	2560 ± 380	2200 ± 300	2650 ± 230	2610 ± 190	2830 ± 230	2890 ± 250	3040 ± 350
35	Fluoranthene	202	293 ± 199	192 ± 25	523	529	666	686	221
36	Pyrene	202	4380 ± 570	5630 ± 850	8370 ± 880	9060 ± 1250	10400 ± 1100	11000 ± 1300	10200 ± 1000
37	Dihdropyrene	204	489 ± 51	456 ± 39	548 ± 41	535 ± 23	640 ± 78	706 ± 29	580 ± 54
38	C ₁ -Dihdropyrene/ fluoranthene	218	--	--	--	--	--	--	--
39	Benzo[b]fluorene, 2- or 4-methylpyrene	216	2130 ± 230	3360 ± 460	4930 ± 460	5450 ± 360	5850 ± 260	6440 ± 300	5730 ± 360

^aRefers to peaks labeled in Figure 4^bIdentifications based on GC retention times and mass spectral data^cNone detected (below approximately 75 ppm), or no data collected^dAverage of three determinations; mean ± standard deviation^eOne determination only

TABLE 8. (Continued)

Peak Number ^a	Compound ^b	Molecular Weight	Concentration (µg/g)							
			Day							
			1	5	10	15	19	24	Composite	
40	C ₁ -Dihydropyrene/ fluoranthene	218	669 ± 60	555 ± 64	674 ± 27	757 ± 54	933 ± 51	1090 ± 140	800 ± 68	
41	1-Methylpyrene	216	226	238 ± 11	298	319	369 ± 16	417 ± 6	378	
42	C ₂ -Pyrenes, C ₁ -benzo- fluorenes	230	--	--	--	--	--	--	--	
43	C ₂ -Dihydropyrenes	232	--	--	--	--	--	--	--	
44	C ₃ -Pyrenes, C ₂ -benzo- fluorenes	244	--	--	--	--	--	--	--	
45	Hexahydrobenzopyrene	258	--	--	--	--	--	--	--	
46	6- or 4-Methylchrysene	242	1060 ± 120	2270 ± 240	3180 ± 200	3280 ± 180	3280 ± 370	3800 ± 160	3320 ± 580	
47	Benzo[j or b]fluoranthene	252	--	--	84	67	98	92	--	
48	Benzo[e]pyrene	252	--	107	162	192	263	319	223	
49	Benzo[a]pyrene	252	--	127	173	188	237	284	174	
50	Indeno[1,2,3-cd]pyrene	276	223	370	521	508	635	732	806	
51	Dibenz[a,h or a,c]anthra- cene	278	--	180	192	270	343	380	236	
52	Benzo[ghi]perylene	276	456 ± 31	1360 ± 250	2560 ± 130	2620 ± 530	2900 ± 1140	4060 ± 210	3160 ± 510	

^aRefers to peaks labeled in Figure 4

^bIdentifications based on GC retention times and mass spectral data

^cNone detected (below approximately 75 ppm), or no data collected

^dAverage of three determinations; mean ± standard deviation

^eOne determination only

while the combined concentration of the indeno[1,2,3-cd]pyrene and benzo[ghi]perylene increased from 679 to 4792 ppm during the duration of the demonstration run. In some cases, these changes in concentration were by a factor of only two or three; in other cases, the changes in concentration were by a factor of nearly nine over the 24 days studied. The most radical changes in composition were noted between the Days 1 and 5 PFL materials, as would be expected from the initial equilibration of operating temperatures. The PFL composition appeared to be the most constant during the period from Days 10 to 19 of the demonstration run. The composition of the PFL composite was most similar to Days 15 and 19 PFL materials.

A comparison of the ratios of the summed concentrations of the methylphenanthrenes, divided by the phenanthrene concentration given in Table 8, to those previously reported for the ITSL recycle solvent by Later (1985) indicated that the CTSL PFL was less alkylated than the ITSL material. The ratios of alkylated to parent phenanthrene concentrations were 1.08 and 1.89 for the CTSL and ITSL internal process stream materials, respectively. In addition, the ratio of dihydrophenalene (mass 168) to fluorene concentrations indicated that the CTSL PFL was also less hydrogenated than the ITSL material; the ratios were 2.94 and 4.26, respectively, for these materials.

The LVMS results for the PAH fractions isolated from Day 1 and from composite PFL materials are shown in Figure 5. The PAH fractions, also analyzed by LVMS, were from Days 5, 10, 15, 19 and 24 PFL materials. Shown in Figure 5 are the major chemical composition changes in the PFL materials that occurred during the 25-day demonstration run. The PAH fractions from the internal process stream material had a higher-molecular-weight distribution as a function of operating time, which was also observable in the GC profiles shown in Figure 4. The average molecular weight of the PFL Day 1 PAH fraction was calculated to be 295 amu, whereas the PFL composite had an average molecular weight of 310 amu. In addition, the relative concentrations of some series of compounds decreased with time. Most notable decreases were found in the series including masses of 208, 222, 236 and 250 (possibly alkylated homologs of dihydrofluorenes, dihydrophenalenes, and/or hexahydrofluoranthenes/pyrenes) and in the series including masses of 248 and 262. Table 9 contains a key to determine postulated structures for the masses shown in Figure 5.

FIGURE 5. LVMS Results for Selected PAH Fractions Isolated from PFL Materials from the HRI CTSL 25-Day Demonstration Run. Top: Day 1; Bottom: Composite. See Table 9 for a key to mass identifications.

TABLE 9. Key to 12-eV Mass Spectra: Nominal Masses for Alkylated Homologous Series of Representative Neutral PAH

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/Phenanthrene	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

^aIn 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.

The LVMS analysis of the PAH fraction isolated from the ITSL recycle solvent (see Later, 1985) showed a similar overall chemical composition to that of the PFL materials from Days 1 and 5, except that the concentration of heavier-molecular-weight components was increased. The major components of the ITSL recycle solvent and of the CTSL PFL from the first few initial days of operation were similar. Decreased concentrations of certain hydroaromatic species with increasing CTSL pilot-plant operation time (as previously described) caused the PFL from subsequent days to vary further from the ITSL recycle solvent.

NPAC. The gas chromatograms from the HRGC analyses of selected NPAC fractions isolated from CTSL PFL materials are shown in Figure 6; the components from the Day 1, Day 10 and composite PFL materials are identified in Table 10. Also given in Table 10 are the quantitative results from the HRGC analyses of PFL materials from Days 5, 15, 19 and 24. Major NPAC compounds identified in the PFL materials by HRGC and GC/MS were carbazole, methylcarbazoles, an azapyrene, and hydrosubstituted isomers of benzoquinoline and carbazole. Again, the HRGC analysis of the NPAC fractions isolated from the PFL materials showed a decreasing concentration of the lower-molecular-weight species, such as the hydroaromatic benzoquinolines, and an increasing concentration of the heavier-molecular-weight species, such as the benzocarbazoles, as a function of pilot-plant operation time. However, unlike the PAH fractions, after 5 to 10 days of operation the NPAC fractions isolated from the PFL materials appeared similar in composition as determined by the quantitative HRGC results in Table 10. NPAC species were generally found in low concentrations in the CTSL post-second-stage internal stream material, as has been the case with all two-stage coal liquefaction materials as compared to single-stage technologies (Later, 1985; Wilson et al., 1984).

The overall chemical composition of the NPAC fractions as determined by LVMS for Day 1 and for the composite PFL materials are shown in Figure 7. The average molecular weight of the Day 1 material was 270 amu; the average molecular weight of the composite was 360 amu. (The component of mass 350 in the PFL composite is believed to be a contaminant.) Again, these results show a trend toward higher-molecular-weight constituents with increasing run time. A key to postulated structures corresponding to the masses shown in Figure 7 is

FIGURE 6. Gas Chromatograms of Selected NPAC Fractions Isolated from PFL. Materials from the HRI CTSL 25-Day Demonstration Run. Top: Day 1; Middle: Day 10; Bottom: Composite. See text for conditions. Peaks numbered are identified in Table 10.

TABLE 10. Concentrations of Selected Components in NPAC Fractions of HRI CTSL PFL from the 25-Day Demonstration Run

Peak Number ^a	Compound ^b	Molecular Weight	Concentration (µg/g)						
			Pressure Filter Liquid (PFL)						Composite
			Day						
			1	5	10	15	19	24	
16	Octahydrobenzoquinoline	187	-- ^c	--	129 ^d	--	131	--	--
17	C ₁ -Dihydroazafluorene	183	--	--	--	--	--	--	--
18	Octahydrobenzoquinoline	187	472 ± 178 ^e	401 ± 109	325	--	256	339 ± 150	232
19	C ₁ -Octahydrobenzoquinoline	201	330 ± 25	127	219	268	83	--	--
20	C ₁ -Dihydroazafluorene	183	--	--	--	--	--	--	--
21	Benzo[h]quinoline	179	--	10	8	15	--	44	--
22	C ₁ -Octahydrobenzoquinoline	201	893 ± 174	606 ± 228	498 ± 8	448 ± 79	430 ± 67	497	420 ± 84
23	C ₁ -Dihydroazafluorene	183	--	--	--	--	--	--	--
24	Tetrahydrocarbazole	171	700 ± 212	300 ± 79	257	238	219 ± 21	223	198
25	Phenanthridine, benzo[f]quinoline	179	--	--	--	--	--	20	--
26	Octahydrobenzoquinoline	187	389 ± 157	268 ± 79	220	225 ± 18	236 ± 25	230 ± 18	--
27	Carbazole	167	1400 ± 260	701	711	683	753	802	634
28	2- or 3-Methylbenzo[f]quinoline	193	185 ± 11	422	221	223	252 ± 37	269	190
29	1-Methylcarbazole	181	485 ± 53	286 ± 179	250	148	159 ± 78	124 ± 6	136
30	3-Methylcarbazole	181	960 ± 396	791	702	626 ± 77	738	389	279 ± 28
31	2-Methylcarbazole	181	674 ± 318	767	705	675	716	190	--
32	4-Methylcarbazole	181	32	477	431	377	280 ± 120	368	--

^aRefers to peaks labeled in Figure 6^bIdentifications based on GC retention times and mass spectral data^cNone detected (below approximately 75 ppm), or no data collected^dOne determination only; mean ± standard deviation^eAverage of three determinations; mean ± standard deviation

TABLE 10. (Continued)

Peak Number ^a	Compound ^b	Molecular Weight	Concentration (µg/g) Pressure Filter Liquid (PFL)						
			Day						Composite
			1	5	10	15	19	24	
33	2-Chloroanthracene, ISTD	212	-- ^c	--	--	--	--	--	--
34	C ₂ -Carbazoles	195	--	--	--	--	--	--	--
35	C ₃ -Carbazoles	209	--	--	--	--	--	--	--
36	1- or 4-Azapyrene	203	185	1110 ± 370	1000	700	1200	1220	960
37	C ₁ -Azapyrenes, azabenzofluorenes	217	--	--	--	--	--	--	--
38	C ₂ -Azapyrenes, C ₁ -Azabenzofluorenes	231	--	--	--	--	--	--	--
39	Benzo[a]carbazole	217	54 ± 13	418 ± 40	396	490	506	500	422
40	Benzo[b]carbazole	217	2	19	133	40	253	142	--
41	Benzo[c]carbazole	217	243	310	570	500	566	526	475
42	C ₃ -Azapyrene, C ₂ -Azabenzofluorene	245	--	--	--	--	--	--	--

^aRefers to peaks labeled in Figure 6^bIdentifications based on GC retention times and mass spectral data^cNone detected (below approximately 75 ppm), or no data collected^dOne determination only; mean ± standard deviation^eAverage of three determinations; mean ± standard deviation

FIGURE 7. LVMS Results for Selected NPAC Fractions Isolated from PFL Materials from the HRI CTSL 25-Day Demonstration Run. Top: Day 1; Bottom: Composite. See Table 11 for a key to mass identification.

