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Preliminary Chemical Analysis and Biological Testing of Materials from the HRI Catalytic Two-Stage Liquefaction (CTSL) Process

**D. W. Later
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January 1985

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PRELIMINARY CHEMICAL ANALYSIS AND BIOLOGICAL
TESTING OF MATERIALS FROM THE HRI CATALYTIC
TWO-STAGE LIQUEFACTION (CTSL) PROCESS

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Pacific Northwest Laboratory
Richland, Washington 99352

SUMMARY

Coal-derived materials from experimental runs of Hydrocarbon Research Incorporated's (HRI) catalytic two-stage liquefaction (CTSL) process were chemically characterized and screened for microbial mutagenicity. This process differs from other two-stage coal liquefaction processes in that catalyst is used in both stages. Samples from both the first and second stages were class-fractionated by alumina adsorption chromatography. The fractions were analyzed by capillary column gas chromatography; gas chromatography/mass spectrometry; direct probe, low voltage mass spectrometry; and proton nuclear magnetic resonance spectrometry. Mutagenicity assays were performed with the crude and class fractions in Salmonella typhimurium, TA98.

Preliminary results of chemical analyses indicate that >80% CTSL materials from both process stages were aliphatic hydrocarbon and polynuclear aromatic hydrocarbon (PAH) compounds. Furthermore, the gross and specific chemical composition of process materials from the first stage were very similar to those of the second stage.

In general, the unfractionated materials were only slightly active in the TA98 mutagenicity assay. Like other coal liquefaction materials investigated in this laboratory, the nitrogen-containing polycyclic aromatic compound (N-PAC) class fractions were responsible for the bulk of the mutagenic activity of the crudes. Finally, it was shown that this activity correlated with the presence of amino-PAH.

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LIST OF ABBREVIATIONS

AH	= Aliphatic hydrocarbon(s)
amino-PAH	= Amino polycyclic aromatic hydrocarbon(s)
CTSL	= Catalytic two-stage liquefaction
eV	= Electron volt
g	= Gram
GC	= Gas chromatography
HRI	= Hydrocarbon Research Inc.
ITSL	= Integrated two-stage liquefaction
MS	= Mass spectrometry
NMR	= Nuclear magnetic resonance spectrometry
N-PAC	= Nitrogen-containing polycyclic aromatic compound(s)
NTSL	= Nonintegrated two-stage liquid
PAH	= Polycyclic aromatic hydrocarbon(s)
PNL	= Pacific Northwest Laboratory
TA98	= Designation for strain of <u>Salmonella typhimurium</u> used in microbial mutagenicity assay
THF	= Tetrahydrofuran

INTRODUCTION

Catalytic two-stage liquefaction (CTSL), as implemented by Hydrocarbon Research Incorporated (HRI), is a coal conversion process in which both reactors are catalytic and no distillation or solids separation is carried out between stages. An objective of the process is to take maximum advantage of catalytic reactions in converting coal. Distillation and solids separation take place after the second stage. Materials sampled from initial runs of the CTSL process operated at Lawrenceville, NJ by HRI are listed in Table 1. These samples were shipped to Pacific Northwest Laboratory (PNL) for preliminary chemical analyses and biological screening using the microbial mutagenicity assay (Ames Test) with Salmonella typhimurium, TA98. A brief sample description as well as a PNL repository number are given in Table 1 for each sample.

Except for 50378-053, all sample materials received were class-fractionated and screened for microbial mutagenicity. Samples 50378-040 and -041 were investigated in more detail; proton nuclear magnetic resonance (NMR) and probe inlet mass spectrometry (MS) analyses, as well as hydroaromatic-specific chemical class fractionations, were performed with these two samples.

In this report, results and data from the HRI samples are presented and, where applicable, compared with corresponding nonintegrated two-stage liquid (NTSL)/integrated two-stage liquefaction (ITSL) results given in PNL-5215, a Status Report on the Wilsonville pilot plant process materials from Runs 241 and 242. For process comparison, the Wilsonville pilot plant was configured as follows: noncatalytic thermal first-stage and catalytic HRI H-Oil hydro-treater second-stage, with critical solvent deashing between the two stages. The Methods section of PNL-5215 (Appendix A of this report) can be referred to for actual experimental details. Results of the HRI samples can be directly compared with the Wilsonville pilot plant data.

TABLE 1. HRI CTSL Samples used in the Preliminary Chemistry/Toxicology Studies

PNL Number	Condition (°F)	Stage	Period	Material ^a
50378-036	1 (650)	1	3	THF ^b extracted filtrate
50378-037	1 (650)	2	3	Topped separator bottoms, pressure filtered
50378-038	2 (550)	1	5	THF extracted filtrate
50378-039	2 (550)	2	5	Topped separator bottoms, pressure filtered
50378-040	3 (750)	1	9	THF extracted filtrate
50378-041	3 (750)	2	9	Topped separator bottoms, pressure filtered
50378-042	4 (750)	1	12	THF extracted filtrate
50378-043	4 (750)	2	12	Pressure filter liquid
50378-053	Run period: 227-18-128			Pressure filter liquid, 15% resid; 975°F+ (not a normal process product)

^a 40 g of each

^b THF = tetrahydrofuran

MICROBIAL MUTAGENICITY ASSAY RESULTS

All CTSL samples received from HRI, with the exception of 50378-053, were assayed for microbial mutagenicity in S. typhimurium, TA98, prior to chemical class fractionation. Dose response and maximum response data for these process materials are given in Table 2. These results can be compared with those of the NTSL/ITSL process materials found in Table 17 of PNL-5215, which is reproduced in Appendix B of this technical memo. In general, the CTSL crudes were relatively inactive; only samples from Condition 4/Period 12 showed significant mutagenic activity. Unlike the ITSL second-stage products, which were inactive, the CTSL second-stage material from Condition 4/Period 12 was more active than the first-stage material. This was also true for the TA98 mutagenicity assay of the chemical class fractions, as well as for replicate analyses of these two materials prior to chemical separation.

Table 3 presents the results from the microbial mutagenicity assays conducted with the chemical fractions of the CTSL crude process materials. As with other coal liquefaction materials, the aliphatic hydrocarbon (AH; A₁) and neutral polycyclic aromatic hydrocarbon (PAH; A₂) chemical classes were either inactive or only slightly active. The nitrogen-containing polycyclic aromatic compound (N-PAC) fraction (A₃), however, was an active mutagen to S. typhimurium, TA98 (see Table 3), and, in general, more active than the NTSL/ITSL N-PAC fractions (see Table 18, Appendix B). Nitrous acid treatment of selected N-PAC fractions (036 and 037) showed this activity to be related to amino-PAH present in these materials. As with the crudes, in two cases (Condition 2/Period 5 and Condition 4/Period 12) the second-stage N-PAC fractions were more mutagenic than the first-stage isolates. Mutagenicities of the CTSL and NTSL/ITSL class fractions can be compared by referring to Table 18 of the NTSL/ITSL Status Report, reproduced in Appendix B of this report.

