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**Two-Stage Coal Liquefaction
Process Materials from the
Wilsonville Facility Operated in
the Nonintegrated and
Integrated Modes: Chemical
Analyses and Biological Testing**

D. W. Later

January 1985

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

**Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute**

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TWO-STAGE COAL LIQUEFACTION PROCESS MATERIALS
FROM THE WILSONVILLE FACILITY OPERATED IN THE
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Pacific Northwest Laboratory
Richland, Washington 99352

FOREWORD

This document reports the results from chemical analyses and biological testing of process materials sampled during operation of the Wilsonville Advanced Coal Liquefaction Research and Development Facility (Wilsonville, Alabama) in both the noncoupled or nonintegrated (NTSL Run 241) and coupled or integrated (ITSL Run 242) two-stage liquefaction operating modes. The Wilsonville R&D Facility is operated by Catalytic, Inc., under subcontract to Southern Company Services, Inc., Birmingham, Alabama. Work at the Wilsonville pilot plant is jointly sponsored by the United States Department of Energy (U.S. DOE) and the Electric Power Research Institute (EPRI).

Mutagenicity and carcinogenicity assays were conducted in conjunction with chromatographic and mass spectrometric analyses to provide detailed, comparative chemical and biological assessments of several NTSL and ITSL process materials. In general, the NTSL process materials were biologically more active and chemically more refractory than analogous ITSL process materials. To provide perspective, the NTSL and ITSL results are compared with those from similar testing and analyses of other direct coal liquefaction materials from the solvent refined coal (SRC) I, SRC II and EDS processes. Comparisons are also made between two-stage coal liquefaction materials from the Wilsonville pilot plant and the C. E. Lummus PDU-ITSL Facility in an effort to assess "scale-up" effects in these two similar processes.

The studies reported in this document were conducted by investigators in the Department of Biology and Chemistry and Department of Environmental Sciences at Pacific Northwest Laboratory (PNL), which is operated by Battelle Memorial Institute for the U.S. DOE. In particular, this work was jointly sponsored by the DOE Office of Fossil Energy and the Office of Health and Environmental Research.

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The author particularly thanks Ed Chess and Cherylyn Wright for assistance in editing the text and compiling the chemistry tables, figures and appendices of this report. D. D. Mahlum, D. D. Dauble, and R. A. Pelroy and D. L. Stewart directed the biological assays and provided results for the carcinogenicity, aquatic toxicity and microbial mutagenicity sections, respectively. T. J. Wozniak and Prof. R. A. Hites of Indiana University collaborated on the class separation and detailed analysis of the hydroaromatic compounds, for which thanks is expressed.

The author also appreciates the technical support and assistance of Richard F. Hickey, who coordinated sample collection and shipment as the "on-site" DOE representative at Wilsonville. C. Clone and T. Forbes of Catalytic, Inc. also assisted in sample collection and shipment. Particular thanks is expressed to J. E. Kimes, Operations Superintendent for Catalytic, Inc. at Wilsonville, for providing detailed information on the engineering aspects of the ITSL and NTSL processes.

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LIST OF ABBREVIATIONS

A ₁	= aliphatic hydrocarbon alumina column fraction
A ₂	= neutral PAH alumina column fraction
A ₃	= N-PAC alumina column fraction
A ₄	= hydroxy-PAH alumina column fraction
amino-PAH	= amino polycyclic aromatic hydrocarbon(s)
amu	= atomic mass unit
APHA	= American Public Health Association
API	= American Petroleum Institute
bp	= boiling point
cm ⁻¹	= reciprocal centimeters (wave numbers); used for infrared spectro- photometry
CSD	= critical solvent deashing
CSF	= Consol synthetic fuel
°F	= degrees Fahrenheit
DNA	= deoxyribonucleic acid
DOE	= U.S. Department of Energy
ECD	= electron capture detector
ECLP	= EDS Coal Liquefaction Pilot Plant
EP	= end boiling point
FID	= flame ionization detector
g	= gram(s)
GC	= gas chromatography
GC/MS	= gas chromatography/mass spectrometry
HD	= heavy distillate
HPLC	= high performance liquid chromatography
HRGC	= high resolution gas chromatography
HTR	= hydrotreater
IBP	= initial boiling point
I/P	= initiation/promotion (mouse skin tumorigenicity assay)
IR	= infrared spectrophotometry
ITSL	= integrated two-stage liquefaction
LSE	= liquid solvent extraction
LTR	= light thermal resid
m	= meter(s)
MAF	= moisture and ash free
MF	= moisture free
µg	= microgram(s)
ml	= milliliter(s)
µl	= microliter(s)
mm	= millimeter(s)
MS	= mass spectrometry
m/z	= mass to charge ratio

NMR = nuclear magnetic resonance spectroscopy
 N-PAC = nitrogen-containing polycyclic aromatic compounds
 NPO = nitrogen-phosphorus detector
 NTSL = nonintegrated two-stage liquefaction

 PA = picric acid/alumina column fraction
 PAC = polycyclic aromatic compound(s)
 PAH = polycyclic aromatic hydrocarbon(s)
 PANH = polycyclic aromatic nitrogen heterocycle(s)
 PAOH = polycyclic aromatic oxygen heterocycle(s)
 PASH = polycyclic aromatic sulfur heterocycle(s)
 PDU = process development unit
 PMA = phorbol myristate acetate
 PNL = Pacific Northwest Laboratory
 ppm = parts per million
 ppt = parts per thousand
 PS = process solvent

 R&D = research and development
 rev/ μ g = revertant colonies detected per microgram of test material in microbial mutagenicity assay

 S9 = metabolic enzyme system used in microbial mutagenicity assay
 SCT = short contact time
 sec = second(s)
 SRC = solvent refined coal

 TA98 = designation for strain of Salmonella typhimurium used in microbial mutagenicity assay
 TC = total carbon
 TLP = total liquid product
 TSL = two-stage liquefaction

 UV = ultraviolet spectrophotometry

 VGO = vacuum gas oil

 WSF = water-soluble fractions

EXECUTIVE SUMMARY

Process materials were obtained from the Advanced Coal Liquefaction R&D Facility at Wilsonville, AL for chemical analyses and biological testing at Pacific Northwest Laboratory. The Wilsonville R&D Facility has recently been operated in a two-stage liquefaction (TSL) configuration, with the first-stage in the short contact time (SCT) mode and the second stage a catalytic hydrogenation reactor. Deashing of the first-stage product prior to second-stage catalytic hydrotreatment was achieved by critical solvent deashing (CSD). Samples were collected during "lined-out" operation of two different TSL process configurations: Run 241, noncoupled two-stage liquefaction (NTSL), and Run 242, coupled or integrated two-stage liquefaction (ITSL). In the NTSL mode, process solvents were distillate products from each of the two stages independently and were recycled within their respective stages; the first-stage process solvent was not hydrogenated. In the ITSL operating mode, a heavy-end distillate product from the second-stage hydrotreater unit was recycled to the first stage and served as the process solvent; the two liquefaction stages were therefore integrally coupled by the hydrogenated process solvent. A single sample set was collected during NTSL operation, and several sample sets were taken under various operating conditions of the ITSL run. Because process flow sheets, internal recycles and desired products differ between the ITSL and NTSL modes, samples taken from the same sampling point do not necessarily represent corresponding materials for the two process modes.

Three bioassays were used to test the biological potency of the NTSL and ITSL process materials: the microbial mutagenicity assay with Salmonella typhimurium TA98, the initiation/promotion (I/P) mouse skin tumorigenicity assay, and an acute toxicity assay with the aquatic organism Daphnia magna. All samples collected were screened for biological activity, using the microbial mutagenicity assay. Furthermore, class-specific chemical fractions from the NTSL and two ITSL sample sets were tested using this assay. As with other coal liquefaction process materials investigated in this laboratory, the nitrogen-containing polycyclic aromatic compound class fractions were responsible for the bulk of the observed microbial mutagenicity of the crude samples. Only the hydrotreater feed and distillation column bottoms from the NTSL and ITSL operating modes were assayed in the I/P tumorigenicity assay. A

<650°F distillate from the C. E. Lummus ITSL process was also tested for tumorigenicity in this assay. In general, the ITSL process materials were less mutagenic and tumorigenic than NTSL materials collected from the same sampling point or the Lummus ITSL samples previously tested. All pilot plant TSL samples tested to date have shown lower mutagenic and tumorigenic potencies than process material from single-stage liquefaction facilities. Comparing the tumorigenicity of the hydrotreater feed and distillate product, the greatest reduction in activity due to catalytic hydrogenation was observed for those materials produced in the ITSL mode. This is assumed to be due to the higher quality process solvent used in the ITSL, compared to the NTSL, mode which optimizes the efficiency of hydrogen incorporation during liquefaction.

The water-soluble fractions of the distillation column overheads from the first and second stages of both the NTSL and ITSL modes (four samples total) were tested for acute toxicity to the water flea, D. magna, in a static aquatic system. As with other direct coal liquefaction process materials tested in this assay, the major aqueous extractable chemical constituents were the hydroxy-substituted compounds, such as phenol, indanol and their alkylated analogs. No difference was observed in the toxicity of first-stage products with respect to process mode; however, second-stage products of the NTSL mode were more toxic than ITSL second-stage materials. The acute toxicities of the four NTSL/ITSL process materials were similar to those observed in previous studies with coal liquids from other processes.

Detailed chemical analyses of the NTSL and ITSL process materials were performed using adsorption liquid chromatography, capillary column gas chromatography, and mass spectrometry. Results from chemical analyses showed that the NTSL/ITSL materials, in general, were highly alkylated and had high levels of hydroaromatic compounds. Higher levels of aliphatic hydrocarbons were observed in the products of the ITSL process than in any previously studied coal liquefaction material with comparable boiling point range. Compared to the Lummus ITSL materials, the pilot plant NTSL and ITSL process materials were more complex, with higher levels of alkylation. As with the Lummus ITSL and EDS processes, where catalytic hydrogenation is employed, concentrations of nitrogen and oxygen heteroatomic compounds were relatively low in the NTSL/ITSL process materials. The major heteroatomic species observed were pyrrolic

compounds, such as carbazole and its alkylated homologs, and the hydroxy-substituted compounds, such as phenol, indanol and their alkylated homologs. Reduced levels of nitrogen-containing compounds resulted in a general reduction in microbial mutagenicity; very low concentrations of amino polycyclic aromatic hydrocarbons were present.

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INTRODUCTION

Both single- and multi-stage direct coal liquefaction processes have been under study in the U.S. Two-stage liquefaction (TSL) processes, which separate initial liquefaction and subsequent hydrogenation steps, are currently being developed as a means of more effectively converting coal by more efficient use of hydrogen and thermal energy. Compared to single-stage processes, TSL can increase the amount of coal liquid produced while greatly reducing the formation of gas and light hydrocarbons. Owing to the enhanced quality of process solvents available in such processes, high coal-conversion rates may be achieved under relatively mild reaction conditions. Both single- and two-stage direct coal liquefaction processes have received major developmental support from offices of the U.S. Department of Energy (DOE). Pacific Northwest Laboratory (PNL), with funding from DOE's Office of Fossil Energy and Office of Health and Environmental Research (OHER), has had an active role in providing detailed chemical and biological analysis of coal liquefaction materials from these processes.