TABLE 11. Key to 12-eV Mass Spectra: Nominal Masses for Alkylated Homologous Series of Representative NPAC

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
Azaphenyl naphthalene	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

^aIn 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 A₃ 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.

given in Table 11. Major NPAC compounds in the PFL materials determined by LVMS were carbazole, alkyl-substituted carbazoles and an alkyl-series based on a possible tetrahydrobenzocarbazole (221 amu) structure. Similar components were found in the NPAC fraction isolated from the ITSL recycle solvent, except that an increased concentration of higher-molecular-weight materials was present. The average molecular weight of the ITSL recycle solvent NPAC fraction was greater than 400 amu (see Later, 1985).

No determinations were made for amino-substituted PAH (amino-PAH). One would expect the concentration of these species to be low, based on previous data, which have indicated that amino-PAH concentrations are low for coal liquefaction materials that have undergone catalytic hydrogenation (Later, 1985; Wright et al., 1985).

Hydroxy-PAH. The 12-eV spectra from the hydroxy-PAH fractions isolated from the Day 1 and composite PFL materials are shown in Figure 8. Table 12 contains the key to determining isomer groups for the hydroxy-PAH fractions. Phenols, indanols, hydroxyfluorenes and other hydroxy-substituted PAH of larger ring sizes were detected in these fractions. The increased concentration of higher-molecular-weight components after initial startup of the plant is shown by comparison of the Day 1 PFL to the PFL composite; the average molecular weight of the hydroxy-PAH fraction isolated from the Day 1 PFL materials was 290 amu; the average molecular weight of the same fraction isolated from the PFL composite material was 370 amu.

Summary. The HRGC and LVMS analyses of chemical class fractions isolated from PFL materials from Days 1, 5, 10, 15, 19, 24 and from a composite sample have indicated that changes occurred in the post-second-stage internal process stream material as a function of pilot plant operation time. The concentration of alkane components in the AH fraction decreased as length of operation increased. The concentrations of parent and alkylated PAH with two rings decreased, while the concentrations of parent and alkylated PAH with four rings or greater increased in the PFL materials over the 25-day demonstration run. All chemical class fractions showed an increased molecular weight distribution as the demonstration run progressed. The changes that occurred in the PFL material samples from the various days of pilot plant operation may be due, in

FIGURE 8. LVMS Results for Selected Hydroxy-PAH Fractions Isolated from PFL Materials from the HRI CTSL 25-Day Demonstration Run. Top: Day 1; Bottom: Composite. See Table 12 for a key to mass identifications.

TABLE 12. Key to 12-eV Mass Spectra: Nominal Masses for Alkylated Homologous Series of Representative Hydroxy-PAH

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
Hydroxyphenan- threnes/Anthra- cenes	194	208	222	236	250	264	278	292	306	320	334	348
Hydroxycyclopenta- phenanthrenes	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
Hydroxyphenyl- naphthalenes	220	234	248	262	276	290	304	318	332	346	360	374
Hydroxybenzo- fluorenes	232	246	260	274	288	302	316	330	344	358	372	386
Hydroxyindeno- pyrenes	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
Hydroxycyclo- pentachrysenes	256	270	284	298	312	326	340	354	368	382	396	410
Hydroxyphenyl- fluorenes	258	272	286	300	314	328	342	356	370	384	398	412
Hydroxybenzo- pyrenes/Benzo- fluoranthenes	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
Hydroxycyclopenta- benzopyrenes	280	294	308	322	336	350	364	378	392	406	420	434
Hydroxydibenzo- fluorenes	282	296	310	324	338	352	366	380	394	408	422	436
Hydroxyindeno- pyrenes	292	306	320	334	348	362	376	390	404	418	432	446
Hydroxybenzo- chrysenes	294	308	322	336	350	364	378	392	406	420	434	448

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

part, to the initial stabilization of temperatures in both stages of the CTSL process. However, stable conditions were achieved by the fourth day of operation, and results from the chemical analyses indicated that the composition of the PFL materials continued to change as a function of pilot-plant operation after this time. Therefore, catalyst deactivation or resid recycle may have contributed to the increasing relative composition of higher-molecular-weight components, most notably the PAH compounds of four rings and greater.

Comparisons of chemical analyses data from the CTSL PFL and the ITSL recycle solvent have indicated that the former materials were of a lower-molecular-weight range and were less alkylated and hydrogenated than the latter. These results were not unexpected, based on the fact that 45 to 50% of the ITSL recycle solvent was undistillable solids and the PFL was solids-free.

Product Distillate Blend (PDB) Materials

Chemical analysis data for the PDB from the CTSL process are presented for the column adsorption chromatographic fractions in the following order: 1) crude, 2) AH, 3) PAH, 4) hydroaromatics, 5) NPAC, and 6) hydroxy-PAH. Selected HRGC, LVMS, and proton NMR data are given, and comparisons are made to the HTR distillation column bottoms materials from the ITSL and NTSL processes previously reported by Later (1985).

Crude. Proton NMR information was acquired for the crude PDB material in addition to the chemical composition data presented in Tables 6 and 7. The high aliphatic, aromatic and hydroaromatic content of the PDB is evidenced by the relatively large peak areas for Regions 1 and 2 in the proton NMR spectrum shown in Figure 9. An explanation of the identified proton regions labeled in the figure is given in Table 13. Minimal response in Region 7 indicated that the PDB material had low concentrations of heteroatomic species. These results are in general agreement with the chemical class fractionation data given in Table 6.

AH. Results of the HRGC analysis of the AH fraction isolated from the HRI CTSL PDB material are given in Figure 10. Selected straight-chain alkane components were identified by GC retention time and GC/MS data. The major

FIGURE 9. Proton NMR Spectrum of the PDB from the HRI CTSL Process. Regions indicated are defined in Table 13.

TABLE 13. Explanation of Hydrogen Environments Designated in Proton NMR Spectra^a

Regions	Structure	Proton Environment
	<p style="text-align: center;"><u>Structure I</u></p> <p style="text-align: center;"><u>Structure II</u></p>
1	-CH ₃	Terminal methyl groups
2	-CH ₂ -	Aliphatic methylene units
3	-CH ₂ -	Protons on saturated cyclic systems or protons adjacent to condensed aromatics
4	-CH-, -CH ₂ -	Highly branched alkanes, or mono- and di-alkanes
5a	-CH-	Aromatic H on nonheteroatom-substituted aromatic systems (e.g., diphenylmethane)
5b	=CH-	Aromatic hydrogen on naphthalene structures (e.g., alpha hydrogen on naphthalene)
6	-CH=	Aromatic hydrogen on multiple-condensed PAH (e.g., 9 and 10 of anthracene)
7	=CH-X	Aromatic hydrogen in proximity to heteroatomic functionalities (e.g., NPAC, hydroxy-PAH, etc.)

^aThis is not intended as an exhaustive or exclusive chemical shift listing but only as a qualitative guide to general chemical shift regions; for complex structures, spectral regions partially overlap.

FIGURE 10. Gas Chromatogram of the AH Fraction Isolated from the HRI CTSL PDB Material. See text for conditions.

components found in the AH fraction isolated by alumina column chromatography were the hydroaromatic compounds. The components of the PDB AH fraction were similar to those of the PFL AH fractions, except that they were of a lower-molecular-weight range (see Figure 3).

The 12-eV spectra of the PDB AH fraction is shown in Figure 11. Parent and alkyl-substituted tetralin, dihydronaphthalene, tetrahydroacenaphthene, dihydrofluorene and/or dihydrophenalene hydroaromatic components were detected. Based on the LVMS results, these hydroaromatic species represented the major components in the fraction. It should be noted, however, that the AH are discriminated against in this method of analysis. Alkanes produce fragment ions (111 amu) under 12-eV ionization conditions; therefore, their total contribution to the fraction cannot be summed in the same way as the molecular ion peaks of the hydroaromatic species. The composition of hydroaromatic compounds in the AH fraction of the PDB material was similar to that in the AH fraction of the PFL composite material (see Figure 4). Both the AH fractions isolated from ITSL and NTSL HTR distillation column bottom materials were of a lower-molecular-weight range than the CTSL PDB. The components of mass 186 represented 100% of the total ion current (TIC) for the ITSL and NTSL product materials (see Later, 1985).

The proton NMR spectrum of the AH fraction isolated from the PDB is shown in Figure 12. The response in Regions 1 through 4 shows the high aliphatic and hydroaromatic content of this fraction.

PAH. Results of the gas chromatographic analyses of the PAH fraction isolated from the CTSL PDB are shown in Figure 13. The components numbered in Figure 13 are identified and quantified in Table 14. Pyrene was the major component, followed by 1,2-dihydrophenalene (identified by synthesis of the standard compound), benzo[b]fluorene or 2- or 4-methylpyrene and 2-methylnaphthalene. The components identified in the PDB PAH fraction were similar to those in the PFL materials, except that there was a significant increase in the concentration of lower-molecular-weight compounds resulting from blending the atmospheric still and separator overheads with the higher-molecular-weight process materials. The ratio of the summed concentrations of the methyl phenanthrenes to the phenanthrene concentration for the CTSL PDB material was the

FIGURE 11. LVMS Results for the AH Fraction Isolated from the HRI CTSL PDB Material

FIGURE 12. Proton NMR Spectrum of the PDB AH Fraction from the HRI CTSL Process. Regions indicated are defined in Table 13.

FIGURE 13. Gas Chromatogram of the PAH Fraction Isolated from the HRI CTSL PDB Material. See text for conditions. Numbers refer to identifications given in Table 14.

TABLE 14. Concentrations of Selected Components in the HRI CTSL PDB PAH Fraction

Peak Number ^a	Compound ^b	Molecular Weight	Concentration (µg/g)
1	Tetralin	132	300 ± 20 ^c
2	Naphthalene	128	342 ± 26
3	2-Methylnaphthalene	142	7270 ± 1100
4	1-Methylnaphthalene	142	1750 ± 220
5	1,2,2a,3,4,5-Hexahydro-acenaphthylene	158	500 ± 53
6	Biphenyl	154	335 ± 20
7	2-Ethyl-naphthalene	156	1950 ± 300
8	2,6- or 2,7-Dimethyl-naphthalene	156	2800 ± 420
9	1,7-Dimethylnaphthalene	156	1260 ± 90 ^d
10	C ₂ -Naphthalenes	156	--
11	C ₃ -Naphthalenes	170	--
12	C ₁ -Hexahydroacenaphthylene	172	830 ± 36
13	C ₃ -Naphthalenes	170	--
14	C ₁ -Hexahydroacenaphthylene	172	440 ± 20
15	Fluorene	166	1770 ± 250
16	1,2-Dihydrophenalene	168	9300 ± 180
17	1,4-Dihydrofluorene, C ₄ -naphthalene	168, 184	--
18	C ₁ -Dihydrophenalene/fluorene	182	--
19	2-Methylfluorene	180	925 ± 243
20	1-Methylfluorene	180	602 ± 279
21	C ₁ -Dihydrophenalene/fluorene	182	6240 ± 840
22	Octahydrophenanthrene	186	770 ± 64
23	Tetrahydrophenanthrene	182	1610 ± 150
24	1,2,3,4-Tetrahydrophenanthrene	182	2110 ± 340
25	Phenanthrene	178	2180 ± 240
26	C ₂ -Fluorenes, C ₂ -dihydro-phenalene/fluorene	194, 196	--
27	3-Methylphenanthrene	192	1540 ± 110
28	2-Methylphenanthrene	192	2050 ± 240

^aRefers to peaks labeled in Figure 13

^bIdentifications based on GC retention times and mass spectral data

^cAverage of three determinations; mean ± standard deviation

^dNone detected (below approximately 75 ppm), or no data collected

^eOne determination only

TABLE 14. (Continued)

Peak Number ^a	Compound ^b	Molecular Weight	Concentration (µg/g)
29	9- or 4-Methylphenanthrene	192	197 ± 8 ^c
30	1-Methylphenanthrene	192	194 ± 1
31	Hexahdropyrene/fluoranthene	208	-- ^d
32	2-Chloroanthracene, ISTD	212	--
33	Hexahdropyrene/fluoranthene	208	--
34	Dihdropyrene/fluoranthene	204	4550 ± 660
35	Fluoranthene	202	975 ± 16
36	Pyrene	202	15300 ± 2800
37	Dihdropyrene	204	1010 ± 90
38	C ₁ -Dihdropyrene/fluoranthene	218	--
39	Benzo[b]fluorene, 2- or 4-methylpyrene	216	9220 ± 1110
40	C ₁ -Dihdropyrene/fluoranthene	218	1220 ± 230
41	1-Methylpyrene	216	564 ± 7
42	C ₂ -Pyrenes, C ₁ -benzofluorenes	230	--
43	C ₂ -Dihdropyrenes	232	--
44	C ₃ -Pyrenes, C ₂ -benzofluorenes	244	--
45	Hexahydrobenzopyrene	258	--
46	6- or 4-Methylchrysene	242	4890 ± 470
47	Benzo[j or b]fluoranthene	252	134 ± 12
48	Benzo[e]pyrene	252	264 ± 140
49	Benzo[a]pyrene	252	230 ± 120
50	Indeno[1,2,3-cd]pyrene	276	180 ^e
51	Dibenz[a,h or a,c]anthracene	278	--
52	Benzo[ghi]perylene	276	538 ± 95

^aRefers to peaks labeled in Figure 13

^bIdentifications based on GC retention times and mass spectral data

^cAverage of three determinations; mean ± standard deviation

^dNone detected (below approximately 75 ppm), or no data collected

^eOne determination only

same as the averaged results from the ITSL and NTSL HTR distillation column bottoms (see Later, 1985). A similar comparison of the concentration ratios of the 1,2-dihydrophenalene to that of fluorene gave the same results. Quali-

tatively, the CTSL PDB PAH fraction chromatogram more closely resembled that of the NTSL than of the ITSL material.