TABLE 2. Microbial Mutagenicity of HRI CTSL Crudes in *S. typhimurium*, TA98

Sample	2- to 50- μ g Dose Range		20- to 500- μ g Dose Range	
	LR Slope ^a Rev/ μ g	MR ^b Rev/(X)	LR Slope ^a Rev/ μ g	MR ^b Rev
First-Stage Condition 1/Period 3 PNL 50378-036	0	76 $\pm$ 0 (50)	0	106 $\pm$ 10(500)
Second-Stage Condition 1/Period 3 PNL 50378-037	0	68 $\pm$ 6 (20)	<1	101 $\pm$ 1(500)
First-Stage Condition 2/Period 5 PNL 50378-038	0	60 $\pm$ 3 (50)	0	71 $\pm$ 4(500)
Second-Stage Condition 2/Period 5 PNL 50378-039	<1	85 $\pm$ 4 (50)	0	103 $\pm$ 4(500)
First-Stage Condition 3/Period 9 PNL 50378-D40	1	96 $\pm$ 8 (50)	0	124 $\pm$ 12(500)
Second-Stage Condition 3/Period 9 PNL 50378-041	<1	84 $\pm$ 2 (50)	<1	120 $\pm$ 5(500)
First-Stage Condition 4/Period 12 PNL 50378-042	2	125 $\pm$ 2 (50)	0	204 $\pm$ 3(500)
Second-Stage Condition 4/Period 12 PNL 50378-043	3	195 $\pm$ 7(500)	0	223 $\pm$ 19 (80)

^aLR = Linear response slope in revertants/ μ g with correlation coefficient >0.70. Values reported are the average of triplicate analyses.

^bMR = Maximum response in revertants/(X) = dose (in μ g) producing maximum response ($\pm$ SE). Background spontaneous TA98 revertants were 42 $\pm$ 2 for these assays. Values reported are the average of triplicate analyses.

TABLE 3. Microbial Mutagenicity of Chemical Class Fractions of the HRI CTSL Process Materials^a

Sample	AH (A ₁)	Neutral PAH (A ₂)	N-PAC (A ₃)	Hydroxy- PAH (A ₄)	Crude	PNL Number
First-Stage Condition 1/Period 3	0	<1	26(4) ^b	<1	<1	50378-036
Second-Stage Condition 1/Period 3	0	<1	6(2) ^b	<1	<1	50378-037
First-Stage Condition 2/Period 5	0	<1	8	0	<1	50378-038
Second-Stage Condition 2/Period 5	0	<1	11	<1	<1	50378-039
First-Stage Condition 3/Period 9	0	0	25	2	2	50378-040
Second-Stage Condition 3/Period 9	0	0	24	1	2	50378-041
First-Stage Condition 4/Period 12	0	0	29	1	2	50378-042
Second-Stage Condition 4/Period 12	0	<1	59	2	3	50378-043

^aResults reported as the linear regression slope in revertants/μg.

^bNumbers in parentheses are the mutagenic activities of the N-PAC Fraction A₃ after treatment with nitrous acid, which selectively eliminated the amino-PAH from the fraction.

CHEMICAL CLASS COMPOSITION OF HRI CTSL PROCESS MATERIALS

The relative chemical composition of each CTSL sample material fractionated by alumina adsorption liquid chromatography is shown in Table 4. The AH (A_1) and neutral PAH (A_2) chemical fractions were typically responsible for >80% of both the first- and second-stage CTSL materials. Conversely, the combined weight of the N-PAC (A_3) and the hydroxy-PAH (A_4) fractions was generally <20% of the total material.

Comparing the chemical composition of first- and second-stage process materials, the second-stage materials generally had higher concentrations of AH components. However, this may be a function only of the recovery; the first-stage recoveries were always 97 to 101%, while the second-stage recoveries were generally between 108 and 113%. This observation suggests that a chemical difference probably exists between the first- and second-stage materials at the chemical constituent level. The exact nature of this change is not apparent at this level of chemical analysis.

For CTSL Samples 036-041, the nitrogen and oxygen heteroatomic functional compounds were present at about the same levels in the first- and second-stage process materials: N-PAC = 5 to 8%, and hydroxy-PAH = 11 to 15%. In Samples -042 and -043, these chemical fractions were of equivalent concentration, 15 to 16%, in both process stage materials.

If the chemical composition of the CTSL and NTSL/ITSL process materials is compared (see Table 4 and Table 29 in Appendix B of this report), the products of the second stage from either process are of comparable gross chemical composition. However, an obvious difference in process material quality, as determined by this chemical analysis, was observed in the first-stage products. The first-stage CTSL samples contained much lower levels of N-PAC (A_3) and hydroxy-PAH (A_4) than their NTSL/ITSL counterparts and were generally more comparable to CTSL and NTSL/ITSL second-stage process materials, which contain high levels of AH and PAH, in overall chemical composition.

TABLE 4. Chemical Composition of HRI CTSL Process Materials

Sample Description	Fractions ^a	Weight Percent Distribution (%)
50378-036	A ₁	53
First-Stage	A ₂	29
Condition 1/Period 3	A ₃	6
THF extracted filtrate	A ₄	<u>13</u>
TOTAL		101
50378-037	A ₁	60
Second-Stage	A ₂	35
Condition 1/Period 3	A ₃	7
Pressure filtered	A ₄	<u>11</u>
Topped separator bottoms	TOTAL	113
50378-038	A ₁	52
First-Stage	A ₂	28
Condition 2/Period 5	A ₃	5
THF extracted filtrate	A ₄	<u>15</u>
TOTAL		100
50378-039	A ₁	64
Second-Stage	A ₂	28
Condition 2/Period 5	A ₃	5
Pressure filtered	A ₄	<u>11</u>
Topped separator bottoms	TOTAL	108
50378-040	A ₁	54
First-Stage	A ₂	22
Condition 3/Period 9	A ₃	8
THF extracted filtrate	A ₄	<u>13</u>
TOTAL		97
50378-041	A ₁	69
Second-Stage	A ₂	24
Condition 3/Period 9	A ₃	7
Pressure filtered	A ₄	<u>11</u>
Topped separator bottoms	TOTAL	111
50378-042	A ₁	32
First-Stage	A ₂	34
Condition 4/Period 12	A ₃	15
THF extracted filtrate	A ₄	<u>16</u>
TOTAL		97
50378-043	A ₁	42
Second-Stage	A ₂	36
Condition 4/Period 12	A ₃	15
Pressure filter liquid	A ₄	<u>16</u>
TOTAL		109

^aKey: A₁ = AH, A₂ = neutral PAH, A₃ = N-PAC, A₄ = hydroxy-PAH.

Results from detailed qualitative chemical analyses by gas chromatography (GC), MS and NMR of the alumina chemical fractions are provided in the following sections.

HYDROAROMATIC CONTENT OF THE HRI CTSL SAMPLES

Table 5 shows the results obtained from further chemical class fractionation of the AH/PAH portion of the process materials by separation on picric acid doped alumina columns. The details of this method are discussed in the Methods section of PNL-5215* (see Appendix A of this report). Briefly, differentiation of the strictly AH (very little unsaturation or olefin property) from the hydro-substituted PAH and fully aromatic PAH is achieved by this method.