BACKGROUND

A major goal for development of advanced direct liquefaction processes is to make more efficient use of thermal energy and available hydrogen for obtaining marketable and environmentally safe fuels from coal. From the process side, several approaches to increased thermal efficiency in coal conversion appear promising, including reduction of initial liquefaction severity by lowering reaction temperature and hydrogen partial pressure. This approach is more feasible when process solvents with high hydrogen-donating activities are available.

Several process developers have chosen to separate, to the greatest extent possible, the initial solvation or liquefaction steps from subsequent hydrogenation or upgrading operations. This strategy allows hydrogen to be more effectively utilized in the second stage since it may be reacted directly with distillate materials. This approach also allows more effective use of catalysts to achieve denitrogenation and desulfurization and/or hydrocracking of aromatic ring systems. TSL catalysts, for example, have generally been

classed as the former type, while EDS catalysts are generally considered hydrogenation catalysts. The difference in products produced by these two types of catalysts are apparent when comparing chemical characterization data (Later et al., 1984; Wilson et al., 1983).

TSL technologies have two major process stages. The first stage is generally a low-severity, thermal liquefaction step, which can be operated under varied residence times and temperatures. The second stage is conventionally a catalytic hydrogenation reaction step. The two liquefaction stages thus far have been "noncoupled," "integrally coupled," or "close-coupled." The terms denote the source of process recycle solvent and placement of distillation and/or deashing steps relative to the two liquefaction stages. Perhaps the most important feature of TSL processes is their versatility in allowing production of a wide range of process recycle solvents with differing physical and chemical properties. The recycle process solvent stream generally constitutes a major portion of the process feed material, and its quality and function as a liquefaction medium and product precursor is of critical importance to overall process performance.

DOE has supported single-stage advanced coal liquefaction pilot plants that produced distillate liquid fuels, including solvent refined coal (SRC) II, H-Coal, and EDS. The first two are considered strictly single-stage processes since the conversion from coal to distillate takes place in a single reactor with coal, a process-derived solvent and hydrogen. EDS is considered a forerunner of the two-stage processes since, in the original configuration, the recycle solvent portion of the product stream was hydrotreated in a separate process unit from the liquefaction reactor. The conversion of coal to distillate product involves a series of reactions, many of which are not well understood. Thus, it has not been obvious that all steps could be optimized in a single reactor. The TSL process, in which the entire product oil stream from a first-stage low-severity liquefaction step is hydrotreated in a second stage, became of interest partly because of the success of EDS. Separation of the primary extraction step from the hydrotreating step showed promise with regard to improving the efficiency of coal conversion and producing higher-quality end products. TSL process strategy development has received major attention and support in the U.S. for approximately the last decade.

The basic TSL concept was first proposed in Germany during World War II in connection with the Pott-Borsche process but was never carried out in the original form (Lowry and Rose, 1947). The Consol Synthetic Fuel (CSF) process, developed by Consolidation Coal Company in the 1950s, was a two-stage process in which integrated operation was successfully established in a pre-pilot-scale program (Lowry and Rose, 1947; U.S. Department of Interior, 1969, 1970). The CSF process was the first attempted application of an expanded-bed hydrocracker for upgrading of a "clean" coal extract. Attempts to scale the process to pilot plant level processing (20 tons/day) were not successful, primarily because of various mechanical problems (U.S. Department of Interior, 1969, 1970).

More recently, a two-stage concept has been under development at the National Coal Board's Coal Research Establishment near Cheltenham in the U.K. (British National Coal Board, 1982, 1983). Liquid solvent extraction (LSE) is currently being evaluated as the initial stage for this technology. As in the EDS technology, the solvent used for extraction in the first stage is recycled from the second stage and regenerated, via hydrotreatment, in a unit separate from the two liquefaction reactors. In the DOE TSL program, initiated in 1975, upgrading operations of the two coal extracts in a prototype LC fining catalytic cracking unit were started in June 1976 and have been conducted under DOE contract by the C. E. Lummus Engineering Development Facility (New Brunswick, NJ). During the last 2 years, the Wilsonville Advanced Coal Liquefaction Research and Development (R&D) Facility pilot plant has been operated in the TSL mode. This status report presents and discusses the results of integrated chemical analyses and biological testing performed on process materials sampled during Run 241, noncoupled (nonintegrated two-stage liquefaction; NTSL), and Run 242, integrated or coupled (integrated two-stage liquefaction; ITSL), at the Wilsonville pilot plant.

CURRENT WORK

In general, coal-derived products have been associated with adverse health effects to a greater degree than have analogous petroleum-based materials (Later et al., 1983; Mahlum, 1981; PNL-3189, 1979; Pelroy, 1981; Pelroy and Wilson, 1981; Wilson et al., 1982). As a component of the overall coal

liquefaction program, DOE-supported National Laboratories and process developers have cooperated in efforts to define potential health effects and industrial hygiene concerns as coal utilization technologies develop. NTSL and ITSL direct coal liquefaction process materials have been supplied by Catalytic, Inc. for biological and chemical evaluation in extramural programs at PNL sponsored by DOE's OHER and the Office of Fossil Energy. The investigations described in this report were performed as part of that effort.

The microbial mutagenicity assay with Salmonella typhimurium TA98, a relatively inexpensive test, has become a standard screening bioassay used at PNL for initially assessing the genetic activity of crude fossil fuel mixtures. All NTSL and ITSL crude process samples collected from the Wilsonville pilot plant were tested in this assay for microbial mutagenicity. In addition, chemical class fractionated process materials from the NTSL and ITSL sample suites were tested.

The carcinogenicity of selected NTSL and ITSL process materials were also investigated using the mouse skin initiation/promotion (I/P) tumorigenicity assay. The hydrotreater (HTR) feed and HTR distillation column bottoms (>450°F) from both the NTSL Run 241 and ITSL Run 242 (four samples total) were tested using the I/P assay. I/P tumorigenicity results are also reported for the <650°F distillate of a total product from the C. E. Lummus ITSL process development unit (PDU).

To complement the in vitro and in vivo biological testing of the NTSL/ITSL materials, the light fuel oils from both the first-stage SRC unit and second-stage HTR unit from both the NTSL and ITSL operation modes (four samples total) were tested in an acute toxicity assay by a static aquatic system with Daphnia magna. The results obtained for the biological assays described are presented and discussed in this status report. In addition, the results obtained for the NTSL/ITSL materials are compared with those from previous studies of other coal liquefaction materials, including SRC I, SRC II, EDS and Lummus ITSL processes. These comparisons will add perspective to the NTSL/ITSL results and emphasize the major differences in chemical composition and biological activity of these materials in relation to process materials from other single- and two-stage coal liquefaction technologies.

Finally, in conjunction with the biological testing, detailed chemical analyses of the NTSL/ITSL process materials were conducted in an effort to understand the chemical basis for the observed biological activities. Although the chemical analyses were performed as a component of the biological assessment portion of these studies, the detailed chemical data provide valuable insights into coal liquefaction chemistry from a process viewpoint. In depth discussions of the process engineering and sample properties are also presented in an effort to correlate the biological and chemical data with process aspects. Again, comparisons of the chemical data from these studies with similar data from other investigations are made so as to qualitatively and quantitatively describe the chemical similarities and differences of the NTSL/ITSL process materials with other direct coal liquefaction materials. Chemical and biological comparisons made between the Wilsonville NTSL/ITSL and the Lummus ITSL process materials studied at PNL provide insights concerning effects of scaling-up the ITSL process from PDU to pilot plant level.

In general, the NTSL/ITSL process materials from the Wilsonville pilot plant were more complex than samples previously analyzed from other coal liquefaction technologies and had a wider range of isomeric polycyclic aromatic compounds (PAC), with high levels of alkylation and hydro-substitution. Furthermore, the particular ITSL process materials tested were less biologically active in the mutagenicity and tumorigenicity assays than, but were of comparable acute toxicity in the aquatic assay with, other direct coal liquefaction materials with similar boiling-point ranges and physical properties.

ENGINEERING

The two-stage liquefaction (TSL) pilot plant at the Advanced Coal Liquefaction Research and Development (R&D) Facility in Wilsonville, AL can be divided into three major process units: 1) the original solvent refined coal (SRC) thermal reactor, which in the integrated two-stage liquefaction (ITSL) operation mode is used as a short contact time (SCT) reactor; 2) the proprietary Kerr-McGee Critical Solvent Deashing (CSD) process unit utilized for efficient solids separation; and 3) an H-Oil[®] ebullated-bed hydrotreater (HTR) used as the second-stage liquefaction reactor for product upgrading by catalytic hydrogenation. The Wilsonville facility is a pilot-scale plant and was designed to process 200 to 400 lb of coal per hour.

Since successful start-up of the HTR unit in May 1981, investigations have primarily focused on testing various process integration options by selective recycle of streams among the three units. Two basic TSL configuration modes of operation that evolved from these studies have been investigated in depth, from both process and conversion perspectives. Figure 1 is a simplified block diagram that illustrates both the ITSL and nonintegrated two-stage liquefaction (NTSL) operational modes. In the NTSL mode, the SRC and catalytic HTR units are decoupled, and the SRC unit distillate solvent and HTR unit hydrotreated solvent are recycled within their respective units. In the ITSL mode, a heavy-end recycle pasting solvent is taken from the high-pressure flash separator after the second-stage HTR unit, recycled to the first stage and used as a solvent for coal slurring, the first-stage distillate process solvent is blended with the CSD deashed SRC product and used as feed for the hydrogenation unit.

NTSL MODE

A schematic of the NTSL operational mode is shown in Figure 2. In this mode, the SRC, CSD, and HTR units were coupled sequentially without recycle of any HTR stream to the SRC unit or feed coal slurry mix tank. Coal was crushed (feed rate: ~400 lb/hr moisture free; MF), slurried in distillate solvent from the SRC unit, mixed with preheated hydrogen, and introduced into the first-stage reaction vessel. The SRC unit, as operated in the NTSL mode, con-

FIGURE 1. Schematic Diagram of the ITSL and NTSL Processes. The dashed lines represent the NTSL recycle modes, whereas the solid line below the dashed lines represents the ITSL recycle mode. KEY: A = ITSL recycle solvent; B = deashed SRC product; C = HTR feed, blend of SRC and/or HTR products; D = HTR distillation vacuum bottoms

FIGURE 2. Detailed Schematic of Run 241, NTSL Mode.

sisted of a slurry preheater and a dissolver unit. Typical residence times in the SRC dissolver were 30 to 40 minutes, at a nominal reactor operating temperature of 805°F at the outlet of the dissolver unit. The product of the SRC reactor was a solvent refined coal, which was passed through a pressure separator to remove C₁-C₅ product gas. The <450°F material from the pressure separator was fractionated in an atmospheric pressure column (T-104); the >450°F portion of the SRC product was vacuum distilled (T-102). The distillate fractionation steps were integrated and produced a naphtha (T-104 overheads; C₅-450°F) and a first-stage product distillate (T-102; Tray 3) as well as a distillate process solvent (T-102; Tray 8) which was recycled to slurry incoming coal. The SRC product, with ash content, was fed to the CSD for deashing.