The LVMS results for the CTSL PDB PAH fraction are shown in Figure 14. Table 9 gives a key to the identification of possible structures for the masses shown in Figure 14. The major components, with masses 216 and 202, respectively, were the methylpyrenes/fluoranthenes or benzofluorenes and pyrene/fluoranthene. The average molecular weight of the PAH fraction was calculated to be 250 amu; these results are similar to the average molecular weight determinations of the ITSL (245 amu) and NTSL (250 amu) HTR distillation column bottoms. The two major components of these other two-stage liquefaction materials were hydroaromatic compounds with masses of 222 and 236, the alkylated hexahydropyrenes/fluoranthenes, respectively.

Proton NMR data from the PAH fraction isolated from the CTSL PDB material indicated the presence of a highly alkylated aromatic and hydroaromatic species (Figure 15).

Hydroaromatics. The hydroaromatic (PA_2) fraction eluted from the picric-acid-coated column adsorption chromatographic separation was analyzed by HRGC and GC/MS. The results of these analyses are given in Figure 16 and Table 15. The components of the PDB were similar to those previously reported for a second-stage CTSL material (see Later and Wilson, 1985). The hydroaromatic components identified ranged from compounds of two to those of four rings; namely, the indanes to dihydropyrenes/fluoranthenes. In addition to the parent compounds mentioned, other hydroaromatics identified in the fraction were hydrogenated species of naphthalene, acenaphthylene (or acenaphthene), fluorene, phenalene and phenanthrene; their alkylated species were also identified.

The analyses of the hydroaromatic fractions isolated from the ITSL and NTSL HTR distillation column bottoms reported by Later (1985) showed that the CTSL product hydroaromatic profile was most similar to that of the NTSL material. The NTSL material did, however, have higher concentrations of the octahydrophenanthrenes than did the CTSL material. In addition, components up to mass 250 were identified.

FIGURE 14. LVMS Results for the PAH Fraction Isolated from the HRI CTSL PDB Material. See Table 9 for a key to mass identifications.

FIGURE 15. Proton NMR Spectrum of the PDB PAH Fraction from the HRI CTSL Process. Regions indicated are defined in Table 13.

FIGURE 16. Gas Chromatogram of the Hydroaromatic Fraction Isolated from the HRI CTSL PDB Material. See text for conditions. Numbered peaks are identified in Table 15.

TABLE 15. Identifications of Selected Components in CTSL PDB Hydroaromatic Fraction

Peak Number ^a	Compound ^b	Molecular Weight
1	Indane	118
2	C ₁ -Indane	132
3	C ₁ -Indane	132
4	Tetralin	132
5	Naphthalene	128
6	C ₂ -Indans and/or C ₁ -tetralins	146
7	2-Methyltetralin	146
8	C ₁ -Tetralins and/or C ₂ -indans	146
9	6-Methyltetralin	146
10	2-Methylnaphthalene, 5-methyltetralin	142,146
11	1-Methylnaphthalene	142
12	2,6-Dimethyltetralin	160
13	C ₂ -Tetralins	160
14	1,2,2a,3,4,5-Hexahydroacenaphthylene	158
15	2-Ethylnaphthalene, C ₂ -tetralin	156,160
16	2,6- or 2,7-Dimethylnaphthalene	156
17	C ₂ -Naphthalenes	156
18	C ₁ -Hexahydroacenaphthylenes, ^c C ₃ -tetralins	172,174
19	C ₃ -Naphthalenes, dihydrofluorenes	170,168
20	C ₁ -Hexahydroacenaphthylenes ^c	172
21	C ₂ -Hexahydroacenaphthylenes, ^c C ₄ -tetralins	188,186
22	Fluorene	166
23	1,2-Dihydrophenalene	168
24	1,4-Dihydrofluorene, C ₄ -naphthalene	168,184
25	C ₁ -Dihydrophenalene and/or C ₁ -dihydrofluorene	182
26	C ₁ -Dihydrophenalene and/or C ₁ -dihydrofluorene	182
27	Tetrahydrophenanthrene	182
28	1,2,3,4-Tetrahydrophenanthrene	182
29	C ₁ -Tetrahydrophenanthrene and/or C ₂ -dihydrophenalene/fluorene	196
30	C ₂ -Tetrahydrophenanthrene and/or C ₃ -dihydrophenalene/fluorene	210
31	Hexahydropyrene/fluoranthene	208
32	Hexahydropyrene/fluoranthene	208
33	Hexahydropyrene/fluoranthene	208
34	Dihydropyrene/fluoranthene	204

^aRefers to peaks labeled in Figure 16

^bTentative identifications based on retention time and mass spectral data

^cOr hexahydrofluorene

NPAC. In the CTSL PDB material NPAC fraction (Figure 17), components containing a nitrogen heteroatom ranged from those with one to those with four rings. Table 16 gives a listing of the compounds identified and quantified in the PDB NPAC fraction. Aniline, indole, carbazole, an azapyrene, the benzo-carbazoles, some hydrogenated NPAC, and alkylated species of the above were present in this fraction. These components were similar to those identified in the ITSL and NTSL HTR distillation bottoms, with two exceptions: 1) no anilines were identified in the ITSL and NTSL materials, and 2) more lower-molecular-weight species were present in the CTSL product material. The concentration ratio of alkylated carbazoles to carbazole for the CTSL PDB was similar to those of the NTSL and ITSL materials (see Later, 1985). The PDB NPAC fraction contained similar components to those of the PFL materials, except that the former had more lower-molecular-weight species.

The 12-eV spectrum obtained from the LVMS analyses of the PDB NPAC fraction is shown in Figure 18. The overall major components of the fraction were determined to be alkyl homologs of carbazole and a series of compounds including mass 221 (possibly a tetrahydrocarbazole). The average molecular weight of the NPAC fraction was determined to be 250, which was comparable to the ITSL and NTSL materials. (However, the LVMS results discriminate against the low-molecular-weight compounds, so that the differences in composition determined by HRGC were not detectable by average molecular weights.) The 12-eV spectra of the NTSL and CTSL NPAC fraction products were the most similar qualitatively (see Later, 1985).

Although no determinations for amino-PAH were performed, the concentration of these species in the CTSL PDB is probably low. Previous studies with coal liquefaction materials that have undergone some form of catalytic hydrogenation have indicated significant reductions of amino-PAH compared to amino-PAH concentrations in materials without catalytic hydrogenation (Later, 1985; Wright et al., 1985).

Hydroxy-PAH. Phenols, indanols, hydroxybiphenyls, hydroxyfluorenes and hydroxyphenanthrenes were detected in the hydroxy-PAH fraction of the CTSL PDB material, as shown by the masses in Figure 19. The LVMS results for the analyses of the same fractions from the ITSL and NTSL products indicated more

FIGURE 17. Gas Chromatogram of the NPAC Fraction Isolated from the HRI CTSL PDB Material. See text for conditions. Numbered peaks are identified in Table 16.

TABLE 16. Concentrations of Selected Components in the HRI CTSL PDB NPAC Fraction

Peak Number ^a	Compound ^b	Molecular Weight	Concentration (µg/g)
1	Aniline	93	1280 ± 60 ^c
2	C ₁ -Aniline	107	5030 ± 490
3	C ₁ -Aniline	107	4050 ± 40
4	C ₂ -Aniline	121	2970 ± 250
5	C ₂ -Anilines	121	-- ^d
6	Tetrahydroquinoline	133	675 ± 132
7	Quinoline plus m/z 135	129	1240 ± 540
8	C ₃ -Anilines	135	--
9	C ₁ -Tetrahydroquinoline	147	--
10	Indole	117	3130 ± 60
11	C ₄ -Anilines, C ₂ -tetrahydroquinolines	149,161	--
12	3-Methylindole	131	4210
13	2-Methylindole	131	4800
14	C ₂ -Indole	145	--
15	2,5- and 2,3-Dimethylindole	145	1790 ± 120
16	Octahydrobenzoquinoline	187	1340 ± 220
17	C ₁ -Dihydroazafluorene	183	--
18	Octahydrobenzoquinoline	187	1950 ± 330
19	C ₁ -Octahydrobenzoquinoline	201	1100 ± 310
20	C ₁ -Dihydroazafluorene	183	--
21	Benzo[h]quinoline	179	--
22	C ₁ Octahydrobenzoquinoline	201	2770 ± 600
23	C ₁ -Dihydroazafluorene	183	--
24	Tetrahydrocarbazole	171	1360 ± 70
25	Phenanthridine, benzo[f]quinoline	179	412 ^e
26	Octahydrobenzoquinoline	187	1340 ± 350
27	Carbazole	167	4380 ± 250
28	2- or 3-Methylbenzo[f]quinoline	193	1080 ± 270
29	1-Methylcarbazole	181	1220 ± 150
30	3-Methylcarbazole	181	3740 ± 410
31	2-Methylcarbazole	181	3450 ± 540
32	4-Methylcarbazole	181	1520 ± 230

^aRefers to peaks labeled in Figure 17

^bIdentifications based on GC retention times and mass spectral data

^cAverage of three determinations; mean ± standard deviation

^dNone detected (below approximately 75 ppm), or no data collected

^eOne determination only

TABLE 16. (Continued)

Peak Number ^a	Compound ^b	Molecular Weight	Concentration (µg/g)
33	2-Chloroanthracene, ISTD	212	-- ^d
34	C ₂ -Carbazoles	195	--
35	C ₃ -Carbazoles	209	--
36	1- or 4-Azapyrene	203	4420 ± 460 ^c
37	C ₁ -Azapyrenes, azabenzofluorenes	217	--
38	C ₂ -Azapyrenes, C ₁ -Azabenzofluorenes	231	--
39	Benzo[a]carbazole	217	1600 ± 190
40	Benzo[b]carbazole	217	710
41	Benzo[c]carbazole	217	1940 ± 550
42	C ₃ -Azapyrene, C ₂ -Azabenzofluorene	245	--

^aRefers to peaks labeled in Figure 17

^bIdentifications based on GC retention times and mass spectral data

^cAverage of three determinations; mean ± standard deviation

^dNone detected (below approximately 75 ppm), or no data collected

^eOne determination only

similarity between the CTSL and NTSL materials than between the CTSL and ITSL material (see Later, 1985). The indanols and alkyl homologs were the major components of the ITSL hydroxy-PAH fraction, whereas the hydroxyfluorenes were the major components of the hydroxy-PAH fractions isolated from the NTSL and CTSL materials. The NTSL material did show more higher-molecular-weight compounds present (average molecular weight, 280 amu); the average molecular weight of the CTSL PDB hydroxy-PAH fraction was determined to be 240 amu (which was also significantly less than the average molecular weight of the PFL composite material).