Levels of AH and hydroaromatic compounds were, again, fairly comparable for the CTSL (Table 5) and NTSL/ITSL (Table 31; see Appendix B) process materials. However, the levels of dihydro-PAH and PAH were generally lower in the CTSL, as compared to the NTSL/ITSL, process materials. This is an indication that hydrogen incorporation is more effectively achieved in the CTSL small pilot facility than in the Wilsonville plant operated in the NTSL/ITSL mode. The fact that hydroaromatic compounds are responsible for the majority of the neutral PAH fraction (A_2 ; see Table 4) in the CTSL samples also supports this view.

Qualitative compound-specific chemical analysis by capillary column GC was used to elucidate the types of chemical constituents present in these fractions. Capillary column gas chromatograms of the PA_1 and PA_2 fractions of CTSL Sample 041 are shown in Figures 1 and 2. The PA_1 fraction is composed primarily of AH ranging from approximately C_{10} up to C_{30} . The complexity of compounds in the C_{16} region results from branched and cyclic saturated hydrocarbons and, possibly, highly alkylated benzene. The PA_2 fraction contained the hydro-substituted PAH; a capillary chromatogram of this isolate from the second-stage (Condition 3/Period 9) material is shown in Figure 2. Specific constituents in this fraction are identified in Table 6. With the exception of boiling point range, this hydroaromatic isolate was very similar in chemical composition to, and had the same hydroaromatic compounds, as found in the first-stage CTSL isolate and similar isolates of second-stage NTSL/ITSL process materials, shown in Figures 10 and 11 of PNL-5215 (reproduced in Appendix B of this report).

Later, DW, Chemical Analysis and Biological Testing of NTSL and ITSL process Materials from the Wilsonville two-stage liquefaction pilot plant, NTIS, Springfield, VA, 1985.

TABLE 5. Hydroaromatic Composition (Weight %) of HRI CTSL Process Materials

Chemical Fraction	Condition 3/Period 4	
	50378-040	50378-041
	First-Stage THF Extracted Filtrate	Second-Stage Pressure Filtered
PA ₁ : AH	38.3 ± 2.0	45.3 ± 4.4
PA ₂ : Hydroaromatic com- pounds	26.2 ± 1.4	32.2 ± 3.4
PA ₃ : Dihydro-PAH/<three- ring PAH	5.5 ± 0.1	7.0 ± 0.1
PA ₄ : >Three-ring PAH/ polar PAH ^a	<u>4.5 ± 0.8</u>	<u>6.1 ± 1.3</u>
TOTAL	74.5%	90.6%
A ₁ + A ₂	74.8%	91.1%

^aSome lower molecular weight, slightly polar compounds also elute in this fraction (e.g., alkylated indoles and azaarenes)

FIGURE 1. Capillary Column Gas Chromatogram of the AH Fraction PA₁ of CTSL Sample 041 (Second-Stage; Condition 3/Period 9)

FIGURE 2. Capillary Column Gas Chromatogram of the Hydroaromatic Compound Fraction PA₂ of CTSL Sample 041 (Second-Stage; Condition 3/Period 9). See Table 6 for peak identification.

TABLE 6. Peak Identifications for Hydroaromatic Compounds in Fraction PA₂ of the CTSI Second-Stage Material (Sample 50378-041; Figure 2) and Selected NTSL/ITSL Samples (Figures 10 and 11, Appendix B)

Peak Number	Molecular Weight	Compound Identification ^a
1	132	C ₁ -Indans
2	132	Tetralin
3	128	Naphthalene
4	146	C ₁ -Tetralins and/or C ₂ -indans
5	146	2-Methyltetralin
6	146	C ₁ -Tetralins and/or C ₂ -indans
7	146	2-Methyl-5,6,7,8-tetrahydronaphthalene
8	146/160	C ₁ - and C ₂ -Tetralins
9	146/142	1-Methyl-5,6,7,8-tetrahydronaphthalene and 2-methylnaphthalene
10	160/142	C ₂ -Tetralin and 1-methylnaphthalene
11	160	C ₂ -Tetralin (dimethyl)
12	160	C ₂ -Tetralins
13	158	Tetrahydroacenaphthene
14	154	Acenaphthene
15	160	C ₂ -Tetralin (dimethyl)
16	170	C ₃ -Naphthalene
17	174/172	C ₃ -Tetralins and 1,2,3,4,4a,9a-hexahydrofluorene (cis or trans)
18	172	1,2,3,4,4a,9a-Hexahydrofluorene (cis or trans)
19	156	C ₂ -Naphthalene
	172	C ₁ -Tetrahydroacenaphthene
	174	C ₃ -Tetralins
20	168	2,4a-Dihydrofluorene
21	170	C ₃ -Naphthalene
22	172	C ₁ -Tetrahydroacenaphthene
23	188	C ₄ -Tetralins
	186	C ₂ -Tetrahydroacenaphthenes and/or C ₁ -hexahydrofluorene
24	188	C ₄ -Tetralin
25	172	C ₁ -Tetrahydroacenaphthene
26	168	1,4-Dihydrofluorene and/or C ₁ -acenaphthene
27	186	C ₁ -Hexahydrofluorenes and/or C ₂ -tetrahydroacenaphthenes
	200	C ₂ -Hexahydrofluorenes and/or C ₃ -tetrahydroacenaphthenes
28	186	C ₁ -Hexahydrofluorene
29	186	1,2,3,4,5,6,7,8-Octahydroanthracene
30	182	C ₁ -Dihydrofluorene
31	186	1,2,3,4,5,6,7,8-Octahydrophenanthrene
32	200	C ₂ -Hexahydrofluorene and/or C ₁ -octahydrophenanthrene
33	182	1,2,3,4-Tetrahydrophenanthrene

^aCompound identifications are based on GC retention data and MS fragmentation patterns.

TABLE 6. (continued)

Peak Number	Molecular Weight	Compound Identification ^a
34	200	C ₁ -Octahydrophenanthrene
35	200	C ₂ -Hexahydrofluorene and/or C ₁ -octahydrophenanthrene
36	196	C ₂ -Dihydrofluorene
37	210	C ₃ -Dihydrofluorene and/or C ₂ -tetrahydrophenanthrenes
	212	C ₃ -Tetrahydrofluorene and/or decahydropyrene/fluoranthenes
	214	C ₃ -hexahydrofluorene and/or C ₄ -tetrahydroacenaphthene
38	208	Hexahydropyrene/fluoranthene
39	208	Hexahydropyrene/fluoranthene
40	226	C ₃ -Hexahydrophenanthrenes and/or C ₄ -tetrahydrofluorene
41	224	C ₃ -Tetrahydrophenanthrene and/or C ₄ -dihydrofluorene
42	208	Hexahydropyrene/fluoranthene
43	222	C ₁ -Hexahydropyrene/fluoranthene and/or hexahydrobenzofluorene
	226	C ₃ -Hexahydrophenanthrenes and/or C ₄ -tetrahydrofluorenes
	240	C ₄ -Hexahydrophenanthrenes and/or C ₅ -tetrahydrofluorenes
44	226	C ₃ -Hexahydrophenanthrene
45	222	C ₁ -Hexahydropyrene/fluoranthene and/or hexahydrobenzofluorene
46	236	C ₂ -Hexahydropyrenes etc. and/or C ₄ -dihydrophenanthrenes
	238	C ₄ -Tetrahydrophenanthrene and/or C ₅ -dihydrofluorene
	250	C ₃ -Hexahydropyrene etc. and/or C ₄ -dihydrophenanthrene

^aCompound identifications are based on GC retention data and MS fragmentation patterns.