After the CSD step, the SRC product was blended in approximately a 1:1 proportion with a second-stage process solvent in the HTR feed blend tank. The SRC/hydrogenated process solvent mixture was next fed into the HTR unit, where it was catalytically reacted with hydrogen at a nominal operating temperature of 780°F. Following the second-stage reaction, the product was fractionated in two steps. First, a high-pressure separator was used to flash off C₁-C₅ product gas. Vacuum bottoms, which constitute the second-stage solid product, were also obtained in this step and drummed for storage. Next, the remaining material was subjected to atmospheric fractionation (T-105), from which an HTR naphtha and distillate bottoms HTR product were recovered. The T-105 distillation column bottoms were recycled to the HTR feed blend tank and used as the process solvent for the HTR unit. The HTR process solvent was blended with the deashed SRC to make feed for the HTR unit. The HTR naphtha or light fuel oil product was tanked and stored. Table 1 summarizes the more important process parameters for Run 241 during the period in which samples were collected for chemical and biological studies. Sample collection points are shown in Figure 2.

ITSL MODE

Several features described for the NTSL mode are similar for the ITSL mode. However unlike the NTSL mode, the two liquefaction stages in the ITSL mode are integrally coupled by recycling process solvent from the second-stage HTR unit to the first-stage coal slurry step. A process schematic for the

TABLE 1. NTSL Nominal Operating Conditions

Parameter	Conditions
<u>SRC-HTR</u>	
Severity combination	LS-LS ^a
<u>THERMAL SRC STAGE</u>	
Soaking factor ^b	0.5
Reactor temperatures (°F)	805
Reactor pressure (psig)	2400
Coal space rate (lb/hr ft ³)	20
Process solvent-to-coal ratio	1.6/1
LTR recycle (lb/lb MF coal) ^c	0.5
<u>CATALYTIC HTR STAGE</u>	
Reactor temperature (°F)	780
Space velocity (lb feed/hr-lb cat)	1.2
Thermal resid in feed (wt %)	50
Catalyst type	Armak/Ketjen (Ni-Mo)

^aLS = low severity

^bThe soaking factor is used to relate reactor temperature, pressure, and space velocity operating parameters to extent of reaction in the thermal stage soaking factor (below; see Rao, Lee et al., 1983 and Rao, Pillai et al., 1983 for a more complete explanation of this term).

Soaking Factor =

$$(1.85 \times 10^{11}) \left(\frac{\text{Pressure}}{1,715} \right)^{0.488} \left(\frac{1}{\text{Space Velocity}} \right) \exp \left(\frac{-30,000}{\text{Temperature}} \right)$$

^cLTR = light thermal resid

ITSL mode is shown in Figure 3. Crushed feed coal (200-mesh) was slurried in the mixing tank with a hydrotreated process solvent recycled from the HTR unit. The blend ratio of solvent to coal was 1.8:1. The mixture was then heated in a slurry preheater and pumped to the SRC thermal reactor, which was operated in the SCT mode by bypassing the dissolver portion of the SRC unit and using only the slurry preheater operated at a nominal outlet temperature of 860°F. Residence time in the first-stage reactor was thus reduced to approximately 6 to 10 minutes.

The resulting SRC product was fractionated by pressure flash separation and atmospheric and vacuum distillation in the same manner as the NTSL-mode SRC product. However, instead of recycling the heavy SRC distillate process solvent to the front end of the process for coal slurry, it was sent directly to the HTR feed blend tank and mixed with the deashed SRC product from the CSD in approximately 1:1 proportions. As in the NTSL mode, a C₁-C₅ product gas and naphtha (T-104 overheads; C₅-450°F) were obtained from the SRC reactor distillation units. However, during "lined-out" ITSL operation, very little first-stage product distillate (Tray 3, T-102) was produced and drawn off. The SRC product was deashed in the CSD unit, as in the NTSL mode, and sent to the second stage as HTR feed.

Hydrogen was added to the HTR feed, which was a mixture of deashed SRC product and SRC distillate process solvent, and passed through the catalytic HTR unit. During the course of Run 242, several HTR reactor temperatures were evaluated, during "lined-out" operating periods, including 680°F, 700°F, 720°F, and 740-750°F. Residence times in the HTR unit were typically 1 to 2 hours. Other key operating parameters are listed in Table 2. The hydrotreated product was prefractionated by a two-stage flash separator. The high-pressure bottoms stream from this two-stage flash separator was recycled to the coal slurry tank via a process solvent blend tank and used as the recycle pasting solvent for the overall integrated process. The vacuum flash bottoms, which constitute the second-stage solid product, were drummed for storage. A C₁-C₅ product gas was also obtained from the flash separation. The intermediate boiling range material was fractionated on an atmospheric column to yield an HTR naphtha (<450°F) and HTR distillate bottoms product (>450°F). In the ITSL mode, the T-105 tower bottoms were recycled to the tower feed tank due to

FIGURE 3. Detailed Schematic of Run 242, ITSL Mode.

TABLE 2. ITSL Nominal Operating Conditions

Parameter	Conditions
SRC stage severity	SCT
<u>THERMAL SRC STAGE</u>	
Dissolver used (%)	0
Reactor outlet temperature (°F)	860 ^a
Inlet hydrogen partial pressure (psi)	2,040
Process solvent-to-coal ratio	1.8/1
Coal space velocity [lb/hr-ft ³ (+ 700°F)]	91 ^b
<u>CATALYTIC HTR STAGE</u>	
Reactor temperature (°F)	720
Inlet hydrogen partial pressure (psi)	2,600
Space velocity (lb feed/hr-lb cat)	1.0
Resid in feed (wt %)	55
Catalyst type	Shell 324M Ni-Mo

^aHeater outlet

^bBased on preheater volume above 700°F

the low feed rates from the catalytic HTR unit flash separator. Sample points for the ITSL process are shown in Figure 3.

NTSL/ITSL: OBJECTIVES AND PERFORMANCE COMPARISONS

The product slate objective for the NTSL process mode was a low-sulfur oil suitable for use as a substitute for petroleum-derived utility fuel oil. Such fuel oil is prepared by blending distillates with hydrotreated resids, thus, resid production is required. However, for the ITSL operational configuration, an "all-distillable" product slate with a minimum production of resids was sought. Table 3 (from Rao, Lee et al., 1983; Rao, Pillai et al., 1983) summarizes the product composition, hydrogen efficiency, and energy rejection for the two process modes.

Higher distillate yields with lower resid and gas make were observed in the ITSL as compared with the NTSL mode; this was consistent with the product slate objectives. Although hydrogen consumption was higher in the ITSL versus the NTSL mode, it appeared to be more efficiently used to form distillable products.

Materials were sampled from both the NTSL and ITSL operational modes at points representative of intermediate- and end-product process streams. The qualitative properties of these sample materials further emphasize the differences between these two direct coal liquefaction processes and will be discussed in detail in the the next section.

TABLE 3. NTSL and ITSL Product Yield Structure

Run	NTSL 241	ITSL 242
Yield (% moisture/ash free [MAF] coal) ^a		
C ₁ -C ₅ gases	9%	6%
Distillates	38%	55%
Resid	23%	5%
Hydrogen consumption	-4.2	-4.9
Hydrogen efficiency		
1b dist/1b H ₂ consumed	9.0	11.0
Energy content of feed coal		
rejected to ash concentrate (%)	20%	23-27%

^aElementally balanced yield structure

PRODUCT COMPOSITION AND SAMPLE MATERIALS

NTSL and ITSL samples were collected during Runs 241 and 242 at the Wilsonville R&D Facility for combined toxicologic and chemical analyses. Sample suites collected are listed in Table 4 along with sampling dates, sampling points, and PNL repository numbers. A single set of samples was collected during "lined-out" operation in the NTSL mode. Several sample sets were collected during the various product work-up periods of Run 242. Sample sets collected during that run correspond to a start-up period and four major subsequent lined-out periods when the temperature of the catalytic HTR unit was incrementally increased, operating at 680°F, 700°F, 720°F and 740-750°F. Additionally, a sample suite was collected during the HTR unit temperature transition period from 700°F to 720°F to investigate the possible effects on product quality during nonequilibrium operating periods.

Samples were collected on site by Catalytic, Inc. personnel. PNL staff assisted in most of the sampling activities. Duplicate 1-L volumes were collected in glass bottles from the designated sample points (Table 4), allowed to cool, blanketed under nitrogen, labeled with Catalytic Inc. sample numbers, individually wrapped in aluminum foil, and placed in a 55-gal drum filled with zeolite packing/adsorbent for shipment by courier service. Samples for the start-up and 680° operational periods, as well as selected other samples, were collected by Catalytic, Inc. in metal containers as grab samples and were later subsampled for PNL. At PNL, each sample was checked for shipping damage, assigned a PNL repository number and immediately placed in cold storage at 4°C.

The sampling points from which NTSL/ITSL process materials were collected are shown in previous Figures 2 and 3. Basically, 10 types of samples were collected; a brief description is given for each in Table 5. Some samples were unique to each operational mode; for example, HTR vacuum flash bottoms were collected in the NTSL mode but not in the ITSL mode. However, a recycle pasting solvent was collected in the ITSL mode. The vacuum bottoms, tanked and stored in the NTSL mode, served as the process solvent in the ITSL mode.