Summary. The chemical analyses of the CTSL PDB indicated that it was a highly alkylated, aromatic and hydroaromatic material with few heteroatoms. The fractions isolated from the PDB had compositions similar to those of the

FIGURE 18. LVMS Results for the NPAC Fraction Isolated from the HRI CTSL PDB Material. See Table 11 for a key to mass identifications.

FIGURE 19. LVMIS Results for the Hydroxy-PAH Fraction Isolated from the HRI CTSL PDB Material. See Table 12 for a key to mass identifications.

PFL chemical class fractions, except for a significantly increased concentration of lower-molecular-weight materials (due to the blending of lower-boiling process materials in this sample). When the analyses of the chemical class fractions were performed, the CTSL PDB more closely resembled the NTSL HTR product than the ITSL product. However, the NTSL material had increased concentrations of heavier-molecular-weight species and increased relative concentrations of some hydroaromatic species, notably the octahydrophenanthrenes.

First- and Second-Stage Materials

First- and second-stage CTSL process materials have been previously analyzed and reported by Later and Wilson (1985). I/P data were not available for any of these samples at that time. The purpose of this section is to present additional chemical analyses data for the two first- and second-stage all-distillate recycle CTSL materials that have been tested in the I/P assay for mouse-skin tumorigenicity. The two samples analyzed were from an experimental run of the CTSL process and were described in the Sample Materials section. The results of the HRGC and LVMS chemical analyses of these two samples are presented in the following order: 1) AH, 2) PAH, 3) NPAC, and 4) hydroxy-PAH. The analyses of the hydroaromatic fractions isolated from these two materials were reported by Later and Wilson (1985); the results of their analyses were similar to the results of the analysis of the PDB hydroaromatic fraction, given above.

AH. The first-stage THF-extracted filtrate AH fraction had a higher concentration of heavier-molecular-weight components than did the second-stage pressure-filtered topped separator bottoms (12-eV spectra, Figure 20). The mass of greatest concentration in the first-stage material was 240 amu, whereas in the second-stage material it was 214 amu. Hydroaromatic species were determined, by LVMS, to be the major components in the AH fractions of both of these materials. Alkane components were also detected based on the presence of fragment ions at 71, 85, 97 and 111 amu. Thus, although the GC profiles for the AH fractions of the first- and second-stage materials were similar, the LVMS results show a shift to lower molecular weight in the second-stage material. These data, along with the increased concentration of AH in the second-stage material (see Table 6), indicate that the second-stage catalytic

FIGURE 20. LVMS Results for the AH Fractions Isolated from First- and Second-Stage Materials from an Experimental Run of the CTSL Process

hydrotreatment had more of an impact on the end product than originally concluded by Later and Wilson (1985). The difference, although subtle, was detectable in the AH fractions.

By comparing Figure 20 to Figure 3, we can compare LVMS results for the AH fraction from the second-stage pressure-filtered topped separator bottoms from the experimental run of the CTSL process to those for the PFL from the 25-day demonstration run. Following the second stage of the demonstration run, the internal process stream material had a higher molecular-weight range than the second-stage material collected during the experimental run.

PAH. The gas chromatograms of the PAH fractions were quite similar to each other for both the first- and second-stage materials from an experimental run of the CTSL process (Figure 21). The components labeled in Figure 21 are identified and quantified in Table 17. The quantitative results in Table 17 also showed the similarity between the two materials: the concentrations of selected components in the PAH fractions isolated from the first- and second-stage materials were nearly identical.

The LVMS results for the PAH fractions from the first- and second-stage CTSL materials are given in Figure 22. The first-stage material was of a higher-molecular-weight range than the second-stage materials, with average-molecular-weight determinations of 250 and 230 amu, respectively. Both fractions had higher average-molecular-weight determinations than did the PFL materials from the 25-day demonstration run (see Figure 5). The series, including components of masses 194, 208, 222 and 236 (the alkylfluorenes or hexahydropyrenes/fluoranthenes) were major components of the PAH fractions from the experimental run materials, whereas these components were minor in the PFL materials after 10 days of the 25-day demonstration run.

NPAC. A more striking difference in the molecular weight ranges of the first- and second-stage products is shown by the LVMS results of the NPAC fractions isolated from the experimental run CTSL materials, shown in Figure 23. The average molecular weight of the first-stage THF-extracted filtrate NPAC fraction was 370 amu; the average molecular weight was 260 amu for the second-stage pressure-filtered topped separator bottoms NPAC fraction.

FIGURE 21. Gas Chromatograms of the PAH Fractions Isolated from the First- and Second-Stage Materials from an Experimental Run of the CTSL Process. See text for conditions. Labeled peaks are identified in Table 17.

TABLE 17. Concentrations of Selected Components in PAH Fractions of First- and Second-Stage CTSI Materials

Peak Number ^b	Compound ^c	Molecular Weight	Concentration (µg/g) ^a	
			First	Second
1	Naphthalene	128	554	498
2	2-Methylnaphthalene	142	1,580	1,390
3	1-Methylnaphthalene	142	478	413
4	Biphenyl	154	727	487
5	2-Ethylnaphthalene	156	231	191
6	2,6- or 2,7-Dimethylnaphthalene	156	1,070	856
7	1,7-Dimethylnaphthalene	156	644	502
8	1,3- or 1,6-Dimethylnaphthalene	156	347	288
9	C ₂ -Naphthalenes	156	-- ^d	--
10	C ₁ -Biphenyls	168	--	--
11	Dibenzofuran	168	990	1,440
12	C ₃ -Naphthalenes	170	--	--
13	Fluorene	166	7,030	7,090
14	1,2-Dihydrophenalene	168	13,700	11,300
15	1,4-Dihydrofluorene	168	4,650	3,770
16	C ₁ -Dihydrophenalene/fluorene	182	--	--
17	2-Methylfluorene	180	6,180	7,480
18	C ₁ -Dihydrophenalene/fluorene	182	10,700	15,500
19	Phenanthrene	178	6,760	7,060
20	C ₂ -Fluorenes, C ₂ -dihydrophenalene/fluorene	194,196	--	--
21	3-Methylphenanthrene	192	5,190	5,320
22	2-Methylphenanthrene	192	4,510	4,760
23	Hexahydropyrene/fluoranthene	208	--	--
24	Hexahydropyrene/fluoranthene	208	--	--
25	2-Chloroanthracene, ISTO	212	--	--
26	Dihydropyrene/fluoranthene	204	9,180	10,700
27	Fluoranthene	202	1,160	1,870
28	Pyrene	202	24,200	30,400
29	C ₁ -Dihydropyrene/fluoranthene	218	--	--
30	Benzo[b]fluorene, 2- or 4-methylpyrene	216	13,400	16,800
31	C ₁ -Dihydropyrene/fluoranthene	218	3,560	4,710
32	1-Methylpyrene	216	1,250	1,160

^a Average of two injections

^b Refers to peaks labeled in Figure 21

^c Identified by GC retention time and GC/MS data

^d No data collected

TABLE 17. (Continued)

Peak Number ^b	Compound ^c	Molecular Weight	Concentration ($\mu\text{g/g}$) ^a	
			Stage	
			First	Second
33	C ₂ -Pyrenes, C ₁ -benzofluorenes	230	-- ^d	--
34	C ₂ -Dihdropyrenes	232	--	--
35	C ₃ -Pyrenes, C ₂ -benzofluorenes	244	--	--
36	Hexahydrobenzopyrene	258	--	--
37	6- or 4-Methylchrysene	242	4,840	5,460
38	Benzo[j or b]fluoranthene	252	281	362
39	Benzo[e]pyrene	252	447	495
40	Benzo[a]pyrene	252	271	415
41	Indeno[1,2,3-cd]pyrene	276	354	305
42	Benzo[ghi]perylene	276	757	836

^aAverage of two injections^bRefers to peaks labeled in Figure 21^cIdentified by GC retention time and GC/MS data^dNo data collected

The low concentration of NPAC species in these materials was evidenced by the fact that the major components of the NPAC fraction appeared as contaminants from the breakthrough of hydroxy-PAH compounds.

The composition of the NPAC fractions isolated from the first- and second-stage CTSL experimental run materials were similar to each other, based on HRGC and GC/MS analyses. The concentrations of selected components in these fractions are given in Table 18.

Hydroxy-PAH. Phenols, indanols, acenaphthenols, hydroxybiphenyls or acenaphthylenols, hydroxyfluorenes, and isomers of hydroxychrysenes were the major components detected by LVMS in the hydroxy-PAH fractions of both the first- and second-stage materials (Figure 24). As with the AH, PAH and NPAC fractions, the first-stage material had an increased heavy-molecular-weight

FIGURE 22. LVMS Results from the Analysis of PAH Fractions Isolated from the First- and Second-Stage Materials from an Experimental Run of the CTSL Process. See Table 9 for a key to mass identifications.

FIGURE 23. LVMS Results from the Analysis of NPAC Fractions Isolated from the First- and Second-Stage Materials from an Experimental Run of the CTSL Process. See Tables 11 and 12 for keys to mass identifications.

TABLE 18. Concentrations of Selected Components in NPAC Fractions of First- and Second-Stage CTSL Materials

Compound ^b	Molecular Weight	Concentration (µg/g) ^a	
		First	Second
Aniline	93	38	8
Quinoline	129	661	536
Indole	117	189	182
8-Methylquinoline	143	77	47
7-Methylindole	131	393	357
3-Methylindole	131	453	435
2,6-Dimethylquinoline	157	881	738
Octahydrobenzoquinoline	187	961	1,090
C ₁ -Octahydrobenzoquinoline	201	1,250	1,570
Carbazole	167	436	630
1-Methylcarbazole	181	486	481
3-Methylcarbazole	181	329	363
1- or 4-Azapyrene	203	944	575
Benzo[a]carbazole	217	138	330
Benzo[b]carbazole	217	129	259
Benzo[c]carbazole	217	479	587

^aAverage of two injections

^bIdentifications based on GC retention time

composition compared to the second-stage material; average molecular weights were 340 and 240 amu, respectively. Both these materials had a significantly lower molecular-weight range than the PFL materials after Day 5 of the 25-day CTSL demonstration run, although similar components were detected (see Figure 8).

Summary. Similar compositions were determined for the chemical class fractions isolated from both the first- and second-stage CTSL experimental run process materials. The first-stage THF-extracted filtrate had a slightly higher molecular-weight range than the second-stage pressure-filtered topped separator bottoms, however. In addition, the chemical class fractions isolated from the second-stage experimental run process material exhibited a sig-

FIGURE 24. LVMS Results from the Analysis of Hydroxy-PAH Fractions Isolated from the First- and Second-Stage Materials from an Experimental Run of the CTSL Process. See Table 12 for a key to mass identifications.

nificantly lower molecular-weight range than did the fractions isolated from the PFL materials after 5 days of the 25-day demonstration run. The molecular-weight range difference between these materials may be an effect of the use of resid recycle during the demonstration run compared to an all-distillate recycle in the first three conditions of the experimental run.

BIOLOGICAL TESTING

Microbial Mutagenicity Assay

The raw dose-response data from the microbial mutagenicity tests with S. typhimurium, TA98 are given in Appendix A for the CTSL materials from the 25-day demonstration run. The positive and negative control data are also included in Appendix A for tests with both strains of S. typhimurium, TA98 and TA100.

The microbial mutagenicity results indicated a general trend of increasing mutagenicity with increased pilot plant operation time and catalyst age. The results of testing crude PFL materials from each day of the demonstration run are given in Table 19. The responses, in revertants/ μg , ranged from approximately 1 to 2 for the first 5 days, 2 to 3 revertants/ μg for the next 5 days, 4 to 6 revertants/ μg for Days 11 through 15, 6 to 10 revertants/ μg for Days 16 through 20 and 9 to 12 revertants/ μg for the last 5 days of the demonstration run. The trend of increasing mutagenic response with time of operation correlates with the chemistry analysis data, which showed that the PFL materials had an increasing heteroatomic (particularly NPAC) composition as the length of pilot plant operation time increased. The microbial mutagenic response of coal liquefaction materials has historically been related to the NPAC chemical class fractions, particularly the amino-PAH, for coal liquefaction materials analyzed using these methods (Later et al., 1982, 1983; Wilson et al., 1984). The mutagenic response of the CTSL PFL after about 10 days of operation was greater than that of the Wilsonville ITSL recycle process solvent, which gave a mutagenic response of 5 revertants/ μg (Later, 1985).