DETAILED CHEMICAL COMPOSITION OF THE CTSL PROCESS MATERIALS

Figure 3 is a chromatogram of the AH fraction of CTSL Sample 040 (first-stage; Condition 3/Period 9). The chemical constituency of this fraction was very similar to the PA₁ fraction, shown in Figure 1, for the analogous second-stage material. Highly branched hydrocarbons as well as alkylated partially and fully saturated cyclic hydrocarbons are most probably responsible for the chemical complexity of these materials in the C₁₆ region.

Figures 4 and 5 are chromatograms of the neutral PAH isolates from the first- and second-stage samples collected during Condition 3/Period 9 (040 and 041). Table 7 provides qualitative peak information for Figures 4 and 5. The compound-specific chemical composition of these two materials is nearly identical. The implication of this observation is that highly efficient hydrocarbon incorporation is taking place in the first stage of liquefaction. Furthermore, the second-stage catalytic reaction does not appear to significantly alter the types of compounds found in this particular fraction. From these results, the major function of the second stage appeared to be further hydrogenation and conversion of the neutral-PAH in the first-stage material to the types of AH and hydroaromatic compounds already present in the first-stage materials. This hypothesis is supported by the increased recoveries of mass in the A₁ fraction of the first- versus the second-stage process materials (see Table 4). Furthermore, the catalyst sequence used in CTSL process configuration (i.e., hydrogenation catalyst in the first stage and hydrocracking catalyst in the second stage) supports this view. In summary, the types of compounds produced in this process appear to be largely determined in the first stage, while the second stage primarily converts first-stage components to AH.

By way of comparison, the compound-specific chemical compositions of these CTSL neutral PAH fractions and the analogous fraction of the ITSL hydro-treater stage distillation column bottoms (Figure 19, Appendix B) are very similar. This is not totally unexpected since an HRI H-Oil hydrotreater unit is the catalytic reactor used in the NTSL/ITSL process configuration.

FIGURE 3. Capillary Column Gas Chromatogram of the AH Fraction A₁ of CTSL Sample 040 (First-Stage; Condition 3/Period 9)

FIGURE 4. Capillary Column Gas Chromatogram of the Neutral PAH Fraction A₂ of CTSL Sample 040 (First-Stage; Condition 3/Period 9). See Table 7 for peak identifications.

FIGURE 5. Capillary Column Gas Chromatogram of the Neutral PAH Fraction A₂ of CTSL Sample 041 (Second-Stage; Condition 3/Period 9). See Table 7 for peak identifications.

TABLE 7. Identifications of Compounds in PAH Fractions Isolated from Selected CTSL (Figures 4 and 5) and NTSL (Figure 19, Appendix B) Process Materials as Determined by GC/MS and Capillary Gas Chromatographic Retention Times

Peak Number	Molecular Weight	Tentative Identification
1	132	C ₁ -Indans
2	132	1,2,3,4-Tetrahydronaphthalene
3	128	Naphthalene
4	146	C ₂ -Indans, C ₁ -tetrahydronaphthalenes
5	142	2-Methylnaphthalene
6	142	1-Methylnaphthalene
7	160	C ₂ -Tetrahydronaphthalenes
8	154	Biphenyl
9	156	2-Ethylnaphthalene
10	156	2,6- or 2,7-Dimethylnaphthalene
11	170	C ₃ -Naphthalenes
12	156	1,7-Dimethylnaphthalene
13	156	1,6- or 1,3-Dimethylnaphthalene
14	156	2,3- or 1,4-Dimethylnaphthalene
15	156	1,2-Dimethylnaphthalene
16	154	Acenaphthene
17	170/168	C ₃ -Naphthalenes, C ₁ -biphenyls
18	172	Hexahydrofluorene
19	166	Fluorene
20	168	1,4-Dihydrofluorene and C ₁ -acenaphthenes
21	180	C ₁ -Fluorenes
22	182	C ₁ -Dihydrofluorenes
23	196	C ₂ -Dihydrofluorenes
24	178	Phenanthrene
25	194/196	C ₂ -Fluorenes, C ₂ -dihydrofluorene
26	192	C ₁ -Phenanthrene
27	212	2-Chloranthracene, ISTD
28	208	C ₃ -Dihydrofluorene and/or tetrahydropyrene
29	206	C ₂ -Phenanthrenes
30	204/208	Dihydrofluoranthene, tetrahydrofluoranthene
31	202	Fluoranthene
32	202	Pyrene
33	220	C ₃ -Phenanthrenes
34	216	Benzo[b]fluorene, 2- or 4-methylpyrene
35	218	Dihydrobenzofluorene
36	216	C ₁ -Pyrenes
37	230	C ₁ -Benzofluorenes, C ₂ -pyrenes
38	244	C ₂ -Benzofluorenes, C ₃ -pyrenes
39	228	Chrysenes
40	258	C ₃ -Benzofluorene, C ₄ -pyrene

TABLE 7. (continued)

Peak Number	Molecular Weight	Tentative Identification
41	242	C ₁ -Chrysenes
42	256	Tetrahydrobenzofluoranthene, C ₂ -chrysene
43	252	Benzofluoranthenes
44	256	Tetrahydrobenzopyrene
45	252	Benzopyrenes
46	276	Indeno[1,2,3-cd]pyrene
47	276	Benzo[g,h,i]perylene

PROTON NMR OF SELECTED CTSL PROCESS MATERIALS

Figures 6 through 15 are proton NMR spectra of various CTSL samples and their chemical class fractions. Figures 6 and 11 are spectra of Samples 040 (first-stage, Condition 3/Period 9) and 041 (second-stage, Condition 3/Period 9) prior to fractionation. Regions 1 through 7 are of significance in interpreting these spectra and are designated in these two figures, with further explanation of their respective proton environments given in Table 8. In general, the crude materials were highly saturated (aliphatic) in nature, as manifested by the quantitatively dominant structure in Regions 1 and 2. Hydroaromaticity (Region 4) and relatively low levels of aromaticity (Regions 5-7) were also observed in the proton NMR spectra of the crude CTSL samples. Overall, only slight differences were observed between the spectra of the first- and second-stage materials.