TABLE 4. Information for NTSL and ITSL Samples Used in the Combined Chemistry/Toxicology Studies

Sample Description	NTSL #241	ITSL	
		#242-Start Up	#242-680 ^a
T-104 Overheads; SRC liquid product; light fuel oil/naphtha	SAMP: 09-22-82 RECD: 10-05-82 #5226-018	SAMP: 11-29-82 RECD: 02-08-83 #5226-073	SAMP: 12-13-82 RECD: 01-26-83 #5226-076
T-102 Tray 8; SRC product; SRC distillate process solvent		SAMP: 11-29-82 RECD: 02-08-83 #5226-072	SAMP: 12-13-82 RECD: 01-26-83 #5226-077
T-102 Tray 3; SRC product; 1st-stage product distillate	SAMP: 09-22-82 RECD: 10-05-82 #5226-019		SAMP: 12-13-82 RECD: 01-26-83 #5226-078
CSD product; deashed SRC, feed to HTR	SAMP: 09-22-82 RECD: 10-05-82 #5226-020	SAMP: 11-29-82 RECD: 02-08-83 #5226-074	SAMP: 12-13-82 RECD: 01-26-83 #5226-080
CSD product; ash concentrate	SAMP: 09-22-82 RECD: 10-05-82 #5226-025	SAMP: 11-29-82 RECD: 02-08-83 #5226-075	SAMP: 12-13-82 RECD: 01-26-83 #5226-079
V-1064; HTR feed; blend of SRC products	SAMP: 09-22-82 RECD: 10-05-82 #5226-021	SAMP: 11-29-82 RECD: 02-08-83 #5226-098	SAMP: 12-13-82 RECD: 01-26-83 #5226-081
T-105 overheads; HTR liquid product; light fuel oil/naphtha	SAMP: 09-22-82 RECD: 10-05-82 #5226-023		
T-105 bottoms; HTR product; distillation col-bottoms	SAMP: 09-20-82 RECD: 10-05-82 PS for TSL #5226-022		
V-1082; HTR product; vacuum flash bottoms	SAMP: 09-22-82 RECD: 10-05-82 #5226-024		
V-1067; recycle pasting Solvent (from HTR unit)	Not applicable	SAMP: 11-29-82 RECD: 02-08-83 #5226-071	SAMP: 12-13-82 RECD: 01-26-83 #5226-082

^aCatalytic HTR operation temperature, °F

TABLE 4. (continued)

Sample Description	ITSL		
	#242-700 ^a	#242-720 ^a A	#242-720 ^a B ^b
T-104 Overheads; SRC liquid product; light fuel oil/naphtha	SAMP: 12-16-82 RECD: 03-15-83 #5226-100	SAMP: 12-20-82 RECD: 01-05-83 #5226-048	SAMP: 01-06-83 RECD: 01-26-83 #5226-055
T-102 Tray 8; SRC product; SRC distillate process solvent	SAMP: 12-16-82 RECD: 03-15-83 #5226-101	SAMP: 12-20-82 RECD: 01-05-83 #5226-049	SAMP: 01-06-83 RECD: 01-26-83 #5226-056
T-102 Tray 3; SRC product; 1st-stage product distillate			SAMP: 01-06-83 RECD: 01-26-83 #5226-057
CSD product; deashed SRC, feed to HTR	SAMP: 12-16-83 RECD: 03-15-83 #5226-102	SAMP: 12-20-82 RECD: 01-05-83 #5226-050	SAMP: 01-06-83 RECD: 01-26-83 #5226-063
CSD product; ash concentrate	SAMP: 12-16-82 RECD: 03-15-83 #5226-104		SAMP: 01-06-83 RECD: 01-26-83 #5226-060
V-1064; HTR feed; blend of SRC products	SAMP: 12-16-82 RECD: 03-15-83 #5226-103	SAMP: 12-20-82 RECD: 01-05-83 #5226-053	SAMP: 01-06-83 RECD: 01-26-83 #5226-061
T-105 overheads; HTR liquid product; light fuel oil/naphtha	SAMP: 12-16-82	SAMP: 12-20-82 RECD: 01-05-83 #5226-051	SAMP: 01-06-83 RECD: 01-26-83 #5226-062
T-105 bottoms; HTR product; distillation col-bottoms	SAMP: 12-16-82	SAMP: 12-20-82 RECD: 01-05-83 #5226-052	SAMP: 01-06-83 RECD: 01-26-83 #5226-059
V-1082; HTR product; vacuum flash bottoms			
V-1067; recycle pasting Solvent (from HTR unit)	SAMP: 12-16-82 RECD: 03-15-82 #5226-105	SAMP: 12-20-82 RECD: 01-05-83 #5226-054	SAMP: 01-06-83 RECD: 01-26-83 #5226-058

^aSamples collected during the initial 8 hours of HTR reactor temperature change from 700^a to 720°C = dynamic sample set

^bSamples collected during "lined-out" condition, with HTR reactor at 720°C

TABLE 4. (continued)

Sample Description	ITSL #242-740°
T-104 Overheads; SRC liquid product; light fuel oil/naphtha	SAMP: 01-10-83 RECD: 02-08-83 #5226-064
T-102 Tray 8; SRC product; SRC distillate process solvent	SAMP: 01-10-83 RECD: 02-08-83 #5226-065
T-102 Tray 3; SRC product; 1st-stage product distillate	SAMP: 01-10-83 RECD: 02-08-83 #5226-066
CSD product; deashed SRC, feed to HTR	SAMP: 01-10-83 RECD: 02-08-83 #5226-067
CSD product; ash concentrate	SAMP: 01-10-83 RECD: 02-08-83 #5226-070
V-1064; HTR feed; blend of SRC products	SAMP: 01-10-83 RECD: 02-08-83 #5226-068
T-105 overheads; HTR liquid product; light fuel oil/naphtha	SAMP: 01-10-83 RECD: 02-08-83 #5226-069
T-105 bottoms; HTR product; distillation col-bottoms	SAMP: 01-10-83 RECD: 02-08-83 #5226-069
V-1082; HTR product; vacuum flash bottoms	
V-1067; recycle pasting Solvent (from HTR unit)	

TABLE 5. Sample Description for NTSL/ITSL Process Materials

Number	Sample Point	Process Unit	Sample Description	Nominal Boiling Range
1	T-104 overheads	SRC	Naphtha or light fuel oil	C ₅ - 450°F
2	T-102 Tray 3	SRC	1st-stage product distillate (slightly heavier than T-104 naphtha)	200 - 450°F
3	T-102 Tray 8	SRC	SRC distillate process solvent	450 - 1000°F
4	Deashed SRC holding tank	CSD	Deashed SRC product	450 - 1000°F
5	Ash concentrate receiver	CSD	CSD ash concentrate	Ash/mineral matter
6	V-1064 (HTR blend tank)	HTR	HTR feed; blend of SRC products	450 - 1000°F
7	T-105 overheads	HTR	Naphtha or light fuel oil	C ₅ - 850°F
8	T-105 bottoms	HTR	Distillation column bottoms	450 - 850°F
9	V-1082	HTR	Vacuum flash bottoms	650°F+/solid resids
10	V-1067	HTR	HTR process solvent or recycle	650°F+/solid resids

In general, the NTSL/ITSL sample sets can be divided into two subgroups: products from the SRC unit and those from the HTR unit. The SRC products included an overhead or naphtha sample (<450°F), a first-stage product distillate, an SRC distillate solvent, and a deashed SRC product used as HTR feed. A CSD ash concentrate sample was also taken during operation in both the NTSL and ITSL modes. Product structure summaries for the SRC unit (Catalytic, Inc., 1983a, b) are given in Table 6 for NTSL Run 241 and Table 7 for ITSL Run 242. In general, the SRC unit product distribution was ~50% SRC product sent to the CSD and ~50% other products. Roughly 10% of the feed coal remained unconverted.

The HTR products included an overhead or naphtha material (<450°F), a distillation column bottoms (>450°F), the vacuum flash bottoms (second-stage solid products, hydrotreated solids) for the NTSL run and a recycle pasting solvent for the ITSL run. Compositional summaries for the HTR products during the PNL sampling periods for NTSL Run 241 and ITSL Run 242 are shown in Tables 8 and 9, respectively (Catalytic, Inc., 1983a,b). Yields and product slates were within the desired ranges for both NTSL and ITSL operating modes. Table 10 provides further details on the operating conditions, product yields, and conversion parameters during the NTSL/ITSL sampling periods.

Illinois No. 6 coal from the Burning Star mine was used as feed during the sample collection periods and throughout Runs 241 and 242. Table 11 presents detailed analysis data on the chemical composition of the feed coal. No significant changes were reported in the feed coal properties during either run (Catalytic, Inc., 1983a,b).

Nominal boiling ranges of the NTSL/ITSL process materials collected are presented in Table 5. Tables 12 through 14 provide more detailed boiling point information on the product composition of key samples. In the NTSL mode, distillate products from the two stages were split into two fractions, with an approximate cut-point of 450°F. The <450°F distillate product fractions were a mixture of naphtha and first-stage product distillate (Tray 3, T-102), and the >450°F fractions were used as distillate process solvents within the respective stages. The 450°F cut-point distillate products and process solvents were separated in the T-102 and T-104 solvent recovery col-

TABLE 6. Estimated Performance and Stability Data for the SRC Unit During NTSL Run 241 (Catalytic, Inc., 1983a)

Date (1982)	Estimated Daily Performance, % MAF Coal								Total Yield
	Hydrogen Consumption ^a	H ₂ O	Gas ^b	Naphtha	1st-Stage Product Distillate	Distillate Solvent	SRC	UC ^c	
September									
1	-1.9	6.8	11.4	3.9	4.3	17.4	51.1	7.2	100.3
2	-1.9	7.2	10.9	4.2	3.6	15.1	52.3	7.1	98.5
11	-1.9	7.0	11.3	3.6	3.7	8.1	56.1	8.1	96.2
12	-1.9	6.2	12.5	4.2	3.9	17.4	48.6	8.3	99.2
13	-1.9	5.3	12.8	4.9	3.7	15.0	51.6	9.2	100.6
14	-1.8	6.4	12.4	4.3	3.3	18.3	48.2	8.3	99.3
15	-1.8	6.9	11.6	4.5	2.7	10.5	58.9	7.9	101.2
16	-1.9	6.7	12.5	4.3	3.1	19.1	49.0	7.6	100.4
17	-1.9	6.0	12.9	5.6	4.3	6.7	57.4	7.7	98.5
18	-1.9	6.1	12.7	4.9	4.4	14.1	51.8	9.2	101.4
19	-1.9	5.6	14.1	5.9	5.2	11.4	50.6	7.4	98.2
20	-1.9	5.8	12.3	3.9	4.4	11.4	50.5	10.9	97.3
21	-1.9	6.5	12.0	4.3	3.8	14.1	50.3	8.5	97.7
22	-1.9	6.4	12.4	3.0	4.6	11.5	54.6	6.8	97.6
23	-1.9	6.3	11.5	3.9	2.7	13.0	54.8	7.0	97.3
24	-1.8	6.4	13.5	4.7	3.9	12.4	53.2	7.6	99.9
25	-1.8	6.2	12.9	4.3	3.5	11.3	54.2	7.4	98.0
26	-2.0	5.9	12.9	4.7	4.4	10.7	54.7	7.8	99.2
27	-1.9	6.6	11.3	3.9	4.2	13.0	53.6	8.1	98.7
28	-1.9	6.1	11.7	4.0	3.3	15.5	53.8	7.9	100.5
29	-1.9	6.5	12.0	3.9	2.8	12.0	49.4	7.0	91.5
30	-1.9	6.8	11.2	3.7	2.5	13.5	57.9	7.5	101.1

^aCalculated using the ethylene injection method. Hydrogen leaks to the atmosphere, 1.5 lb/hr, were corrected.

^bProduct gas losses to the atmosphere, 4 lb/hr, were corrected.