The CTSL PDB had a higher mutagenic response with S. typhimurium, TA98 than materials representative of Wilsonville (bp, $>450^{\circ}\text{F}$) and Lummus PDU (bp,

TABLE 19. CTSL Process Material Microbial Mutagenicity Data with *S. typhimurium*, TA98

PFL Sample #50378-	Day	Revertants/ μ g	Maximum Response ^a (μ g, Background)
064	1	1.5	334 $\pm$ 3 (500, 61 $\pm$ 8)
065	2	1.7	320 $\pm$ 29 (500, 61 $\pm$ 8)
066	3	1.1	312 $\pm$ 23 (500, 61 $\pm$ 8)
067	4	1.1	282 $\pm$ 21 (500, 61 $\pm$ 8)
068	5	1.1	350 $\pm$ 52 (500, 50 $\pm$ 14)
069	6	1.7	260 $\pm$ 36 (500, 50 $\pm$ 14)
070	7	1.5	287 $\pm$ 29 (500, 50 $\pm$ 14)
071	8	3.2	429 $\pm$ 30 (500, 50 $\pm$ 14)
072	9	1.9	483 $\pm$ 16 (500, 50 $\pm$ 14)
073	10	2.0	351 $\pm$ 22 (500, 61 $\pm$ 8)
074	11	5.4	624 $\pm$ 7 (500, 52 $\pm$ 14)
075	12	5.0	571 $\pm$ 162 (500, 52 $\pm$ 14)
076	13	5.7	627 $\pm$ 75 (500, 52 $\pm$ 14)
077	14	4.0	695 $\pm$ 92 (500, 52 $\pm$ 14)
078	15	6.0	680 $\pm$ 95 (500, 52 $\pm$ 14)
079	16	5.8	514 $\pm$ 34 (200, 52 $\pm$ 14)
080	17	8.2	830 $\pm$ 69 (500, 52 $\pm$ 14)
081	18	7.3	651 $\pm$ 104 (500, 52 $\pm$ 14)
082	19	7.0	963 $\pm$ 108 (500, 52 $\pm$ 14)
083	20	10.4	852 $\pm$ 38 (200, 52 $\pm$ 14)
084	21	9.5	906 $\pm$ 41 (200, 36 $\pm$ 2)
085	22	10.7	862 $\pm$ 8 (200, 36 $\pm$ 2)
086	23	12.2	1263 $\pm$ 101 (500, 36 $\pm$ 2)
087	24	9.4	857 $\pm$ 31 (500, 36 $\pm$ 2)
088	25	11.6	824 $\pm$ 21 (200, 36 $\pm$ 2)
089 ^b		5.1	493 $\pm$ 43 (500, 36 $\pm$ 2)
090 ^c		1.7	315 $\pm$ 17 (500, 36 $\pm$ 2)

^aRevertants/plate

^bPFL composite

^cPDB

>400°F) ITSL final products: approximately 2 revertants/ μ g for the CTSL versus 0 revertants/ μ g for the ITSL materials (see Later, 1985; Wilson et al., 1983). The PDB did, however, have a lower mutagenic response than that of a NTSL (bp, >450°F) final product (6 revertants/ μ g; Later, 1985).

All crude materials from the 25-day CTSL demonstration run were also tested for mutagenic response with S. typhimurium, TA100. Although none of the materials tested gave a response twice that of background, the maximum response data indicated that higher numbers of revertant colonies were produced with the PFL materials from the later days of the demonstration run (Table 20).

Microbial mutagenicity was determined for the chemical class fractions isolated from selected CTSL demonstration run materials (Table 21). A comparison of the crude mutagenic responses given in Table 21 to those in Table 19 shows the variability of the biological assay. In general, there was good trend correlation of data. The data in Table 21 also show the increasing mutagenic potency of the CTSL PFL with increasing pilot plant operation time. The mutagenic response of the unfractionated crudes ranged from 0 (Day 1) to ~21 (Day 24) revertants/ μ g for the PFL materials. The majority of microbial mutagenicity was associated with the NPAC fractions of these materials, as has been the case with the other coal liquefaction materials studied to date. Some direct-acting (no S9) mutagenic response was noted in the CTSL PDB material. Significantly higher levels of mutagenic response were produced in the hydroxy-PAH fractions of the PFL materials after 10 days of the 25-day demonstration run.

The microbial mutagenicity of the first- and second-stage CTSL experimental run process materials were given in Later and Wilson (1985). These samples exhibited similar microbial mutagenicity to that of the PFL materials from the early days of the demonstration run. Few differences were noted between the samples.

I/P Tumorigenicity Assay

The results are shown in Figure 25 for the I/P mouse skin tumorigenicity assay of Days 5, 15, 24 and the composite PFL materials from the 25-day demonstration run of the HRI CTSL process. The cumulative skin-tumor yield data (the total number of tumors, normalized to a population of 30 mice) indicated a general trend of increasing tumorigenicity with increasing length of pilot plant operation and catalyst age. These I/P results are in general agreement

TABLE 20. CTSL Process Material Maximum Response Microbial Mutagenicity Data with S. typhimurium, TA100

PFL Sample #50378-	Day	µg/Plate	Revertant Colonies ^a	Background (Revertants)
064	1	20	382 ± 8	309 ± 31
065	2	8	394 ± 5	309 ± 31
066	3	50	390 ± 3	309 ± 31
067	4	20	392 ± 1	309 ± 31
068	5	50	374 ± 1	309 ± 31
069	6	8	395 ± 9	309 ± 31
070	7	50	397 ± 20	309 ± 31
071	8	20	404 ± 8	309 ± 31
072	9	20	409 ± 2	309 ± 31
073	10	50	357 ± 31	309 ± 31
074	11	50	392 ± 15	309 ± 31
075	12	50	378 ± 15	309 ± 31
076	13	50	380 ± 15	309 ± 31
077	14	50	387 ± 15	309 ± 31
078	15	50	423 ± 13	281 ± 12
079	16	50	412 ± 20	281 ± 12
080	17	50	480 ± 26	281 ± 12
081	18	50	482 ± 21	281 ± 12
082	19	50	501 ± 20	281 ± 12
083	20	50	505 ± 27	281 ± 12
084	21	50	430 ± 21	281 ± 12
085	22	50	525 ± 81	281 ± 12
086	23	50	481 ± 77	281 ± 12
087	24	50	486 ± 11	281 ± 12
088	25	50	499 ± 4	281 ± 12
089 ^b		50	387 ± 53	281 ± 12
090 ^c		50	347 ± 17	281 ± 12

^aRevertants/plate with 20 µl S9

^bPFL composite

^cPDB

with the chemistry results that showed that PFL materials had decreased AH content, increased molecular weight distribution and increased heteroatomic composition with increasing length of pilot plant operation and catalyst age.

TABLE 21. Microbial Mutagenicity Data with *S. typhimurium*, TA98 of Chemical Class Fractions Isolated from CTSI Process Materials from the 25-Day Demonstration Run

PFL Sample #50378-	Day	Revertants/ μ g ^a				
		Crude	AH	Chemical Class Fraction		
				PAH	NPAC	Hydroxy-PAH
064	1	0 (176 $\pm$ 43)	0 (47 $\pm$ 1)	0.2 (64 $\pm$ 3)	25.3 (147 $\pm$ 5)	0.2 (173 $\pm$ 22)
068	5	0.5 (360 $\pm$ 19)	0 (79 $\pm$ 5)	0 (123 $\pm$ 14)	15.6 (151 $\pm$ 7)	0.7 (374 $\pm$ 3)
073	10	3.6 (251 $\pm$ 19)	0.3 (138 $\pm$ 3)	0 (153 $\pm$ 13)	29.0 (505 $\pm$ 11)	3.8 (798 $\pm$ 7)
078	15	16.9 (1068 $\pm$ 134)	0 (50 $\pm$ 1)	0.6 (110 $\pm$ 17)	24.3 (779 $\pm$ 22)	3.7 (996 $\pm$ 98)
082	19	17.6 (1419 $\pm$ 51)	0 (36 $\pm$ 3)	0.6 (135 $\pm$ 9)	39.2 (1012 $\pm$ 21)	5.2 (1293 $\pm$ 69)
087	24	21.1 (1381 $\pm$ 129)	0 (40 $\pm$ 1)	0.5 (139 $\pm$ 11)	32.3 (963 $\pm$ 89)	4.0 (986 $\pm$ 10)
089 ^b		12.4 (403 $\pm$ 35)	0 (38 $\pm$ 0)	0.8 (163 $\pm$ 0)	27.2 (834 $\pm$ 5)	3.4 (1118 $\pm$ 39)
090 ^c		1.9 (772 $\pm$ 27)	0 (44 $\pm$ 3)	1.7 (467 $\pm$ 42)	10.8 (483 $\pm$ 41)	0.6 (330 $\pm$ 6)
		1.5 (489 $\pm$ 35) ^d		0.2 (109 $\pm$ 12) ^d	6.9 (182 $\pm$ 5) ^d	0.3 (200 $\pm$ 20) ^d

^aMaximum revertants/plate given in parentheses; values reported with S9 activation, except as otherwise noted.

^bPFL composite

^cPDB

^dValue reported without S9 activation

The tumor yield data for the PFL composite correlated with the tumor yield data for the PFL Day 15 material. The percent tumor incidences were similar

FIGURE 25. Mouse-Skin Tumor Response after Initiation with Coal Liquefaction Materials from the 25-Day Demonstration Run of the HRI CTSL Process. Top: Cumulative skin-tumor yield (normalized to 30 mice/group) versus time. Bottom: Percent tumor incidence versus time. See Figure 26 for experimental control data.

for all the PFL materials tested; however, Day 5 results were slightly lower and Day 15 results were slightly higher than the rest.

The skin-tumor initiating activity of the PDB (also shown in Figure 25) was significantly less than that of any PFL materials tested when judged by either tumor yield or tumor incidence; this is predictable from the significantly increased bp range of the PFL (>975°F) versus that of the PDB (<850°F) materials. All coal liquefaction materials tested from 25-day demonstration run #227-20 showed significantly greater tumorigenic potential than the negative solvent control (Figure 26).

Figure 26 shows the I/P results for the first- and second-stage process materials from an experimental run of the HRI CTSL process. Preliminary chemical analyses and mutagenicity testing of these two materials have been previously reported by Later and Wilson (1985), and additional chemical analysis data are presented in this report. The initiating activity of these two process materials appeared to be quite similar. The first-stage material, however, gave slightly higher tumor-yield and tumor-incidence results after 177 days. These I/P results are in general agreement with the chemistry results, which showed that the first-stage material was similar in composition to the second-stage material, except for a slightly higher molecular weight range.

The initiating activities of the first- and second-stage materials from an experimental run of the CTSL process were lower than those expressed by the PFL materials from the 25-day CTSL demonstration run. This may be an effect of the different operating conditions, primarily all-distillate versus resid-containing recycle, used to obtain the samples or an effect of the length of pilot plant operation time before the samples were taken. The initiating activity of the PFL materials was evaluated after 5 days of operation, and chemistry data showed that concentrations of heavier-molecular-weight components increased with the length of operating time. I/P results of the first- and second-stage materials and the PFL materials were also in agreement with chemistry data that showed the former were of a generally lower-molecular-weight and bp range and had higher AH content than the latter.

FIGURE 26. Mouse-Skin Tumor Response after Initiation with Coal Liquefaction Materials from an Experimental Run of the HRI CTSL Process. Top: Cumulative skin-tumor yield (normalized to 30 mice/group) versus time. Bottom: Percent tumor incidence versus time.