Figures 7 through 10 and 12 through 15 are proton NMR spectra of the picric acid alumina column fractions PA₁ through PA₄. As anticipated, hydrogen in the AH fractions was in environments which gave rise to signals almost entirely in Regions 1 and 2 (Figures 7 and 12). The PA₂ fraction (Figures 8 and 13) likewise had hydrogen in Regions 1 and 2; however, strong hydroaromatic character was also present in Regions 3 and 4. The dihydro-PAH/<three-ring-PAH fractions (PA₃; Figures 9 and 14) had nearly equal levels of Regions 1-4 and Regions 5-7 hydrogen, indicating the presence of PAH with hydro- and alkyl- substitution. Finally, the PA₄ fractions (Figures 10 and 15) contained mostly multiple-ring aromatic hydrogen in Regions 5 and 6 with some hydrogen in the proximity of heteroatoms in Region 7.

FIGURE 6. Proton NMR Spectrum of CTSL Sample 040 (Condition 3/Period 9): Crude

FIGURE 7. Proton NMR Spectrum of CTSL Sample 040, Fraction PA₁: AH

FIGURE 8. Proton NMR Spectrum of CTSL Sample 040, Fraction PA₂: Hydroaromatic Compounds

FIGURE 9. Proton NMR Spectrum of CTSL Sample 040, Fraction PA₃: Dihydro-PAH/<Three-Ring PAH

FIGURE 10. Proton NMR Spectrum of CTSL Sample 040, Fraction PA₄: >Three-Ring PAH/Polar PAH

FIGURE 11. Proton NMR Spectrum of CTSL Sample 041 (Condition 3/Period 9): Crude

FIGURE 12. Proton NMR Spectrum of CTSL Sample 041, Fraction PA₁: AH

FIGURE 13. Proton NMR Spectrum of CTSL Sample 041, Fraction PA₂: Hydroaromatic Compounds

FIGURE 14. Proton NMR Spectrum of CTSL Sample 041, Fraction PA₃: Dihydro- PAH/<Three-Ring PAH

FIGURE 15. Proton NMR Spectrum of CTSL Sample 041, Fraction PA₄: >Three-Ring PAH/Polar PAH

TABLE 8. Explanation of Hydrogen Environments Designated in Figures 6 and 11^a

Regions	Structure	Proton Environment
	<p style="text-align: center;">Structure I</p> <p style="text-align: center;">Structure II</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., nine and ten positions of anthracene)
7	=CH-X	Aromatic hydrogen in proximity to heteroatomic functionalities (e.g; N-PAC, 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, partial overlapping of the spectral regions occurs.

PROBE INLET MASS SPECTRA OF SELECTED CTSL PROCESS MATERIALS

Low-voltage probe mass spectral data, obtained by averaging 30 or more scans, are shown in Figures 16 through 19 for first-stage samples 50378-036, -038, -040, and -042. The base peak (m/z 222) in three of the four samples corresponded to a C_1 -hexahydrofluoranthene/pyrene or an equivalent isomeric hydrocarbon. Ion signals from the fully aromatic analog of these species, at m/z 216, were generally approximately 80% as intense. In addition, there were substantial differences in the relative intensities of the ion signals from other hydroaromatic species, such as those at m/z 182 and 196: C_1 -dihydrofluorenes and C_2 -dihydrofluorenes, respectively). The compounds present in these materials can be determined by comparing the ion masses with chemical structures listed in Table 9. Molecular weight for hydroaromatic species can be obtained by incrementing the given mass by one atomic mass unit per additional hydrogen atom; e.g., dihydrofluorene is m/z 168--two mass units greater than fluorene at m/z 166.

In separate analyses, under slightly different conditions (lower ionization potential as compared to the above experiments), first-stage crude Sample 040 (Figure 20A) was compared to its second-stage counterpart, Sample 041 (Figure 20B). In these samples, differences detected by probe mass spectral analyses are minimal. This result is consistent with those obtained on matched sets of samples by GC analyses. It is important to note in this regard that the unconverted materials (appearing as particulate in the THF extracts) would not be expected to show in either the electron impact mass spectral data or in the GC data because of their relative involatility.

HRI96W. 0 31-JUL-84 CAL: C731
HRI 50378=036, 12EV, 7KV, 1.5K, PROBE

STR: A. BG SCAN = 3

0:18

FIGURE 16. Low-Voltage (12 eV) Probe Inlet Mass Spectrum of CTSL Sample 036 (Condition 1/Period 3)

HRI38W. 0 31-JUL-84 CAL: C731
HRI 50378-038, 12EV, 7KV, 1.5K, PROBE

STA: A. BG SCAN = 0

0:24

FIGURE 17. Low-Voltage (12 eV) Probe Inlet Mass Spectrum of CTSL Sample 038 (Condition 2/Period 5)

FIGURE 18. Low-Voltage (12 eV) Probe Inlet Mass Spectrum of CTSL Sample 040 (Condition 3/Period 9)

FIGURE 19. Low-Voltage (12 eV) Probe Inlet Mass Spectrum of CTSL Sample 042 (Condition 4/Period 12)

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	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/Fluor- anthene	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]fluor- anthene	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
Cyclopentachry- senes/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
Cyclopentabenz- pyrenes	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/ Cyclopenta- chrysenes	276	290	304	318	332	346	360	374	388	402	416	430
Dibenzanthra- cenes/Phenan- threnes	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.

FIGURE 20A. Low-Voltage (12 eV) Probe Inlet Mass Spectrum of CTSL Samples: 040, First Stage

L41CW . 0 07-SEP-84 CAL: C97 STA: A. BG SCAN = 0
50378-041/CRUDE; HRI, 2ND STAGE, COND. 3, 12EV, 5KV

0:19

FIGURE 20B. Low-Voltage (12 eV) Probe Inlet Mass Spectrum of CTSI Samples: 041, Second Stage

APPENDIX A
EXPERIMENTAL METHODS SECTION FROM PNL-5215

EXPERIMENTAL METHODS

BIOLOGICAL ASSAYS

The biological activity of the NTSL and ITSL process materials was evaluated using three assays. The mutagenic potencies for all of the sampled crude materials were estimated using the standard plate incorporation microsomal assay. Chemical class fractions of the process materials sampled during Run 241, Run 242-720°F and Run 242-740°F were also assayed for microbial mutagenicity. The I/P mouse skin tumorigenicity assay was employed to evaluate the carcinogenic potency of four selected NTSL and ITSL pilot plant process materials, as well as the <650°F total liquid product (TLP) distillate from the C. E. Lummus PDU. Finally, the toxicity of four NTSL/ITSL sample materials was evaluated in a static aqueous test system with D. magna. The experimental details of these three assays are provided below.

Standard Microbial Mutagenicity Test

Standard agar plate mutagenicity assays were performed as described by Ames et al. (1965) using the S. typhimurium TA98 microbial tester strain. Dimethylsulfoxide was used as a solvent. In addition to the mutagens used to check the phenotype of Salmonella TA98 strain, fixed concentrations of 2-aminoanthracene, benzo[a]pyrene and a complex basic fraction from SRC II heavy distillate were tested, with Aroclor-induced rat liver (S9) homogenates used for metabolic activation. Optimal levels for S9 were established and monitored daily during the course of the experiments. Typical amounts of S9 homogenate used were 5, 10, 20 and 100 µl. Negative controls included the Salmonella TA98 test strain with and without microsomal enzymes (S9), and appropriate solvent controls. Revertant colonies per petri plate were counted electronically using a Biotran II automated colony counter.