^cUnconverted coal

TABLE 7. Estimated Performance and Stability Data for the SRC Unit During ITSL Run 242 (Catalytic, Inc., 1983b)

Date	Estimated Daily Performance, % MAF Coal								Total Yield
	Hydrogen Consumption ^a	H ₂ O	Gas	Naphtha	1st-Stage Product Distillate	Distillate Solvent	SRC	UC ^b	
November									
23	-0.5	4.1	2.5	1.3	1.1	19.2	57.0	18.0	102.7
27	-0.6	4.5	4.2	2.2	1.1	13.8	63.5	10.3	99.0
29	-0.8	5.3	4.3	3.4	2.0	15.8	48.6	12.7	91.4
30	-0.9	6.1	4.1	3.3	3.5	18.4	59.6	10.3	104.4
December									
1	-0.9	5.8	4.8	5.1	5.5	4.2	66.3	10.0	100.7
3	-0.3	5.8	6.8	7.0	8.8	17.0	53.1	10.2	108.9
6	-0.5	5.3	6.7	5.2	2.6	12.2	58.8	8.4	98.8
8	-0.4	5.3	6.3	4.8	4.0	20.4	44.0	9.0	93.3
11	-0.4	7.2	6.6	3.2	4.6	12.2	51.4	6.9	91.9
14	-0.4	6.4	7.2	3.7	5.8	17.8	43.1	7.6	91.2
15	-0.4	5.5	7.5	2.3	5.3	12.7	50.5	7.1	90.6
16	-0.4	6.2	6.9	2.5	4.3	14.2	55.3	7.3	96.2
18	-0.5	4.4	6.5	3.6	5.0	15.7	51.0	6.3	92.0
19	-0.5	5.1	6.7	3.3	4.6	17.6	52.6	7.1	96.7
20	-0.3	5.8	6.3	3.7	5.3	20.8	44.3	6.9	92.8
21	-0.4	5.4	6.6	3.2	4.5	18.3	48.8	6.7	93.2
23	-0.3	4.8	7.7	3.5	4.2	15.2	49.5	6.5	91.1
25	-0.3	5.2	6.4	4.0	4.5	8.3	57.5	6.9	92.5
26	-0.4	4.8	7.5	3.9	5.1	18.3	56.5	5.3	101.0
28	-0.4	5.8	6.9	4.2	4.9	21.4	47.1	6.5	96.5
29	-0.4	5.1	7.0	3.1	3.7	15.1	54.3	6.8	94.7
31	-0.4	6.3	7.6	4.4	5.0	12.9	51.2	9.3	96.3

^aCalculated using the ethylene injection method^bUnconverted coal

TABLE 7. (continued)

Date	Estimated Daily Performance, % MAF Coal								Total Yield
	Hydrogen Consumption ^a	H ₂ O	Gas	Naphtha	1st-Stage Product Distillate	Distillate Solvent	SRC	UC ^b	
January									
2	-0.3	7.3	7.7	4.8	4.7	12.1	49.9	8.3	94.4
5	-0.3	4.8	7.3	3.4	5.1	12.6	55.6	7.6	96.1
6	-0.3	4.4	7.2	3.1	4.2	10.7	57.7	8.8	95.7
7	-0.4	4.5	6.8	2.8	3.4	14.3	56.6	6.2	94.2
8	-0.4	5.7	6.3	3.6	4.6	12.3	54.9	7.4	94.4
9	-0.4	5.7	6.2	3.6	4.5	12.5	55.9	10.3	98.4
10	-0.4	5.2	6.7	3.3	4.3	13.4	52.9	9.1	94.5
12	-0.4	4.4	7.0	4.0	4.2	13.4	47.6	10.2	90.5
13	-0.4	5.5	6.8	4.4	3.7	15.7	52.9	9.9	98.5
15	-0.4	5.1	7.0	3.0	3.6	10.1	54.4	9.1	91.9
17	-0.4	5.5	9.1	2.9	3.7	18.2	51.4	10.2	100.6
19	-0.5	4.6	5.5	1.1	1.2	15.6	61.9	11.9	101.4
21	-0.7	6.9	6.0	3.9	3.0	12.7	58.0	14.3	104.3

^aCalculated using the ethylene injection method^bUnconverted coal

TABLE 8. Estimated Performance and Stability Data for the HTR Unit During NTSL Run 241 (Catalytic, Inc., 1983a)

Date	Total Out/ In, %	Solvent- Free SRC, lb/hr	Solvent in, lb/hr	Distillate Yield, % SRC by Fraction			HTR SRC		Sour Water, % SRC	C ₁ -C ₅ Gas, % SRC	Hydrogen Consump- tion ^a % SRC	Flare Knockout Liquids, % SRC
				<350	350-450°F	>450°F	Solvent, % SRC	SRC, % SRC				
Sept.												
1	100	135	132	5.6	2.3	27.2	6.9	62.7	2.3	2.3	4.6	4.4
2	98	146	144	8.6	3.0	29.0	4.9	49.3	2.6	2.2	4.5	5.3
11	100	158	160	2.3	5.8	21.7	4.2	58.2	6.8	6.8	3.9	4.1
12	102	139	147	8.0	3.7	17.6	4.1	55.9	8.9	7.8	4.0	5.4
13	104	127	135	7.4	3.9	33.3	3.0	55.1	9.0	8.5	4.5	6.4
14	100	139	148	6.1	2.4	24.2	3.9	52.1	7.3	7.0	4.7	4.7
15	101	133	136	8.3	2.9	32.4	3.4	56.2	5.5	5.9	4.6(4.1)	7.1
16	102	136	134	8.2	3.0	31.2	1.3	58.3	8.6	5.7	4.5	6.3
17	103	142	141	8.9	4.4	25.3	3.6	59.0	9.1	5.2	4.4	7.7
18	102	165	167	8.0	3.2	19.2	4.3	56.8	8.3	5.9	3.9	6.4
19	103	163	170	12.1	3.6	16.6	4.1	57.9	8.5	6.0	3.9	5.5
20	103	149	150	7.8	2.7	25.0	5.2	54.9	9.0	7.4	4.2	7.6
21	100	144	144	8.1	5.4	26.8	4.6	54.2	2.1	7.7	4.1	8.7
22	100	142	140	8.7	3.5	25.0	5.4	56.0	3.1	5.0	4.2(3.7)	7.3
23	99	144	148	9.2	4.0	22.7	4.1	54.2	3.3	4.9	4.0	7.4
24	100	141	143	8.8	3.8	26.3	4.4	58.9	2.8	4.1	4.2	7.1
25	100	144	149	8.4	3.7	22.6	3.3	59.8	3.6	4.0	4.1	7.1
26	99	147	155	8.2	3.5	20.1	6.1	59.8	3.4	5.8	4.0	6.5
27	99	140	146	9.3	3.4	16.0	5.2	60.4	3.0	6.1	4.0	6.3
28	99	155	163	8.4	3.3	13.5	4.3	60.0	2.4	5.2	3.7	6.1
30	102	146	144	7.3	4.6	26.2	3.6	63.2	1.2	6.0	3.1	4.9

^aAs determined by make-up hydrogen meter less flare hydrogen (by ethylene injection). The values in parentheses were determined by elemental balance.

TABLE 9. Estimated Performance and Stability Data for the HTR Unit During ITSL Run 242 (Catalytic, Inc., 1983b)

Date	Total out/ in, %	Solvent- Free SRC, lb/hr	Solvent Input, lb/hr	Distillate Product % Feed SRC by Fraction			HTR SRC, % SRC	Sour Water, % SRC	C ₁₋₅ Gas, % SRC	Hydrogen Consump- tion, % SRC	Flare Knockout Liquids % SRC
				<350°F	350-450°F	>450°F					
December											
7	1.03	178	168	1.9	0.9	29.8	89.2	4.4	0.6	3.6	1.3
8	1.01	210	199	2.5	1.0	29.6	79.9	5.7	0.6	3.3	1.3
10	1.01	215	199	2.5	1.2	24.8	82.9	4.2	0.7	3.4	2.6
11	0.99	208	199	2.1	2.0	17.3	82.7	4.1	0.7	2.9	1.4
12	1.01	216	217	1.9	1.4	24.2	84.8	2.7	0.7	2.9	2.2
13	1.01	209	207	2.8	1.2	22.3	85.3	1.5	0.7	2.7	2.3
19	1.03	221	169	5.0	2.7	35.2	74.9	4.8	0.8	3.6	3.0
20	1.01	213	157	3.0	1.6	33.6	74.6	3.7	1.4	3.2	3.0
21	0.99	214	155	4.5	1.3	27.3	72.8	2.4	1.5	3.2	3.1
22	0.99	214	154	3.8	2.0	24.4	76.6	3.2	1.5	3.1	2.8
23	1.01	214	168	3.5	1.9	25.6	78.2	2.4	1.5	3.1	5.7
24	1.03	240	183	3.0	1.6	21.7	82.8	2.4	1.3	2.8	3.8
25	0.99	236	186	3.0	1.8	17.3	76.2	3.0	1.4	3.0	3.7
26	1.01	203	161	3.7	2.3	27.5	76.5	2.3	1.1	3.4	4.6
27	1.02	201	160	3.6	2.2	27.7	88.8	0.2	1.1	3.3	4.7
28	0.98	192	140	3.3	2.1	36.0	73.7	3.7	1.2	3.4	4.6
29	0.98	206	157	3.3	1.8	25.2	73.6	3.5	1.3	3.2	4.7
30	0.99	224	170	3.4	2.2	28.0	76.2	3.1	1.1	3.0	4.6
31	1.00	183	130	4.2	2.0	29.9	82.0	3.8	1.3	3.4	5.0

TABLE 9. (continued)

Date	Total out/ in, %	Solvent- Free SRC, lb/hr	Solvent Input, lb/hr	Distillate Product % Feed SRC by Fraction			HTR SRC, % SRC	Sour Water, % SRC	C ₁₋₅ Gas, % SRC	Hydrogen Consump- tion, % SRC	Flare Knockout Liquids % SRC
				<350°F	350-450°F	>450°F					
January											
1	1.00	236	176	3.3	2.1	26.0	79.9	3.0	1.2	2.8	3.6
2	1.02	207	151	3.3	1.4	28.7	82.8	3.2	1.4	3.2	5.3
3	0.98	224	160	3.0	1.2	17.2	83.8	1.4	1.1	3.0	3.9
4	1.01	212	169	4.4	2.4	23.6	78.5	2.5	1.3	3.1	4.4
5	1.01	210	148	3.3	2.0	34.5	77.5	2.4	1.2	2.9	4.2
6	1.01	216	144	2.9	2.1	35.0	79.7	2.3	1.0	3.0	2.3
8	1.01	232	174	4.6	2.8	30.3	75.1	3.1	2.2	3.5	1.6
9	1.02	229	172	4.9	2.7	32.1	70.9	4.4	2.2	3.4	1.5
10	1.00	212	160	5.2	2.7	31.2	69.8	3.5	2.6	3.5	1.5
11	1.02	213	159	5.1	2.5	34.3	69.5	4.3	2.6	3.3	1.8
12	1.01	204	154	7.0	2.6	26.9	72.3	2.9	2.3	---	1.6
14	1.01	224	172	4.7	2.1	26.5	75.0	1.7	2.3	---	1.5
15	1.02	224	172	3.5	1.7	30.6	73.9	3.0	2.3	---	1.6
16	0.97	248	193	3.0	1.5	19.1	69.8	3.2	1.9	---	1.6
17	0.99	222	170	4.9	2.8	23.8	73.7	3.0	2.2	2.8	2.4
18	1.01	206	163	4.3	2.2	25.9	74.8	2.4	2.3	2.9	2.3
19	1.00	173	135	4.7	2.5	29.4	68.9	2.5	4.0	2.9	3.0
20	1.01	193	151	4.1	2.0	29.5	75.7	3.3	1.8	3.1	1.6
21	0.99	198	158	5.6	2.9	19.3	71.6	1.7	1.8	3.3	2.8