I/P data complementary to those given in Figures 25 and 26 are given in Table 22 in the form of mean number of tumors per mouse. Again, the following three observations can be made: 1) there was a general trend of increasing initiating activity with increasing pilot plant operating time; 2) the PDB material (representative of a final CTSL coal liquefaction product) expressed lower initiating activity than did the PFL materials (representative of post-second-stage internal process stream materials); and 3) both the first- and second-stage process materials from a previous experimental run of the HRI CTSL process showed lower initiating activity than did the PFL materials tested from the 25-day demonstration run.

Also included in Table 22 are the mean number of tumors per mouse for the ITSL and NTSL HTR feed (first-stage product) and distillation column bottoms (second-stage product) from Later (1985) and for the ITSL TLP from Wilson et al. (1983), with nominal bp information for all samples. The CTSL PDB appeared to have less tumor-initiating activity than did the NTSL or ITSL products. This result is in agreement with the chemistry data, which indicated that the CTSL material had a decreased concentration of high-molecular-weight compounds compared to the ITSL and NTSL materials. Increased tumorigenic potential has been correlated with increased bp and increased concentrations of heavier-molecular-weight species in coal liquefaction materials by Mahlum (1983a). The results of the I/P analyses of all CTSL materials have been in general agreement with this finding.

A more significant reduction in tumorigenicity was noted between the first- and second-stage products for both the Wilsonville ITSL and NTSL processes compared to the CTSL process (see Table 22). Later (1985) showed that catalytic hydrogenation reduced the tumorigenic potential of coal liquefaction materials. The data presented here indicate that the addition of a catalyst to the solvation reactor may help to reduce the tumorigenicity of first-stage coal liquefaction products, since the initiating activities were similar between the materials from both stages of the CTSL process. The similarity of tumorigenic response (no reduction) between the first- and second-stage CTSL experimental process materials may also have been an effect of the THF extraction of the first-stage product, which may discriminate against heavy-molecular-weight (insoluble) species.

TABLE 22. I/P Results (Mean Number of Tumors per Mouse) for HRI CTSL Materials

Sample	Nominal bp Range (°F)	Tumors/Mouse ^a
50378-068 PFL Day 5	500-975+	1.37
50378-078 PFL Day 15	500-975+	1.62
50378-087 PFL Day 24	500-975+	2.27
50378-089 PFL Composite	500-975+	1.59
50378-090 PDB	<850	0.57
50378-040 First-stage THF extracted filtrate	IBP 850+	0.67
50378-041 Second-stage pressure-filtered topped separator bottoms	IBP 850+	0.52
Negative Control		0.10
5226-021 NTSL HTR feed	450-1000	2.2 ^b
5226-022 NTSL HTR distillation column bottoms	450- 850+	1.3 ^b
5226-061 ITSL HTR feed	450-1000	3.2 ^b
5226-056 ITSL HTR distillation column bottoms	450- 850+	1.1 ^b
3399-095 ITSL TLP (Lummus PDU)	~400- 850+	2.6 ^c

^aMean of tumor results for 30 mice per test material

^bFrom Later (1985)

^cFrom Wilson et al. (1983)

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APPENDIX A

RAW, UNTRANSFORMED DOSE-RESPONSE MICROBIAL MUTAGENICITY DATA

TABLE A1. Average Positive and Negative Control Data for Salmonella typhimurium, TA98 Microbial Mutagenicity Data of Table A2

Controls	S9 (μ l)	μ g/Plate	Number of Revertant Colonies
2-AA	10	1	2131 $\pm$ 369
BaP	100	10	413 $\pm$ 32
NTG	0	1	28 $\pm$ 6
030 A ₃	20	1	179 $\pm$ 30
None	20		49 $\pm$ 14
None	100		52 $\pm$ 10
None	0		29 $\pm$ 5

KEY:

2-AA = 2-Aminoanthracene

BaP = Benzo[a]pyrene

NTG = n-Methyl-N'-nitro-N-nitrosoguanidine

030 A₃ = Nitrogen-containing polycyclic aromatic compound fraction of solvent refined coal-II 850°F+ distillate cut

TABLE A2. Raw Dose-Response Data for the *Salmonella typhimurium*, TA98 Mutagenicity Testing of Crude CTSL Process Materials from the 25-Day Demonstration Run

$\mu\text{g}/\text{Plate}$	Number of Revertant Colonies with 20 μl S9 in Sample #50378-			
	064	065	066	067
	PFL Day			
	1	2	3	4
0	61 $\pm$ 8	61 $\pm$ 8	61 $\pm$ 8	61 $\pm$ 8
2	68 $\pm$ 18	68 $\pm$ 9	57 $\pm$ 0	46 $\pm$ 2
4	71 $\pm$ 13	69 $\pm$ 10	63 $\pm$ 8	58 $\pm$ 1
8	57 $\pm$ 1	52 $\pm$ 3	50 $\pm$ 2	39 $\pm$ 1
10	60 $\pm$ 6	74 $\pm$ 0	53 $\pm$ 4	50 $\pm$ 2
20	109 $\pm$ 14	102 $\pm$ 8	96 $\pm$ 9	70 $\pm$ 10
50	166 $\pm$ 5	145 $\pm$ 12	136 $\pm$ 4	121 $\pm$ 1
20	130 $\pm$ 14	136 $\pm$ 10	123 $\pm$ 7	120 $\pm$ 16
40	144 $\pm$ 9	178 $\pm$ 41	113 $\pm$ 5	129 $\pm$ 5
80	187 $\pm$ 14	200 $\pm$ 49	171 $\pm$ 11	149 $\pm$ 25
100	187 $\pm$ 4	177 $\pm$ 17	154 $\pm$ 17	204 $\pm$ 10
200	299 $\pm$ 23	251 $\pm$ 36	231 $\pm$ 22	236 $\pm$ 15
500	334 $\pm$ 3	320 $\pm$ 29	312 $\pm$ 23	282 $\pm$ 21

	Number of Revertant Colonies with 20 μl S9 in Sample #50378-			
	068	069	070	071
	PFL Day			
	5	6	7	8
0	50 $\pm$ 14	50 $\pm$ 14	50 $\pm$ 14	50 $\pm$ 14
2	49 $\pm$ 1	53 $\pm$ 8	46 $\pm$ 1	56 $\pm$ 3
4	43 $\pm$ 3	53 $\pm$ 0	59 $\pm$ 2	63 $\pm$ 1
8	43 $\pm$ 2	65 $\pm$ 8	34 $\pm$ 0	46 $\pm$ 2
10	56 $\pm$ 3	67 $\pm$ 4	48 $\pm$ 4	69 $\pm$ 4
20	63 $\pm$ 3	85 $\pm$ 11	82 $\pm$ 5	129 $\pm$ 9
50	104 $\pm$ 7	155 $\pm$ 26	105 $\pm$ 9	176 $\pm$ 23
20	95 $\pm$ 4	86 $\pm$ 10	121 $\pm$ 7	127 $\pm$ 5
40	109 $\pm$ 0	110 $\pm$ 23	117 $\pm$ 25	137 $\pm$ 2
80	124 $\pm$ 0	171 $\pm$ 14	184 $\pm$ 19	163 $\pm$ 5
100	182 $\pm$ 30	155 $\pm$ 2	248 $\pm$ 39	201 $\pm$ 25
200	195 $\pm$ 17	248 $\pm$ 8	231 $\pm$ 0	288 $\pm$ 43
500	350 $\pm$ 52	260 $\pm$ 36	287 $\pm$ 29	429 $\pm$ 30

PFL = Pressure filter liquid

TABLE A2. (Continued)

$\mu\text{g}/\text{Plate}$	Number of Revertant Colonies with 20 μl S9 in Sample #50378-			
	072	073	074	075
	PFL Day			
	9	10	11	12
0	50 $\pm$ 14	61 $\pm$ 8	52 $\pm$ 14	52 $\pm$ 14
2	54 $\pm$ 2	55 $\pm$ 1	62 $\pm$ 8	50 $\pm$ 3
4	87 $\pm$ 5	75 $\pm$ 1	75 $\pm$ 4	103 $\pm$ 9
8	55 $\pm$ 1	72 $\pm$ 8	89 $\pm$ 1	63 $\pm$ 15
10	70 $\pm$ 8	82 $\pm$ 7	134 $\pm$ 11	120 $\pm$ 5
20	120 $\pm$ 4	105 $\pm$ 13	155 $\pm$ 12	160 $\pm$ 6
50	132 $\pm$ 5	173 $\pm$ 3	235 $\pm$ 25	281 $\pm$ 2
20	177 $\pm$ 15	146 $\pm$ 25	244 $\pm$ 1	198 $\pm$ 6
40	215 $\pm$ 0	135 $\pm$ 7	170 $\pm$ 59	227 $\pm$ 37
80	264 $\pm$ 50	198 $\pm$ 31	384 $\pm$ 43	388 $\pm$ 99
100	288 $\pm$ 67	229 $\pm$ 2	357 $\pm$ 88	287 $\pm$ 106
200	452 $\pm$ 12	295 $\pm$ 1	498 $\pm$ 23	544 $\pm$ 2
500	483 $\pm$ 16	351 $\pm$ 22	624 $\pm$ 7	571 $\pm$ 162

	Number of Revertant Colonies with 20 μl S9 in Sample #50378-			
	076	077	078	079
	PFL Day			
	13	14	15	16
0	52 $\pm$ 14	52 $\pm$ 14	52 $\pm$ 14	52 $\pm$ 14
2	55 $\pm$ 2	62 $\pm$ 17	61 $\pm$ 8	61 $\pm$ 7
4	100 $\pm$ 8	99 $\pm$ 21	91 $\pm$ 16	95 $\pm$ 2
8	58 $\pm$ 4	60 $\pm$ 4	82 $\pm$ 8	79 $\pm$ 3
10	82 $\pm$ 9	96 $\pm$ 9	113 $\pm$ 8	128 $\pm$ 6
20	173 $\pm$ 26	153 $\pm$ 3	196 $\pm$ 26	162 $\pm$ 22
50	337 $\pm$ 19	225 $\pm$ 6	334 $\pm$ 2	360 $\pm$ 9
20	187 $\pm$ 21	267 $\pm$ 5	258 $\pm$ 35	254 $\pm$ 35
40	202 $\pm$ 10	253 $\pm$ 90	321 $\pm$ 39	374 $\pm$ 25
80	338 $\pm$ 16	409 $\pm$ 67	420 $\pm$ 11	274 $\pm$ 2
100	394 $\pm$ 0	518 $\pm$ 56	477 $\pm$ 18	478 $\pm$ 86
200	467 $\pm$ 43	553 $\pm$ 61	628 $\pm$ 26	514 $\pm$ 34
500	627 $\pm$ 75	695 $\pm$ 92	680 $\pm$ 95	453 $\pm$ 122

PFL = Pressure filter liquid

TABLE A2. (Continued)

$\mu\text{g}/\text{Plate}$	Number of Revertant Colonies with 20 μl S9 in Sample #50378-			
	080	081	082	083
	PFL Day			
	17	18	19	20
0	52 $\pm$ 14	52 $\pm$ 14	52 $\pm$ 14	52 $\pm$ 14
2	67 $\pm$ 13	80 $\pm$ 7	92 $\pm$ 5	72 $\pm$ 5
4	68 $\pm$ 3	90 $\pm$ 14	135 $\pm$ 20	125 $\pm$ 6
8	95 $\pm$ 3	121 $\pm$ 1	122 $\pm$ 37	110 $\pm$ 0
10	139 $\pm$ 11	150 $\pm$ 10	145 $\pm$ 28	173 $\pm$ 4
20	240 $\pm$ 28	163 $\pm$ 23	198 $\pm$ 2	288 $\pm$ 18
50	395 $\pm$ 55	306 $\pm$ 2	375 $\pm$ 57	526 $\pm$ 2
20	325 $\pm$ 51	322 $\pm$ 25	354 $\pm$ 53	385 $\pm$ 48
40	413 $\pm$ 67	427 $\pm$ 46	394 $\pm$ 27	540 $\pm$ 27
80	569 $\pm$ 0	536 $\pm$ 54	574 $\pm$ 38	641 $\pm$ 43
100	503 $\pm$ 20	559 $\pm$ 33	703 $\pm$ 4	746 $\pm$ 12
200	789 $\pm$ 78	598 $\pm$ 174	870 $\pm$ 31	852 $\pm$ 38
500	830 $\pm$ 69	651 $\pm$ 104	963 $\pm$ 108	840 $\pm$ 36