The specific mutagenic activity of crude products and chemical fractions were expressed as revertant colonies of S. typhimurium, TA98/µg of test material. Doses of crudes and chemical fractions ranged from 0.1 µg to 500 µg/plate. A positive test was one that had a maximum mutagenic response in revertant colonies twofold (or greater) that of background. Mutagenic potency

was estimated by linear regression analysis of dose response data. The complete set of raw data are presented in Appendix A for all NTSL and ITSL materials tested with TA98, along with data on positive and negative controls.

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 doubling of dose concentration; a correlation coefficient of 0.8 or greater; an intercept on the response (ordinate) axis within 20% of the negative control for the day. To estimate recovery of genetic activity, mutagenicity experiments were replicated several times to obtain an average value for the slope of the regression line, or mutagenic potency in revertants/ μ g.

I/P Mouse Skin Carcinogenicity Assay

Carcinogenesis consists of at least two stages, initiation and promotion. Investigation in this laboratory and others has shown that the ability of coal-derived materials to initiate skin tumorigenesis correlates well with their ability to act as complete skin carcinogens (Barenblum, 1941; Calkins et al., 1980; Mahlum et al., 1983). The I/P assay has therefore been used in this study to assess the potential carcinogenicity of materials derived from the NTSL and ITSL processes.

Female CD-1 mice (Charles River Laboratories, Portage, MI), approximately 6 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 dichloromethane, 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. The controls received 50 μ l of dichloromethane. Two weeks after initiation, 5- μ g doses of phorbol myristate acetate (PMA; Sigma Chemical Co., 0.1 mg/ml of acetone) were applied to the initiated area, twice weekly for 24 weeks. The mice were shaved as necessary throughout the study, usually weekly. Animals were observed regu-

larly for tumor growth, and the number of tumors per animal was counted bi-weekly.

The coal liquids from the Wilsonville pilot plant tested for initiating activity were: 1) the NTSL HTR feed (PNL#5226-021); 2) the NTSL distillation column bottoms (PNL#5226-022); 3) the ITSL HTR feed (PNL#5226-061); and 4) the ITSL distillation column bottoms (PNL#5226-059). A <650°F distillate (PNL#3399-135) of the TLP from the Lummus ITSL PDU in New Brunswick, NJ was also tested in this set of experiments.

Aquatic Toxicity Assay

Ecological screening bioassays were conducted with the distillation column overheads from both stages of the NTSL and ITSL process. The samples tested are listed in Table 15. Water-soluble fractions (WSF) were generated from the four coal liquids, using methods previously described by Dauble et al. (1982, 1983). Briefly, WSF were generated by adding 100 ml of sample material to 10 L of well water (1:100 ratio) in a 15-L glass carboy. The mixture was stirred at 90 rpm with a teflon-coated rod for 4 hours. After a 1-hour settling period, 8 L of the respective WSF were siphoned from the center of the carboy, chemically analyzed, and used for ecological testing. Exposure solutions for testing were made by diluting WSF with well water. Dilutions were based on total carbon concentrations in the WSF (stock solution).

Total carbon (TC) of the WSF was determined by direct aqueous injection into a Beckman 915B carbon analyzer. Detailed chemical analysis of the WSF by gas chromatography (GC) was conducted to determine phenol and hydrocarbon composition (methodology outlined in Dauble et al., 1982, 1983). Total phenols in selected test exposure solutions were estimated by the direct photometric method (American Public Health Association [APHA] Method 2220) at test initiation and again at 48 hours to monitor the relative stability of solubilized materials.

Acute toxicity of WSF derived from the test materials was determined by static bioassays with the freshwater invertebrate D. magna. All tests were conducted at 20°C with a 16:8-hour light:dark cycle. The test consisted of

placing five first-instar D. magna in each of four 100-ml-capacity glass jars at six treatment levels, plus a control (4 x 7 matrix, 20 organisms per treatment level).

To allow direct comparison of toxicological response of daphnids to the four process materials, all tests were conducted concurrently. The 48-hour LC₅₀ determinations were determined by probit analysis (Finney, 1971), and 95% confidence intervals were estimated to provide comparisons of acute toxicity between comparable process materials. Toxicity thresholds were expressed as percent WSF and TC, based on dilution.

CHEMICAL ANALYSES

Fractionation Methods

The NTSL and ITSL samples were chemically analyzed and prepared for biological testing using an integrated analytical approach based on separation according to chemical class. This method was developed for the qualitative and quantitative measurement of components in complex coal liquefaction process materials. The development of these analytical methods has been principally directed by the requirements of identifying the biologically active agents in coal conversion materials.

An overview of the separation scheme used to class-fractionate the NTSL and ITSL samples is shown in Figure 4. All crude process materials except the CSD ash concentrate were adsorbed on 3 g of neutral alumina, packed on top of an additional 6 g of alumina and eluted with the solvent scheme, as shown in Figure 4. The CSD ash concentrate was first solvent-extracted in a Soxhlet device for 24 hours with benzene:methanol (3:1); the extract was then separated by alumina adsorption column chromatography. The organic extractables in the ash ranged from ~6 to 16% by weight. Separation on neutral alumina of the major chemical classes that generally occur in coal conversion materials is achieved by this method (Later et al., 1981): (A₁) aliphatic hydrocarbons, (A₂) neutral polycyclic aromatic hydrocarbons (PAH), (A₃) N-PAC, and (A₄) polar or hydroxy-PAC. The neutral alumina used for the separation of NTSL/ITSL

FIGURE 4. Schematic Diagram for the Chemical Class Separation of PAC on Neutral Alumina

materials was standardized with respect to adsorbent activity (Later et al., 1983) to insure reproducible class separations.

The various classes of PAC determined in this study are listed in Table 16, along with typical structures and the acronyms used in this report. Capillary column GC and mass spectrometry (MS) were used for the detailed identification and quantitative determination of specific compounds in each class-specific isolate obtained from the adsorption column chromatographic separations. This fractionation approach has been applied to the chemical characterization of coal liquefaction materials from the SRC I, SRC II, ITSL PDU and EDS processes.

A separation method developed for the isolation of hydroaromatic PAH from synthetic fuels was also used to fractionate selected crude samples. This method, as developed and described by Wozniak and Hites (1983), was used due to the high content of hydroaromatic PAH in the NTSL/ITSL sample materials. High levels of hydroaromatics in these materials are a direct result of the integrated, second-stage catalytic hydrogenation process.

Figure 5 is a schematic diagram of this separation method, which uses a layered adsorption column of picric-acid-coated alumina over alumina. With the elution parameters given in Figure 5, class separation was achieved for aliphatic hydrocarbons (PA_1), hydroaromatic compounds (PA_2), dihydro-PAH and PAH with less than three aromatic rings (PA_3) and other PAH and N-PAC (PA_4). In general, those hydroaromatic compounds with a high degree of saturation were eluted in the aliphatic hydrocarbon fraction, A_1 , of the original alumina adsorption scheme. Differentiation of aliphatic hydrocarbons and partially saturated PAH was achieved by the picric acid/alumina. Hydroaromatic compounds and PAH complex with picric acid to form picrates; the aliphatic hydrocarbons do not undergo picrate complexation. Therefore, the hydroaromatic compounds and PAH can be retained on the adsorption column while the aliphatic hydrocarbons are eluted with polar solvents. The degree of saturation of a hydroaromatic compound determines the strength of the picrate complex and, thus, its elution from the column. In general, the hydroaromatic compounds with greater than dihydro substitution elute together, and the dihydro-PAH and PAH co-elute.