TABLE 10. HTR Unit Operating Conditions and Yields

Date:	NTSL 241		ITSL 242		
	09/15/82	09/24/82	12/20/82	01/02/83	01/10/83
H/C atomic ratio:	1.44	1.43	1.35	1.36	1.37
<u>Fraction, wt%</u>					
<450°F	2.8	2.9	0.1	0.4	0.2
450-650°F	33.9	35.9	16.8	22.4	15.1
>650°F	63.3	61.2	83.1	77.2	68.7
<u>Activity, % THF Conversion</u>					
Kinetic test	72.7	68.6	71.5	72.1	68.7
Equilibrium test	80.7	78.2	86.9	83.7	83.6
<u>Operating Conditions</u>					
CSD SRC rate, lb/hr (% solvent)	140.4(3.2)	152.9(5.3)	247.3(12.0)	240.3(11.6)	246.5(14.4)
Feed rate, lb/hr	284	299	399	389	380
Concentration, wt% SRC	47.8	48.4	54.6	54.6	55.6
Recycle gas, Mscf/ton SRC	65.5	62.9	51.2	57.0	66.3
Hydrogen purity, mole %	73.2	74.8	90.3	90.3	86.5
Water injection rate, lb/lb feed	0.24	0.25	0.17	0.26	0.27
Seal oil, % SRC feed	1.4	1.3	0.8	0.9	0.9

TABLE 10. (continued)

Date:	NTSL 241		ITSL 242		
	09/15/82	09/24/82	12/20/82	01/02/83	01/10/83
<u>Reaction</u>					
Space velocity (lb feed/hr)/lb cat	1.14	1.20	0.99	0.98	0.99
Temperature, °F average	781	780	719	720	249
Hydrogen partial press., psi at inlet	2,220	2,250	2,601	2,597	2,509
Catalyst age, lb SRC/lb catalyst	260 ^a	387 ^a	248	441	546
<u>Results</u>					
SRC conversion, %	42.5	42.5	26.8	19.5	29.9
Hydrogen consumption, % feed SRC ^b	4.1(4.6) ^b	3.7(4.2)	3.1(2.9)	3.2(3.2)	3.1(3.2)
Sulfur, % of SRC product	0.27	0.37	0.24	0.33	0.32
<u>Yields, % of Feed SRC</u>					
<u>Gases</u>					
NH ₃ , H ₂ S	1.9	1.8	1.3	1.2	1.3
C ₁ -C ₅	5.8	5.8	1.3	1.2	1.3

^aIncludes 84 lb SRC/lb catalyst when temperature was less than 750°F

^bBy elemental balance; the values in parentheses are determined by make-up hydrogen meter less flare hydrogen

TABLE 10. (continued)

Date:	NTSL 241		12/20/82	ITSL 242	
	09/15/82	09/24/82		01/02/83	01/10/83
<u>Liquids</u>					
Water	4.3	4.4	4.4	4.3	2.6
Naphtha	8.0	8.5	3.0	3.2	5.2
1st-stage product distillate	2.7	3.6	1.7	2.1	2.7
Distillate solvent	23.9	22.1	18.0	10.5	19.1
<u>SRC (Solvent-Free)</u>					
Nondistillable oil	29.1	22.1	40.7	43.4	33.8
Asphaltenes	26.2	29.7	25.9	33.0	32.0
Preasphaltenes	2.2	5.6	6.7	4.0	4.1
Unreacted Coal	0.02	0.02	0.1	0	0.1
Ash	0.04	0.06	0.1	0.1	0.1

^aIncludes 84 lb SRC/lb catalyst when temperature was less than 750°F

^bBy elemental balance; the values in parentheses are determined by make-up hydrogen meter less flare hydrogen

TABLE 11. Feed Coal Analysis for NTSL Run 241 and ITSL Run 242 (from Catalytic, Inc., 1983a,b)

Illinois No. 6 Coal Burning Star Mine	NTSL		ITSL	
	09/15/82	09/24/82	12/20/82	01/10/83
<u>Proximate analyses, wt%</u>				
Volatile matter	39.52	34.95	36.02	35.63
Fixed carbon	47.87	51.07	50.51	50.81
Ash	10.90	10.97	10.49	10.65
Moisture	1.71	3.01	2.98	2.91
<u>Ultimate analysis, wt%</u>				
Carbon	68.29	68.20	68.67	66.87
Hydrogen	4.46	4.48	4.49	4.24
Nitrogen	1.18	1.41	1.02	1.34
			(1.41) ^a	(1.58) ^a
Sulfur	3.50	3.50	3.42	3.40
Chlorine	0.06	0.06	0.11	0.08
Ash	11.09	11.30	10.80	10.96
Oxygen (by difference)	11.42	11.05	11.49	13.11
H/C atomic ratio	0.78	0.79	0.78	0.76
Dry heating value, Btu/lb	12,724	12,325	12,668	12,508
<u>Sulfur forms, wt%^a</u>				
Pyritic	1.17	1.11	1.08	1.06
Sulfate	0.11	0.10	0.13	0.20
Sulfide	<0.01	<0.01	0.02	<0.01
Organic	2.15	2.14	2.28	2.05
<u>Mineral analysis, wt% (ignited basis)</u>				
Phos. pentoxide, P ₂ O ₅	0.06	0.05	0.06	0.13
Silica, SiO ₂	48.45	47.97	48.27	47.69
Ferric oxide, Fe ₂ O ₃	16.31	16.74	17.20	16.77
Alumina, Al ₂ O ₃	16.88	18.12	18.13	18.45
Titania, TiO ₂	0.93	0.98	0.80	0.91
Lime, CaO	7.44	6.96	6.26	6.03
Magnesia, MgO	0.97	0.97	0.59	0.82

^aData from Galbraith analyses

^bThirty minutes at 750°F; 2:1 solvent-to-coal ratio. The solvent is 25% tetralin and 75% 1-methylnaphthalene.

TABLE 11. (continued)

Illinois No. 6 Coal Burning Star Mine	NTSL		ITSL	
	09/15/82	09/24/82	12/20/82	01/10/83
Sulfur trioxide, SO_3	4.67	4.15	6.12	6.27
Potassium oxide, K_2O	1.88	1.95	2.23	2.49
Sodium oxide, Na_2O	0.66	0.85	0.60	0.63
Vanadium oxide, V_2O_5	0.04	0.06	0.05	0.05
Undetermined	1.71	1.20	----	----
<u>Trace metal analysis, ppm</u>				
Arsenic	2	2	2	2
Reactivity, % THF conversion (by the equilibrium test) ^b	80.4	77.3	73.2	74.8

^aData from Galbraith analyses

^bThirty minutes at 750°F; 2:1 solvent-to-coal ratio. The solvent is 25% tetralin and 75% 1-methylnaphthalene.

TABLE 12. Elemental and Boiling Point Product Analyses of the NTSL Process Materials (Catalytic, Inc., 1983a)

	09/15/82				09/24/82			
	Naphtha/ 1st-Stage Product Distillate		Distillate Process Solvent		Naphtha/ 1st-Stage Product Distillate		Distillate Process Solvent	
	SRC ^a	HTR ^b	SRC ^c	HTR ^d	SRC ^a	HTR ^b	SRC ^c	HTR ^d
<u>Elemental Analysis, Wt%</u>								
Carbon	82.0	85.70	83.43	87.21	82.60	86.70	85.98	87.90
Hydrogen	11.38	13.02	9.16	10.56	10.92	12.91	9.28	10.56
Nitrogen		0.06	1.93	0.26	0.39	0.06	0.50	0.46
Sulfur	0.42	0.03	0.29	0.01	0.85	0.02	0.26	0.04
Oxygen (by difference)		1.19	5.19	1.96	5.24	0.31	3.98	1.04
<u>GC Analysis</u>								
<u>Boiling Fraction, Wt%</u>								
(IBP, °F)	(70)	(70)	(368)	(381)	(83)	(83)	(365)	(385)
IBP-200°F	20.56	17.21	0	0	17.84	15.90	0	0
200-350°F	40.84	41.44	0.2	0.05	35.50	44.84	0.2	0.04
350-450°F	37.92	35.93	13.6	2.78	44.65	30.96	14.1	2.90
450-550°F	0.68	5.42	56.5	14.11	1.93	8.01	50.8	15.20
550-650°F	0	0	24.9	19.82	0.08	0.26	24.8	20.70
650°F-EP	0	0	4.8	63.24	0	0.03	10.1	61.16
(EP, °F)	(460)	(478)	(740)	(1008)	(466)	(531)	(773)	(949)
API gravity, degrees	35.0	49.0	10.4	13.8	33.6	42.1	11.7	13.2
Kjeldahl nitrogen, wt%	---	---	---	0.25	---	---	---	---
Sodium, ppm	---	---	---	<4	---	---	---	---
Titanium, ppm	---	---	---	<1	---	---	---	---

^aSample point: T-102, Tray 3; PNL#5226-019^bSample point: T-105, Overheads; PNL#5226-023^cSample point: T-102, Tray 8; PNL Sample: not collected^dSample point: T-105, Bottoms; PNL#5226-022

TABLE 13. Elemental and Boiling Point Product Analyses of the ITSL Process Materials (Catalytic, Inc., 1983b)

	12/20/82			01/10/82		
	SRC Unit		HTR Unit	SRC Unit		HTR Unit
	T-104 (OVHD)	T-102 (Tray 8)	T-105 (Feed)	T-104 (OVHD)	T-102 (Tray 8)	T-105 Feed
<u>Elemental Analysis, Wt%</u>						
Carbon	83.42	87.19	87.69	82.74	88.13	87.50
Hydrogen	11.36	9.64	12.18	11.26	9.65	12.23
Nitrogen	0.13	0.23	0.13	0.08	0.37	0.04
Sulfur	0.42(0.79)	0.19(0.26)	-(0.06)	0.36(0.77)	0.20(0.29)	0.04(0.024)
Oxygen (by difference)	4.67	2.75	---	5.56	1.65	0.19
<u>GC Analysis</u>						
<u>Boiling Fraction, Wt%</u>						
IBP, °F	68	464	97	70	460	97
IBP-200°F	14.7	---	3.9	16.1	---	4.6
200-350°F	23.5	---	12.9	24.4	---	10.4
350-450°F	54.5	---	9.0	51.7	0.3	8.2
450-550°F	7.3	9.0	23.6	7.8	7.3	20.2
550-650°F		16.9	27.0	---	14.6	22.1
650°F-EP		74.1	23.6	---	77.8	34.5
EP, °F	468	1001	864	476	1021	890
API gravity, degrees	31.9	9.4	25.2	33.0	8.5	24.7