	Number of Revertant Colonies with 20 μl S9 in Sample #50378-			
	084	085	086	087
	PFL Day			
	21	22	23	24
0	36 $\pm$ 2	36 $\pm$ 2	36 $\pm$ 2	36 $\pm$ 2
2	96 $\pm$ 10	108 $\pm$ 2	97 $\pm$ 11	76 $\pm$ 1
4	130 $\pm$ 10	162 $\pm$ 8	177 $\pm$ 20	128 $\pm$ 10
8	148 $\pm$ 19	147 $\pm$ 15	141 $\pm$ 7	136 $\pm$ 11
10	169 $\pm$ 4	185 $\pm$ 8	155 $\pm$ 21	130 $\pm$ 1
20	220 $\pm$ 10	290 $\pm$ 26	319 $\pm$ 16	254 $\pm$ 16
50	504 $\pm$ 40	522 $\pm$ 15	438 $\pm$ 18	378 $\pm$ 19
20	559 $\pm$ 33	501 $\pm$ 8	696 $\pm$ 21	483 $\pm$ 19
40	687 $\pm$ 56	708 $\pm$ 43	709 $\pm$ 50	510 $\pm$ 1
80	621 $\pm$ 20	655 $\pm$ 7	842 $\pm$ 40	660 $\pm$ 1
100	694 $\pm$ 10	760 $\pm$ 12	1040 $\pm$ 45	755 $\pm$ 22
200	906 $\pm$ 41	862 $\pm$ 8	1029 $\pm$ 58	883 $\pm$ 34
500	750 $\pm$ 34	860 $\pm$ 2	1263 $\pm$ 101	857 $\pm$ 31

PFL = Pressure filter liquid

TABLE A2. (Continued)

$\mu\text{g}/\text{Plate}$	Number of Revertant Colonies with 20 μl S9 in Sample #50378-		
	088 PFL Day 25	089 PFL Composite	090 PDB
0	36 $\pm$ 2	36 $\pm$ 2	36 $\pm$ 2
2	89 $\pm$ 4	49 $\pm$ 1	37 $\pm$ 7
4	127 $\pm$ 9	71 $\pm$ 7	49 $\pm$ 3
8	124 $\pm$ 13	84 $\pm$ 7	53 $\pm$ 6
10	172 $\pm$ 6	93 $\pm$ 1	59 $\pm$ 3
20	310 $\pm$ 19	167 $\pm$ 11	67 $\pm$ 5
50	595 $\pm$ 29	206 $\pm$ 14	91 $\pm$ 5
20	395 $\pm$ 39	228 $\pm$ 4	113 $\pm$ 5
40	536 $\pm$ 14	308 $\pm$ 24	139 $\pm$ 9
80	612 $\pm$ 43	322 $\pm$ 15	126 $\pm$ 4
100	777 $\pm$ 41	363 $\pm$ 9	182 $\pm$ 7
200	824 $\pm$ 21	388 $\pm$ 5	224 $\pm$ 1
500	767 $\pm$ 8	493 $\pm$ 43	315 $\pm$ 17

KEY:

PFL = Pressure filter liquid

PDB = Product distillate blend

TABLE A3. Average Positive and Negative Control Data for Salmonella typhimurium, TA100 Microbial Mutagenicity Data

Controls	S9 (μl)	μg/Plate	Number of Revertant Colonies
2-AA	10	1	3554 ± 762
BaP	100	10	1422 ± 124
NTG	0	1	634 ± 85
030 A ₃	20	1	347 ± 43
None	20		295 ± 31
None	100		242 ± 15
None	0		369 ± 18

KEY:

2-AA = 2-Aminoanthracene

BaP = Benzo[a]pyrene

NTG = n-Methyl-N'-nitro-N-nitrosoguanidine

030 A₃ = Nitrogen-containing polycyclic aromatic compound fraction of solvent refined coal-II 850°F+ distillate cut

TABLE A4. Average Positive and Negative Control Data for Salmonella typhimurium, TA98 Microbial Mutagenicity Data of Tables A5 Through A7

Compound	S9 (μl)	μg/Plate	Number of Revertant Colonies
2-AA	10	1	2873 ± 920
BaP	100	10	488 ± 129
NTG	0	1	51 ± 22
030 A ₃	20	1	238 ± 72
1-NP	0	1	2719 ± 1086
6-AC	5	0.05	405 ± 207
None	20		50 ± 23
None	100		42 ± 17
None	0		40 ± 22

KEY:

2-AA = 2-Aminoanthracene

BaP = Benzo[a]pyrene

NTG = n-Methyl-N'-nitro-N-nitrosoguanidine

030 A₃ = Nitrogen-containing polycyclic aromatic compound fraction of solvent refined coal-II 850°F+ distillate cut

1-NP = 1-Nitropyrene

6-AC = 6-Aminochrysene

TABLE A5. Raw Dose-Response Data for the *Salmonella typhimurium*, TA98 Mutagenicity Testing of CTSI Pressure Filter Liquid Materials from Days 1, 5 and 10 of the 25-Day Demonstration Run

Fraction	S9 (μl)	μg/Plate	Number of Revertant Colonies, Sample #50378-		
			064	068	74
			Day		
			1	5	10
AH	100	0	29 ± 3	68 ± 1	68 ± 6
		20	37 ± 2	79 ± 5	99 ± 15
		40	47 ± 1	77 ± 5	109 ± 1
		80	23 ± 6	105 ± 0	104 ± 1
		100	32 ± 3	68 ± 3	104 ± 6
		200	31 ± 3	76 ± 16	138 ± 3
		500	35 ± 0	71 ± 1	115 ± 1
	0	0	22 ± 3	56 ± 10	89 ± 7
		20	35 ± 0	54 ± 0	110 ± 2
		40	25 ± 3	55 ± 8	113 ± 15
		80	31 ± 1	73 ± 5	107 ± 9
		100	38 ± 0	67 ± 9	101 ± 7
		200	34 ± 0	66 ± 4	110 ± 3
		500	39 ± 0	63 ± 1	112 ± 8
PAH	100	0	29 ± 3	68 ± 1	68 ± 6
		20	47 ± 13	117 ± 6	176 ± 20
		40	47 ± 4	117 ± 7	172 ± 15
		80	55 ± 8	90 ± 4	172 ± 60
		100	55 ± 9	94 ± 2	143 ± 11
		200	64 ± 3	112 ± 5	153 ± 13
		500	57 ± 6	123 ± 14	151 ± 2
	0	0	22 ± 3	56 ± 10	89 ± 7
		20	34 ± 6	73 ± 4	118 ± 7
		40	31 ± 5	68 ± 3	121 ± 11
		80	26 ± 1	76 ± 2	116 ± 6
		100	31 ± 1	70 ± 2	110 ± 3
		200	24 ± 2	69 ± 4	109 ± 16
		500	33 ± 1	66 ± 6	109 ± 2

KEY:

AH = Aliphatic hydrocarbon
PAH = Polycyclic aromatic hydrocarbon

TABLE A5. (Continued)

Fraction	S9 (μl)	μg/Plate	Number of Revertant Colonies, Sample #50378-		
			064	068	74
			0ay		
			1	5	10
NPAC	20	0	33 ± 2	64 ± 8	96 ± 21
		2	119 ± 9	134 ± 14	158 ± 1
		4	109 ± 2	178 ± 6	180 ± 1
		8	104 ± 6	155 ± 11	189 ± 5
		10	124 ± 5	223 ± 7	252 ± 5
		20	171 ± 4	234 ± 15	309 ± 5
		50	253 ± 4	285 ± 15	505 ± 11
	0	0	22 ± 3	56 ± 10	89 ± 7
		2	23 ± 4	74 ± 11	118 ± 4
		4	25 ± 5	63 ± 2	107 ± 2
		8	29 ± 2	69 ± 5	101 ± 4
		10	31 ± 4	72 ± 3	99 ± 14
		20	33 ± 6	70 ± 6	112 ± 6
		50	33 ± 1	68 ± 5	115 ± 2
	20	0	33 ± 2	64 ± 8	96 ± 21
		0.2	44 ± 4	71 ± 5	106 ± 3
		0.4	44 ± 8	93 ± 5	121 ± 13
		0.8	42 ± 2	84 ± 7	133 ± 17
		1	56 ± 1	98 ± 7	140 ± 8
		2	92 ± 7	101 ± 16	163 ± 1
		5	147 ± 5	151 ± 7	239 ± 1
	0	0	20 ± 3	56 ± 10	89 ± 7
		0.2	30 ± 1	69 ± 12	93 ± 1
		0.4	30 ± 4	77 ± 9	80 ± 1
		0.8	28 ± 6	67 ± 1	85 ± 6
		1	26 ± 2	66 ± 0	94 ± 12
		2	28 ± 1	65 ± 2	96 ± 3
		5	27 ± 5	68 ± 6	90 ± 4

KEY:

NPAC = Nitrogen-containing polycyclic aromatic compounds
 Hydroxy-PAH = Hydroxy-substituted polycyclic aromatic hydrocarbon

TABLE A5. (Continued)

Fraction	S9 (μl)	μg/Plate	Number of Revertant Colonies, Sample #50378-		
			064	068	74
			Day		
			1	5	10
Hydroxy-PAH	100	0	29 ± 3	68 ± 1	68 ± 6
		20	72 ± 9	123 ± 15	126 ± 8
		40	105 ± 14	136 ± 31	252 ± 18
		80	98 ± 29	132 ± 12	501 ± 5
		100	92 ± 4	168 ± 14	503 ± 1
		200	131 ± 7	260 ± 1	575 ± 6
		500	173 ± 22	374 ± 3	798 ± 7
	0	0	22 ± 3	56 ± 10	89 ± 7
		20	28 ± 1	68 ± 10	119 ± 1
		40	37 ± 5	73 ± 7	91 ± 9
		80	45 ± 1	73 ± 6	123 ± 1
		100	41 ± 12	75 ± 7	116 ± 6
		200	30 ± 1	78 ± 13	101 ± 14
		500	46 ± 5	85 ± 9	108 ± 14
Crude	20	0	33 ± 2	64 ± 8	96 ± 21
		20	136 ± 5	177 ± 18	134 ± 12
		40	171 ± 16	197 ± 6	153 ± 5
		80	119 ± 21	174 ± 17	127 ± 1
		100	132 ± 9	209 ± 23	147 ± 7
		200	166 ± 13	253 ± 12	204 ± 24
		500	176 ± 43	360 ± 19	251 ± 19
	0	0	22 ± 3	56 ± 10	89 ± 7
		20	37 ± 5	69 ± 6	105 ± 14
		40	30 ± 3	73 ± 9	104 ± 7
		80	36 ± 2	88 ± 2	112 ± 6
		100	29 ± 4	65 ± 1	98 ± 5
		200	33 ± 2	74 ± 3	96 ± 9
		500	28 ± 1	78 ± 10	111 ± 14

KEY:

Hydroxy-PAH = Hydroxy-substituted polycyclic aromatic hydrocarbon

TABLE A6. Raw Dose-Response Data for the *Salmonella typhimurium*, TA98 Mutagenicity Testing of CTSI Pressure Filter Liquid Materials from Days 15, 19 and 24 of the 25-Day Demonstration Run