TABLE 16. PAC Classes in Coal-Derived Materials

STRUCTURE	CLASS	ACRONYM
<u>NEUTRAL PAH</u>
POLYCYCLIC AROMATIC HYDROCARBONS	PAH
POLYCYCLIC AROMATIC SULFUR HETEROCYCLES	PASH
POLYCYCLIC AROMATIC OXYGEN HETEROCYCLES	PAOH
<u>N-PAC</u>
3°-POLYCYCLIC AROMATIC NITROGEN HETEROCYCLES	3°-PANH
2°-POLYCYCLIC AROMATIC NITROGEN HETEROCYCLES	2°-PANH
AMINO POLYCYCLIC AROMATIC HYDROCARBONS	AMINO-PAH ^(a)
<u>HYDROXY-PAH</u>
HYDROXY POLYCYCLIC AROMATIC HYDROCARBONS	HYDROXY-PAH

^(a)ALSO COMMONLY REFERRED TO AS PRIMARY AROMATIC AMINES (PAA)

FIGURE 5. Schematic Diagram of the Picric Acid/Alumina Separation Scheme

Column parameters for this method, including percent picric acid content and adsorbent activity, were optimized for these analyses. Further details on this separation technique are available elsewhere (Wozniak and Hites, 1983). This separation method was applied in an effort to differentiate the strictly hydrocarbon-type compounds by chemical class and to more completely determine the effects of process configuration on chemical composition.

Gas Chromatography (GC)

High resolution GC was performed using a Hewlett-Packard (HP) 5880 GC equipped with a 25 m x 0.25 mm i.d. fused silica capillary column coated with DB-5 at a film thickness of 0.25 μ m (J & W Scientific, Inc.). The capillary vaporization injection system was operated in the splitless mode at 260°C for sample introduction. In general, the oven temperature was held for 2 minutes at 50°C, then temperature-programmed at a rate of either 3 or 4°C/minute to 280°C. Other temperature programs employed for specific GC analyses are defined in appropriate figure legends. A flame ionization detector (FID) was used to analyze for neutral PAC and N-PAC fractions. A nitrogen-specific detector (NPD) was used in conjunction with the FID to verify that the N-PAC components eluted entirely in the proper fraction (A_3 ; Figure 4). Both FID and NPD detectors were operated at 285°C.

A retention index system, specially designed for the determination of PAC in complex mixtures using temperature-programmed capillary GC (Lee et al., 1979; Vassilaros et al., 1982), was one of two means used to identify NTSL/ITSL sample constituents. This retention system uses the intervals between naphthalene, phenanthrene, chrysene, and picene PAH standards to calculate indices of retention for other PAC. Using standard compounds, a retention index library of approximately 500 PAC compounds has been established (Lee et al., 1979; Vassilaros et al., 1982). PAC in the sample fractions were identified by comparing retention indices of actual sample components with library values and those of authentic reference compounds.

A second GC method, based on absolute retention and calibrated internal standard data (assisted by the HP 5880 computerized integrator), was used for both the quantitative and qualitative analyses of the majority of fractionated

NTSL/ITSL samples. An internal standard, 2-chloroanthracene, added to all fractions at a final concentration of 50 ng/ μ l, was used in conjunction with calibrated response factors, as measured with standard compounds, for quantitative analysis of sample components. The absolute retention times of all available PAC standard compounds were measured, and detector response factors were calculated at eight concentration levels, ranging over two orders of magnitude for each standard. These values were then used to identify and quantify sample constituents with respect to the 2-chloroanthracene internal standard. A related or average response factor of a closely eluting or similar compound was used to quantify components for which standard compounds were not available. For example, a response factor was calculated for benzo[b]fluorene from the available standard; however, a benzo[a]fluorene standard compound was not available, so the same response factor was used for both quantitative calculations. All samples were analyzed at two or more dilutions (1.0, 2.5, 5.0 or 10.0 mg/ml) to ensure that analyses were within the range of the calculated response factors. Results are reported in parts per million (ppm), μ g/g, or in parts per thousand (ppt), mg/g, as noted for a given fraction or crude, with a minimum detectable limit of approximately 20 ppm. The mean and standard deviations for at least three determinations are given for each component quantified in the fractions.

Gas Chromatography/Mass Spectrometry (GC/MS)

GC identifications were supplemented with MS identification, using coupled GC/MS. The GC/MS analyses were performed on an HP 5982A quadrupole MS interfaced with an HP 5710 GC equipped with a 15 m x 0.30 mm i.d., DB-5 fused-silica capillary column. 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. This modification enhanced the resolution and interpretability of the GC/MS chromatograms. Gas chromatographic conditions were similar to those previously described for GC analyses. 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. Identifications were assigned to sample components, based on their similarity with mass spectra in

the EPA/NIH library or with spectra of authentic reference compounds run under identical GC/MS conditions.

Probe Inlet MS

To determine compounds present in higher molecular weight materials which were not be amenable to GC owing to their low volatilities, and to compare the relative average molecular weights of the samples, the crude materials and alumina fractions were analyzed by probe inlet MS on a VG ZAB 1-F double-focusing MS. The ZAB system was typically 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 at 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 MS was scanned repetitively 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, representing the entire sample. These averaged spectra were then used to estimate the mean molecular weight of each sample and were compared to GC data to confirm the rank order of the average molecular weights assigned to the various samples.

Averaged spectra were acquired for most samples, using ionizing electron energies of both 70 and 10-12 eV. The 70-eV spectra display the molecular ions, the major fragments, and the doubly charged ions for each species, thus providing structural information. However, 70-eV spectra do not accurately depict either the average molecular weight profiles of the samples or the relative concentration of alkylated and hydroaromatic components, as represented by the intensities of their molecular ions. The 10- to 12-eV spectra are composed primarily of signals representing molecular ions, resulting in a profile that more accurately represents the average molecular weight distribution of the sample.

APPENDIX B
SELECTED TABLES AND FIGURES FROM PNL-5215

TABLE 17. Microbial Mutagenicity of NTSL/ITSL Crudes in *S. typhimurium* TA98 (rev/μg; linear regression of dose response data)^a

Sample Description	NTSL	ITSL					
		242~ Start Up	242~ 680°	242~ 700°	242~ 720°A	242~ 720°B	242~ 740°
SRC Product: Light fuel oil T-104 overheads	0	0	0	0	0	2	1
SRC Product: Distillate process solvent T-102, Tray 8	--	0	2	0	0	3	2
SRC Product: 1st-stage product distillate T-102, Tray 3	0	--	>1	--	--	0	--
Deashed SRC: Feed to HTR CSD unit	4	1	7	1	2	0	5
CSD Product: Ash concentrate	6	0	2	2	<1	3	0
HTR Feed: Blend of SRC pro- ducts V-1064	9	--	2	1	0	0	0
HTR Product: Light fuel oil T-105 overheads	0	--	--	--	0	0	0
HTR Product: Distillate column bottoms T-105 bottoms	6	--	--	--	0	0	0
HTR Product: Vacuum flash bottoms V-1082	5	--	--	--	--	--	--
HTR Product: Recycle pasting solvent V-1067	--	0	4	1	0	0	--

^aThe comparative mutagenicity of National Bureau of Standards coal tar was 2 rev/μg in TA98.