TABLE 14. Product Analysis of the ITSL Process Solvents (Catalytic, Inc., 1983b)

	SRC Distillate Process Solvent SRC: T-102, Tray 8 PNL: 5226-056		ITSL Recycle Process Solvent HTR: V-1067 PNL: 5226-058	
	12/20/82	01/10/82	12/20/82	01/10/82
<u>Boiling Fractions, Wt%</u>				
IBP, °F	463.7	460.0	465.8	492.0
IBP-450°F	0	0.3	0.2	0.1
450-550°F	9.0	7.3	3.1	2.2
550-650°F	16.9	14.6	9.0	8.0
650°F-EP	71.1	74.8	43.0	47.1
Residual, >EP	3.0	3.0	44.7	42.6
EP, °F	1001.0	1021.0	991.5	958.0
Hydrogen, %	9.64	9.65	9.39(10.25) ^a	8.85(10.10)
Carbon, %	87.19	88.13	89.41(88.09)	89.41(88.38)
H/C atomic ratio	1.318	1.305	1.251(1.387)	1.179(1.362)
Specific gravity	1.004	1.011	1.116	---

^aThe values in parentheses are for the distillate portion of the sample (600°F at 0.1 mm Hg).

umns of the SRC unit and in the T-105 fractionation column of the HTR unit (see Figures 2 and 3). Table 12 gives a detailed boiling point breakdown of the <450°F and >450°F NTSL products from both the SRC and HTR stages. The naphtha and product distillates from both stages are composed of material boiling from 70-450°F (>99% of total material). The T-104 overheads (PNL# 5226-018) are of similar composition and quality. The distillate process solvents for the two stages are somewhat different. The SRC process solvent is a 350-740°F material, with ~95% of the product in the 350-650°F boiling point range. Conversely, ~60-70% of the HTR unit distillate product boils above 650°F. From the elemental analyses, the NTSL HTR distillate products have significantly lower oxygen, nitrogen and sulfur content than the same SRC unit NTSL materials and correspondingly higher H/C ratios. The HTR feed in the NTSL mode (PNL#5226-021) is a blend (approximately 1:1) of the deashed SRC product and the HTR >450°F fraction from distillation (T-105); therefore it has intermediate properties. In general, the HTR feed can be considered a 450-1000°F material.

As in the NTSL mode, distillate products and process solvents in the ITSL mode were also split into <450°F and >450°F fractions in both the first and second process stages. The separated sample materials were again taken from T-102, T-104 and T-105 fractionation columns (see Figure 3). Elemental analysis and boiling point distribution data for the SRC and HTR distillate products are shown in Table 13 for time periods corresponding to collection of PNL sample series 242-700°F, 242-720°F and 242-740°F. The SRC overheads are, again, a 70-450° material (PNL#5226-055; examples of sample numbers in this section are given only for Run 242-720°B. See Table 4 for other sample numbers). Approximately 75% of the SRC distillate process solvent (PNL#5226-056) was in the 650-1000°F boiling range. The HTR products collected were distilled materials that received their feed from the HTR unit flash separator. Distillation tower T-105 split the flash separator feed into column overheads, 100-450°F boiling point range (PNL#5226-062), and column bottoms, 450-850°F boiling point range (PNL#5226-059). Product analyses of the distillation column feed are shown in Table 13. Approximately 25% of the feed goes to overheads with 75% distillate column bottoms.

The flash separator bottoms stream from the HTR unit (see Figure 3) was the process solvent for the SRC unit during ITSL Run 242 operation. Approximately 50% of this stream consisted of hydrotreated SRC residue, with approximately 90% of the total material boiling above 650°F. When sufficient quantities of this process solvent were unavailable (mostly during start-up periods), it was supplemented with distillate process solvent from Tray 8 of the SRC unit T-102 distillation column. Additionally, SRC distillate process solvent was also blended with the deashed SRC product, in a 1:1 ratio, to make the HTR unit feed. The product analysis for these two process solvents is shown in Table 14 for the same time periods given in Table 13.

A comparison of the distillation properties and elemental compositions of the NTSL and ITSL process materials, as summarized in Tables 12 through 14, indicates a significant improvement in the quality of both the SRC and HTR products in the ITSL mode. In general, the heteroatom contents are lower and the H/C ratios are higher for the ITSL, as compared to NTSL, process materials. The improved quality of the ITSL materials is probably a direct result of integrated operation, in which a heavy-end hydrotreated process solvent was recycled from the HTR stage and used as the slurry and process solvent in the SRC stage, which was operated as an SCT reactor. Furthermore, hydrogen consumption in the first stage of the ITSL was reduced as compared to the NTSL mode (Catalytic, Inc., 1983b). This is probably attributable to the active hydroaromatic species in the ITSL hydrogenated process solvent which serve as hydrogen donors and shuttlers. The net result of these factors is a more efficient use of hydrogen in the ITSL process and higher quality intermediate- and end-products.

Several sample materials from other direct coal liquefaction processes were also used for comparative biological and chemical analyses. Such samples include SRC I, SRC II, EDS and Lummus ITSL materials. Descriptions of these sample materials have been provided in previous PNL Status Reports (Later et al., 1984; Mahlum, 1981; Weimer et al., 1980; Wilson et al., 1983). All NTSL and ITSL samples collected from the Wilsonville R&D facility, as well as other process materials used for comparisons, are research materials and should not be considered representative of direct coal liquefaction products that may eventually be produced on a commercial scale. In particular, samples selected

for analysis have boiling point ranges that differ significantly from those projected for products from a commercial facility.

METHODS AND BACKGROUND

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 determined 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 initiation/promotion (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

TABLE 15. Description of TSL Materials Used For Ecotoxicity Testing

Process Mode	Sample Point	PNL #	Nominal Boiling Point Range (°F)
NTSL	T-104 first-stage SRC overhead product	5226-018	C ₅ - 450°F
	T-105 second-stage HTR overhead product	5226-023	C ₅ - 450°F
ITSL	T-104 first-stage SRC overhead product	5226-055	C ₅ - 450°F
	T-105 second-stage HTR overhead product	5226-062	C ₅ - 450°F

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 (A₃; 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.

RESULTS AND DISCUSSION

BIOLOGICAL TESTING

Microbial Mutagenicity Assays

All crude sample materials collected by PNL from the Wilsonville R&D Facility during NTSL Run 241 and ITSL Run 242 (see Table 4) were assayed for microbial mutagenicity with S. typhimurium TA98. Table 17 provides the results of these assays. Overall, the NTSL process materials had higher mutagenic potencies than ITSL process materials taken from the same sampling location. The NTSL SRC (first-stage) and HTR (second-stage) light fuel oils and the SRC first-stage product distillate were either inactive or only slightly active in this microsomal test system. However, the other NTSL process materials from both the SRC and HTR units showed positive responses with TA98. The NTSL HTR feed, which was a blend of deashed SRC and process solvent from the HTR unit, was the most mutagenic crude tested, with an activity comparable to that of SRC I process solvent (Later et al., 1982).

The majority of ITSL process materials collected and tested for microbial mutagenicity were either inactive or only slightly active. Except for the deashed SRC product, none of the ITSL crudes were more mutagenic than their corresponding NTSL materials. As for the NTSL crudes, the naphthas and light fuel oils, as well as the first-stage product distillate from both the SRC and HTR units, were not significantly mutagenic in this assay. Almost no mutagenic activity was detected in the second-stage process material and products from the ITSL mode. Of the ITSL materials sampled during periods when the HTR unit was operated at various temperatures, the 680°F crudes from Run 242 were the most mutagenic.

Figure 6 shows the effect of HTR operating temperature on the microbial mutagenicity of the unfractionated deashed SRC product in the ITSL mode. From 680° up to 720°F, as the HTR unit temperature incrementally increased, the mutagenic activity of the deashed SRC product and HTR feed decreased. However, when the HTR unit temperature was increased from 720°F to 740°F, the

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.

FIGURE 6. Comparative Microbial Mutagenicity of the Deashed SRC Product at Different HTR Unit Operating Temperatures. (See Appendix A for dose-response raw data.)

activity of deashed SRC product increased (Figure 6). Furthermore, the analogous NTSL crude material from the period when the HTR unit was operated at 780°F had an activity of 4 rev/μg. This suggests that it may be possible to minimize the mutagenicity of some distillate products by properly selecting the operating conditions of the hydrotreater. However, this may affect the mutagenicity of other products not evaluated here. Similar observations were previously reported for the Lummus ITSL PDU samples; process materials produced during a thermal excursion of the catalytic HTR were more mutagenic in *S. typhimurium* TA98 than samples collected during normal operation (Wilson et al., 1981). The data presented in Table 17 and Figure 6 also indicate that it may be possible to minimize the net mutagenic hazard by adjusting conditions appropriately, but this would require a comprehensive study, specifically directed toward such a goal. Similar trends were also supported by the results obtained from bioassays conducted with chemical class fractions of the crude materials.

The NTSL crudes and two sets of ITSL crudes were class-fractionated by alumina adsorption column chromatography, and the chemical fractions were assayed for microbial mutagenicity. Mutagenic responses for the fractionated SRC and CSD unit process materials are shown in Table 18. Table 19 presents similar mutagenicity data for the alumina fractions of the HTR unit process materials. As with other direct coal liquefaction process materials tested in this laboratory, the most mutagenic class fraction of both the NTSL and ITSL process materials were the N-PAC isolates. In some cases, mutagenic activity was detected in the N-PAC isolates of inactive crudes (for example, the SRC unit light fuel oil; see Table 18). Significant levels of microbial mutagenicity were also detected in several hydroxy-PAH isolates, particularly in the NTSL deashed SRC product and HTR feed as well as in the NTSL vacuum flash bottoms. Appendix A contains complete sets of raw dose-response data used to calculate mutagenic potencies by linear regression analysis for materials shown in Tables 18 and 19.