Fraction	S9 (μl)	μg/Plate	Number of Revertant Colonies, Sample #5D378-					
			078		082		087	
			Day					
			15		19		24	
AH	100	0	36 ±	8	37 ±	2	23 ±	2
		20	50 ±	1	27 ±	4	40 ±	1
		40	41 ±	2	35 ±	2	32 ±	1
		80	43 ±	2	36 ±	3	23 ±	4
		100	40 ±	5	30 ±	9	23 ±	1
		200	34 ±	1	34 ±	2	35 ±	2
		500	43 ±	7	32 ±	2	38 ±	4
	0	0	41 ±	0	28 ±	3	24 ±	3
		20	42 ±	8	26 ±	2	27 ±	2
		40	41 ±	2	21 ±	2	23 ±	2
		80	43 ±	3	34 ±	4	34 ±	3
		100	35 ±	6	32 ±	2	33 ±	2
		200	35 ±	3	28 ±	3	26 ±	4
		500	29 ±	2	33 ±	1	35 ±	2
PAH	100	0	23 ±	2	37 ±	2	23 ±	2
		20	63 ±	10	62 ±	1	52 ±	1
		40	74 ±	13	81 ±	9	77 ±	7
		80	96 ±	7	111 ±	3	71 ±	4
		100	94 ±	1	92 ±	4	86 ±	3
		200	102 ±	5	114 ±	15	130 ±	15
		500	110 ±	17	135 ±	9	139 ±	11
	0	0	24 ±	3	28 ±	3	24 ±	3
		20	36 ±	5	30 ±	4	36 ±	0
		40	29 ±	2	34 ±	7	26 ±	0
		80	30 ±	1	30 ±	2	40 ±	1
		100	32 ±	2	31 ±	3	29 ±	1
		200	49 ±	3	38 ±	1	36 ±	5
		500	41 ±	3	44 ±	4	46 ±	1

KEY:

AH = Aliphatic hydrocarbon
PAH = Polycyclic aromatic hydrocarbon

TABLE A6. (Continued)

Fraction	S9 (μl)	μg/Plate	Number of Revertant Colonies, Sample #50378-					
			078		082		087	
			Day					
			15		19		24	
NPAC	20	0	51 ±	5	30 ±	6	27 ±	2
		2	101 ±	18	128 ±	16	71 ±	6
		4	165 ±	3	219 ±	12	199 ±	47
		8	280 ±	9	380 ±	1	290 ±	12
		10	331 ±	3	420 ±	15	330 ±	8
		20	460 ±	1	631 ±	22	530 ±	22
		50	779 ±	22	1012 ±	21	963 ±	89
	0	0	41 ±	0	28 ±	3	24 ±	3
		2	34 ±	3	28 ±	1	32 ±	0
		4	42 ±	1	23 ±	3	22 ±	3
		8	44 ±	1	28 ±	2	36 ±	6
		10	36 ±	0	33 ±	5	28 ±	0
		20	43 ±	8	32 ±	0	42 ±	9
		50	40 ±	2	36 ±	5	35 ±	7
	20	0	51 ±	5	30 ±	6	27 ±	2
		0.2	59 ±	13	43 ±	2	35 ±	6
		0.4	56 ±	7	48 ±	9	41 ±	8
		0.8	65 ±	9	67 ±	11	52 ±	10
		1	73 ±	1	73 ±	2	56 ±	5
		2	108 ±	13	112 ±	14	110 ±	6
		5	174 ±	2	256 ±	3	204 ±	2
	0	0	41 ±	0	28 ±	3	24 ±	3
		0.2	33 ±	2	32 ±	1	25 ±	0
		0.4	23 ±	4	32 ±	2	23 ±	2
		0.8	37 ±	5	33 ±	3	23 ±	2
		1	35 ±	4	33 ±	5	31 ±	1
		2	53 ±	1	27 ±	3	29 ±	3
		5	40 ±	2	27 ±	2	25 ±	4

KEY:

NPAC = Nitrogen-containing polycyclic aromatic compounds

TABLE A6. (Continued)

Fraction	S9 (μl)	μg/Plate	Number of Revertant Colonies, Sample #50378-					
			078		082		087	
			Day					
			15		19		24	
Hydroxy-PAH	100	0	36 ±	8	37 ±	2	23 ±	2
		20	133 ±	10	142 ±	13	96 ±	15
		40	255 ±	33	276 ±	3	172 ±	15
		80	365 ±	18	412 ±	5	394 ±	11
		100	473 ±	102	593 ±	31	459 ±	11
		200	692 ±	23	620 ±	72	712 ±	37
		500	996 ±	98	1293 ±	69	986 ±	10
	0	0	41 ±	0	28 ±	3	24 ±	3
		20	41 ±	4	40 ±	0	23 ±	5
		40	51 ±	17	29 ±	5	27 ±	7
		80	39 ±	1	42 ±	1	24 ±	2
		100	37 ±	1	31 ±	7	33 ±	8
		200	45 ±	3	32 ±	3	32 ±	7
		500	55 ±	12	48 ±	2	27 ±	2
Crude	20	0	51 ±	5	30 ±	6	135 ±	8
		20	351 ±	22	413 ±	14	717 ±	48
		40	452 ±	28	523 ±	42	735 ±	31
		80	605 ±	16	718 ±	28	1082 ±	41
		100	608 ±	19	861 ±	31	1029 ±	20
		200	805 ±	49	932 ±	26	1360 ±	155
		500	1068 ±	134	1419 ±	51	1381 ±	129
	0	0	41 ±	0	28 ±	3	24 ±	3
		20	32 ±	1	29 ±	3	33 ±	9
		40	44 ±	1	32 ±	4	30 ±	1
		80	60 ±	6	48 ±	6	35 ±	0
		100	55 ±	10	31 ±	1	37 ±	2
		200	48 ±	2	30 ±	5	39 ±	9
		500	71 ±	10	38 ±	7	33 ±	1

KEY:

Hydroxy-PAH = Hydroxy-substituted polycyclic aromatic hydrocarbon

TABLE A6. (Continued)

Fraction	S9 (μl)	μg/Plate	Number of Revertant Colonies, Sample #50378-					
			078		082		087	
			Day					
			15		19		24	
Crude	20	0	51 ±	5	30 ±	6	27 ±	2
		2	94 ±	17	87 ±	4	73 ±	14
		4	119 ±	24	153 ±	5	149 ±	2
		8	209 ±	3	217 ±	9	235 ±	23
		10	207 ±	13	235 ±	21	280 ±	10
		20	400 ±	14	339 ±	24	360 ±	22
		50	444 ±	14	541 ±	5	625 ±	39
	0	0	41 ±	0	28 ±	3	24 ±	3
		2	44 ±	5	37 ±	4	28 ±	1
		4	44 ±	1	33 ±	2	28 ±	5
		8	43 ±	2	34 ±	4	32 ±	2
		10	42 ±	5	37 ±	2	40 ±	1
		20	40 ±	0	38 ±	1	36 ±	5
		50	41 ±	4	34 ±	1	34 ±	8

TABLE A7. Raw Dose-Response Data for the Salmonella typhimurium, TA98 Mutagenicity Testing of CTSI Pressure Filter Liquid and Product Distillate Blend Materials from an Intermediate Period of the 25-Day Demonstration Run

Fraction	S9 (μl)	μg/Plate	Number of Revertant Colonies, Sample #50378-	
			089 PFL	D90 PDB
AH	100	0	34 ± 4	41 ± 11
		20	35 ± 0	36 ± 1
		40	29 ± 3	44 ± 3
		80	35 ± 3	32 ± 4
		100	33 ± 1	36 ± 6
		200	38 ± 0	38 ± 1
		500	34 ± 6	32 ± 4
	0	0	26 ± 0	
		20	25 ± 9	
		40	28 ± 2	
		80	31 ± 5	
		100	27 ± 6	
		200	29 ± 0	
		500	29 ± 1	
PAH	100	0	34 ± 4	41 ± 11
		20	74 ± 1	244 ± 35
		40	92 ± 3	266 ± 2
		80	103 ± 5	223 ± 32
		100	122 ± 6	328 ± 18
		200	133 ± 6	464 ± 38
		500	163 ± 0	467 ± 42
	0	0	26 ± 0	31 ± 2
		20	33 ± 1	43 ± 2
		40	33 ± 6	56 ± 1
		80	38 ± 1	57 ± 1
		100	43 ± 1	64 ± 7
		200	41 ± 6	86 ± 5
		500	62 ± 2	109 ± 12

KEY:

PFL = Pressure filter liquid
PDB = Product distillate blend
AH = Aliphatic hydrocarbon
PAH = Polycyclic aromatic hydrocarbon

TABLE A7. (Continued)

Fraction	S9 (μl)	μg/Plate	Number of Revertant Colonies, Sample #50378-	
			089 PFL	090 PDB
NPAC	20	0	47 ± 4	55 ± 7
		2	94 ± 5	93 ± 1
		4	143 ± 3	98 ± 11
		8	273 ± 3	97 ± 12
		10	309 ± 9	139 ± 7
		20	479 ± 40	239 ± 31
		50	834 ± 5	483 ± 41
	0	0	26 ± 0	31 ± 2
		2	31 ± 7	60 ± 6
		4	31 ± 1	59 ± 12
		8	32 ± 1	71 ± 2
		10	32 ± 7	72 ± 7
		20	33 ± 0	116 ± 12
		50	35 ± 3	182 ± 5
	20	0	47 ± 4	55 ± 7
		0.2	35 ± 2	49 ± 5
		0.4	43 ± 1	39 ± 3
		0.8	62 ± 8	41 ± 1
		1	72 ± 2	53 ± 3
		2	97 ± 15	75 ± 23
		5	184 ± 16	120 ± 2
	0	0	26 ± 0	31 ± 2
		0.2	24 ± 1	42 ± 2
		0.4	23 ± 3	37 ± 3
		0.8	22 ± 1	38 ± 5
		1	33 ± 3	43 ± 11
		2	33 ± 1	58 ± 4
		5	24 ± 0	81 ± 2

KEY:

PFL = Pressure filter liquid

PDB = Product distillate blend

NPAC = Nitrogen-containing polycyclic aromatic compounds

TABLE A7. (Continued)

Fraction	S9 (μl)	μg/Plate	Number of Revertant Colonies, Sample #50378-	
			089 PFL	090 PDB
Hydroxy-PAH	100	0	34 ± 4	41 ± 11
		20	150 ± 3	66 ± 5
		40	176 ± 12	72 ± 19
		80	352 ± 6	55 ± 2
		100	444 ± 42	107 ± 2
		200	607 ± 22	177 ± 20
		500	1118 ± 39	330 ± 6
	0	0	26 ± 0	31 ± 2
		20	21 ± 2	52 ± 8
		40	17 ± 3	48 ± 3
		80	23 ± 4	59 ± 3
		100	27 ± 4	83 ± 8
		200	35 ± 2	94 ± 10
		500	23 ± 1	200 ± 20
Crude	20	0	47 ± 4	55 ± 7
		20	287 ± 19	204 ± 19
		40	319 ± 20	273 ± 0
		80	433 ± 5	236 ± 34
		100	464 ± 14	337 ± 43
		200	511 ± 9	627 ± 7
		500	682 ± 49	772 ± 27
	0	0	26 ± 0	31 ± 2
		20	32 ± 6	130 ± 6
		40	26 ± 4	174 ± 0
		80	31 ± 6	191 ± 2
		100	36 ± 4	273 ± 21
		200	35 ± 7	400 ± 58
		500	32 ± 3	489 ± 35

KEY:

PFL = Pressure filter liquid

PDB = Product distillate blend

Hydroxy-PAH = Hydroxy-substituted polycyclic aromatic hydrocarbon

TABLE A7. (Continued)

Fraction	S9 (μ l)	μ g/Plate	Number of Revertant Colonies, Sample #50378-	
			089 PFL	090 PDB
Crude	20	0	47 $\pm$ 4	55 $\pm$ 7
		2	62 $\pm$ 11	80 $\pm$ 7
		4	147 $\pm$ 5	88 $\pm$ 18
		8	192 $\pm$ 30	72 $\pm$ 13
		10	179 $\pm$ 30	116 $\pm$ 27
		20	249 $\pm$ 10	171 $\pm$ 4
		50	403 $\pm$ 35	280 $\pm$ 6
	0	0	26 $\pm$ 0	31 $\pm$ 2
		2	21 $\pm$ 3	46 $\pm$ 7
		4	25 $\pm$ 1	54 $\pm$ 5
		8	30 $\pm$ 2	76 $\pm$ 5
		10	27 $\pm$ 1	81 $\pm$ 10
		20	24 $\pm$ 3	118 $\pm$ 2
		50	37 $\pm$ 7	194 $\pm$ 7

KEY:

PFL = Pressure filter liquid
PDB = Product distillate blend

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