TABLE 18. Microbial Mutagenicity of Chemical Class Fractions of the SRC Unit Process Materials (First Stage)

Sample Description	Process Description	Mutagenic Response <i>S. typhimurium</i> TA98 (rev/μg)					
		Aliphatic Hydrocarbons	PAH	N-PAC	Hydroxy-PAH	Crude	PNL #
Light fuel oil T-104 overheads	NTSL	0	0	0	0	0	5226-023
	ITSL-720°B	0	0	11	0	2	5226-055
	ITSL-740°	0	0	11	0	1	5226-064
SRC distillate Process solvent T-102, Tray 8	NTSL	--	--	--	--	--	--
	ITSL-720°B	0	0	27	0	3	5226-056
	ITSL-740°	0	<1	16	0	3	5226-065
1st-stage product distillate T-102, Tray 8	NTSL	0	0	0	0	0	5226-019
	ITSL-720°B	0	0	39	0	0	5226-057
	ITSL-740°	--	--	--	--	--	--
Deashed SRC product HTR feed CSD unit	NTSL	0	<1	15	5	4	5226-020
	ITSL-720°B	0	0	0	0	0	5226-063
	ITSL-740°	0	0	0	0	5	5226-066 ^a
CSD ash Concentrate	NTSL	0	0	3	<1	3	5226-025 ^a
	ITSL-720°B	0	0	0	0	3	5226-060
	ITSL-740°	0	0	0	0	0	5226-067

^aValues reported are the average obtained from two different sets of assays.

TABLE 29. Chemical Composition for the NTSL and Select ITSL Process Materials

Sample Description ^a	Fractions ^b	Weight Percent Distribution		
		NTSL 241	ITSL 242-720°B	ITSL 242-750°
		(5226-018)	(5226-055)	(5226-064)
SRC: Light fuel oil	A ₁	23	15	22
SP: T-104, Overheads	A ₂	16	22	23
	A ₃	2	10	12
	A ₄	24	24	24
	Total	65%	69%	81%
		(5226-056)	(5226-065)	
SRC: Distillate process solvent	A ₁	---	34	38
	A ₂	---	49	46
SP: T-102, Tray 8	A ₃	---	6	9
	A ₄	---	13	18
	Total	---	102%	111%
		(5226-019)	(5226-057)	
SRC: 1st-stage product distillate	A ₁	34	44	---
	A ₂	30	29	---
SP: T-102, Tray 3	A ₃	13	7	---
	A ₄	29	20	---
	Total	106%	100%	---
		(5226-020)	(5226-063)	
SRC: Deashed SRC Product	A ₁	<1	11	2
Second-stage HTR feed	A ₂	10	36	33
SP: CSD unit holding tank	A ₃	33	32	45
	A ₄	36	22	24
	Total	80%	101%	104%
		(5226-025)	(5226-060)	(5226-067)
CSD: Ash concentrate	A ₁	4	2	3
SP: CSD unit ash concentrate receiver	A ₂	6	18	13
	A ₃	20	29	25
	A ₄	66	27	28
	Total	96%	76%	69%

^aSP = Sampling point^bValues reported are the average of two, three or more individual separations.Key: A₁ = aliphatic hydrocarbons, A₂ = neutral PAH, A₃ = N-PAC, and A₄ = hydroxy-PAH

TABLE 29. (continued)

Sample Description ^a	Fractions ^b	Weight Percent Distribution		
		NTSL 241	ITSL 242-720°B	ITSL 242-750°
		(5226-021)	(5226-061)	5226-070)
HTR: HTR feed	A ₁	22	14	15
SP: V-1064	A ₂	24	38	36
	A ₃	19	27	27
	A ₄	35	23	23
	Total	100%	102%	101%
		(5226-023)	(5226-062)	(5226-068)
HTR: Light fuel oil	A ₁	51	51	53
SP: T-105, Overheads	A ₂	47	11	44
	A ₃	<1	2	1
	A ₄	5	9	7
	Total	103%	73%	105%
		(5226-022)	(5226-059)	(5226-069)
HTR: Distillation column bottoms	A ₁	45	63	65
	A ₂	34	26	24
SP: T-10P bottoms	A ₃	7	5	7
	A ₄	15	9	15
	Total	101%	103%	111%
		(5226-024)	(5226-058)	
NTSL: Vacuum flash bottoms	A ₁	1	21	---
SP: V-1082	A ₂	29	28	---
ITSL: Recycle pasting solvent	A ₃	50	22	---
SP: V-1067	A ₄	18	17	---
	Total	98%	88%	---

^aSP = Sampling point^bValues reported are the average of two, three or more individual separations.Key: A₁ = aliphatic hydrocarbons, A₂ = neutral PAH, A₃ = N-PAC, and A₄ = hydroxy-PAH

TABLE 31. Hydroaromatic Composition of ITSL and NTSL Process Materials

Chemical Fraction	Deashed SRC Product		HTR Feed		HTR Distillate Column Bottoms	
	NTSL (020)	ITSL (063)	NTSL (021)	ITSL (061)	NTSL (022)	ITSL (059)
PA ₁ : Aliphatic hydrocarbons	15	3	<1	11	37	51
PA ₂ : Hydroaromatics	<1	3	17	13	40	30
PA ₃ : Dihydro-PAH plus <3-ring PAH	1	8	7	12	13	7
PA ₄ : >3-ring PAH plus polar compounds ^a	<u>10</u>	<u>24</u>	<u>13</u>	<u>23</u>	<u>9</u>	<u>11</u>
<u>Total:</u>	27%	38%	38%	59%	99%	99%
Sum of A ₁ plus A ₂ : (aliphatic plus PAH)	11%	47%	46%	52%	79%	89%

^aSome lower molecular weight polar compounds also eluted in this fraction.

FIGURE 10. Capillary Chromatogram of the Hydroaromatic Compound Fraction, PA₂, of the HTR Distillation Column Bottoms from the NTSL Process. See Table 32 for peak identifications.

FIGURE 11. Capillary Chromatogram of the Hydroaromatic Compound Fraction, PA₂, of the HTR Distillation Column Bottoms from the ITSL Process. See Table 32 for peak identifications.

FIGURE 19. Capillary Chromatograms of the PAH Fractions of (Top) the HTR Light Fuel Oil (PNL #5226-023) and (Bottom) the HTR Distillate (PNL #5226-022) Process Materials for NTSL Run 241. (See Table 33 for peak identifications.)

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