The effect of HTR reactor temperature on the mutagenic activity previously discussed for the crudes was also observed for the N-PAC fractions of the HTR distillate column bottoms. When the HTR was operated at 780°F in the NTSL mode, the mutagenic activity of the N-PAC fraction was 65 rev/μg. The

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)					PNL #
		Aliphatic Hydrocarbons	PAH	N-PAC	Hydroxy-PAH	Crude	
Light fuel oil T-104 overheads	NTSL	0	0	0	0	0	5226-023
	ITSL-720 ^o B	0	0	11	0	2	5226-055
	ITSL-740 ^o	0	0	11	0	1	5226-064
SRC distillate Process solvent T-102, Tray 8	NTSL	--	--	--	--	--	--
	ITSL-720 ^o B	0	0	27	0	3	5226-056
	ITSL-740 ^o	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 ^o B	0	0	39	0	0	5226-057
	ITSL-740 ^o	--	--	--	--	--	--
Deashed SRC product HTR feed CSD unit	NTSL	0	<1	15	5	4	5226-020
	ITSL-720 ^o B	0	0	0	0	0	5226-063
	ITSL-740 ^o	0	0	0	0	5	5226-066 ^a
CSD ash Concentrate	NTSL	0	0	3	<1	3	5226-025 ^a
	ITSL-720 ^o B	0	0	0	0	3	5226-060
	ITSL-740 ^o	0	0	0	0	0	5226-067

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

TABLE 19. Microbial Mutagenicity of Chemical Class Fractions of the HTR Unit Process Materials (Second Stage)

Sample Description	Process Description	Mutagenic Response <i>S. typhimurium</i> TA98 (rev/μg)					PNL #
		Aliphatic Hydrocarbons	PAH	N-PAC	Hydroxy-PAH	Crude	
HTR feed	NTSL	0	0	6	2	9	5226-021 ^a
SRC blend	ITSL-720°B	0	0	0	0	0	5226-061
V-1064	ITSL-740°	0	0	0	0	0	5226-070
Light fuel oil T-105, overheads	NTSL	0	0	0	0	0	5226-023
	ITSL-720°B	0	0	--	0	0	5226-062
	ITSL-740°	0	0	0	0	0	5226-068
58 Distillate column Bottoms T-105, bottoms	NTSL	0	0	65	<1	6	5226-022
	ITSL-720°B	0	0	3	0	0	5226-059
	ITSL-740°	0	0	14	0	0	5226-069
Vacuum flash Bottoms V-1082	NTSL	0	0	3	3	3	5226-024 ^a
	ITSL-720°B	--	--	--	--	--	--
	ITSL-740°	--	--	--	--	--	--
Recycle pasting Solvent V-1067	NTSL	--	--	--	--	--	--
	ITSL-720°B	0	0	0	0	0	5226-058
	ITSL-740°	--	--	--	--	--	--

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

mutagenic response was reduced to 3 rev/ μ g for the 242-720°B (steady-state) ITSL N-PAC fraction. However, when the HTR temperature was increased in the ITSL mode to 740-750°F, the mutagenic activity of the same fraction of the distillate column bottoms increased to 14 rev/ μ g.

In previous work at this and other laboratories, it has been demonstrated that the amino-PAH are the determinant microbial mutagens in the N-PAC isolates of coal liquids (Later et al., 1982; Wilson et al., 1981). These data suggest that there is an optimal operating temperature for the HTR with regard to elimination of mutagenic amino-PAH from the product material.

Although the neutral PAH fractions isolated from the crude ITSL/NTSL process materials contained significant levels of mutagenic compounds such as benzo[a]pyrene, mutagenic responses for these fractions were not detected. Inactivity of neutral PAH fractions, using the standard plate incorporation microbial assay, have also been reported for coal liquefaction materials from other processes investigated in this laboratory (Mahlum, 1981; Wilson et al., 1983). The failure of mutagenic PAH constituents to be expressed in complex mixtures may be due to antagonistic matrix effects of other parent, alkylated and/or hydro-substituted PAH present in the fractions.

To determine the effects of hydrotreatment on mutagenic PAH, hydroaromatic derivatives of benzo[a]pyrene and two catalytically hydrogenated products of benzo[a]pyrene were assayed for microbial mutagenicity in S. typhimurium TA98. All compounds and hydrotreated compounds were assayed under identical experimental conditions and within the same time period. Table 20 provides the results of these mutagenicity assays.

The mild hydrogenate of benzo[a]pyrene had eight to ten major constituents, as determined by capillary column GC. From GC and GC/MS data, the most concentrated constituent in the mildly hydrotreated product was 4,5-dihydrobenzo[a]pyrene. Tetra-, hexa-, octa- and tetradecahydrobenzo[a]pyrene isomers were the other components of the mildly hydrogenated benzo[a]pyrene. The severely hydrogenated benzo[a]pyrene product was a complex mixture of hydroaromatic benzo[a]pyrene-derived compounds. An isomer of octahydrobenzo[a]pyrene was the most concentrated derivative specie, with many other isomers

TABLE 20. Microbial Mutagenicity of Benzo[a]pyrene and Selected Hydroaromatic Derivatives.

Compound	Dose Response (rev) ^a						Linear Response (rev/ μ g) ^b	Correlation Coefficient
	0.2 μ g	0.4 μ g	0.8 μ g	1.0 μ g	2.0 μ g	5.0 μ g		
Benzo[a]pyrene	74 $\pm$ 3	<u>96 $\pm$ 4</u>	<u>158 $\pm$ 3</u>	<u>204 $\pm$ 2</u>	<u>220 $\pm$ 19</u>	<u>243 $\pm$ 29</u>	158	0.99
4,5-Dihydrobenzo[a]pyrene	57 $\pm$ 2	51 $\pm$ 11	71 $\pm$ 4	<u>74 $\pm$ 5</u>	<u>104 $\pm$ 1</u>	<u>85 $\pm$ 23</u>	30	0.96
7,8,9,10-Tetrahydrobenzo[a]pyrene	53 $\pm$ 7	53 $\pm$ 4	63 $\pm$ 5	57 $\pm$ 13	<u>75 $\pm$ 4</u>	57 $\pm$ 1	15	0.87
Mildly hydrotreated ^c benzo[a]pyrene	33 $\pm$ 5	26 $\pm$ 4	50 $\pm$ 9	56 $\pm$ 3	63 $\pm$ 3	<u>76 $\pm$ 2</u>	9	0.73
	(2 μ g) ^e	(4 μ g)	(8 μ g)	(10 μ g)	(20 μ g)	(50 μ g)		
Severely hydrotreated ^d benzo[a]pyrene	45 $\pm$ 4	50 $\pm$ 7	61 $\pm$ 3	61 $\pm$ 11	<u>80 $\pm$ 10</u>	<u>83 $\pm$ 7</u>	2	0.99

^aTester strain was *S. typhimurium* TA98 with 100- μ l S9 enzyme activation medium. Solvent blank produced 41 $\pm$ 5 spontaneous revertants; underlined values were significant responses as determined by comparison with a negative historical control data base

^bLinear response reported was calculated with only those points in the linear portion of the dose-response curve

^cBenzo[a]pyrene (~200 mg) reacted in an autoclave at 80°C under 800 psi H₂ for 30 hr with a Pd/PtO₂ catalyst (100 mg 10% on carbon/60 mg) in 50 ml of cyclohexane solvent.

^dBenzo[a]pyrene (~200 mg) reacted in an autoclave at 350°C under 1500 psi H₂ for 24 hr with 250 mg of Co/Mo (on alumina) catalyst in 50 ml cyclohexane solvent.

^eDose for severely treated benzo[a]pyrene

of dihydro- through tetradecahydrobenzo[a]pyrene present. Furthermore, hydrogenation products resulting from excision and addition of methylene units were also observed in the severely hydrotreated sample. Residual benzo[a]pyrene was present following both mild and severe hydrogenation.

As shown in Table 20, a significant reduction in mutagenic potency was observed in this test system as hydro-substitution increased. Both the dihydro- and tetrahydro- derivative compounds showed a significant reduction in mutagenicity as compared to the fully aromatic parent benzo[a]pyrene. More than a 90% reduction in the mutagenic activity of benzo[a]pyrene was observed for the products from both the mild and severe catalytic hydrogenations. In general, these data show a significant reduction in the mutagenicity of the putative PAH mutagen benzo[a]pyrene upon hydrotreatment and/or hydro-substitution. Preliminary results will be presented and discussed in the next section for these same test compounds and for hydrotreated benzo[a]pyrene products in the I/P mouse skin tumorigenicity assay.

One goal of pilot plant ITSL Run 242 was to simulate the Lummus PDU ITSL operation. Table 21 compares the mutagenicity of selected crude process materials from the NTSL and ITSL pilot plant operating modes with results previously reported (Wilson et al., 1981) for similar process materials from the ITSL PDU facility. The NTSL and PDU ITSL materials were generally more mutagenic than those from the ITSL pilot plant. Comparing the NTSL and PDU ITSL materials, the HTR feeds appeared to be of equivalent activity. The PDU ITSL recycle process solvent was much more mutagenic than the corresponding NTSL material. Overall, the ITSL pilot plant crudes were the least mutagenic in this microsomal assay.

Finally, a comparative summary of process materials with fairly equivalent boiling point ranges from various direct coal liquefaction technologies is presented in Table 22. Those process materials from technologies that employ some form of catalytic hydrogenation (ITSL, NTSL, EDS) were less mutagenic than nonhydrotreated process materials (SRC I, SRC II), which were nearly equivalent in distillation temperature range. In general, the pilot plant ITSL crudes and chemical fractions were the least mutagenic of these materials, shown in Table 22.

TABLE 21. Comparative Microbial Mutagenicity of Selected Process Materials from Different TSL Operating Modes

Process Material Description	Mutagenic Response TA98 (rev/μg)		
	NTSL 241	ITSL 242 (720°B)	ITSL Lummus PDU ^a
SRC Product: Light fuel oil	0	2	--
SRC distillate process solvent	--	3	3 ^b
SRC Product: 1st-stage product distillate	0	0	--
Deashed SRC product	4	0	--
HTR feed	9	0	9 ^c
HTR Product: Light fuel oil	0	0	--
HTR Product: Distillation column bottoms	6	0	3 ^d
Recycle process solvent	5 ^e	0	18

^aMutagenicity data for ITSL Lummus PDU process materials are from PNL-4553 (Wilson et al., 1983).

^b8" BDU bottoms from SCT used as the equivalent PDU process material

^cLC finer feed used as the equivalent PDU process material

^dLC finer TLP used as the equivalent PDU process material

^eHTR vacuum flash bottoms used as the equivalent NTSL process material

TABLE 22. Comparative Microbial Mutagenicity of Different Direct Liquefaction Process Materials

Process Material Description	Boiling Point Range	Crude	Aliphatic Hydrocarbons	PAH	N-PAC	Hydroxy-PAH
NTSL Pilot Plant HTR vacuum flash bottoms	>650°F	5	0	0	5	2
HTR distillation column bottoms	450-850°F	6	0	0	65	<1
ITSL Lummus PDU ^a Recycle solvent	>650°F	18	0	<1	43	3
LC finer TLP	~400-850+°F	<1	0	0	0	0
ITSL Pilot Plant ^b Recycle process solvent	>650°F	0	0	0	0	0
HTR distillate column bottoms	450-850°F	0	0	0	3	0
SRC II heavy distillate	500-850°F	38	0	0	193	12
SRC I process solvent	450-850+°F	15	0	0	65	0
EDS bottoms recycle process solvent ^c	400-1000°F	2	0	0	40	0

^aData from PNL-4553 (Wilson et al., 1983)

^bData reported for Run 242-720°B

^cData from PNL-4960

I/P Tumorigenicity Assay

Representative first- and second-stage products from the NTSL and ITSL operating modes were tested for mouse skin tumor initiating activity in the I/P assay. The materials selected were the HTR feed and the HTR distillation column bottoms. In addition, a <650°F distillate of the ITSL TLP from the Lummus PDU was assayed for tumorigenicity. The results of these I/P assays are graphed in Figure 7 for the NTSL process materials and in Figure 8 for the three ITSL crudes tested. A summary of the tumor responses at sacrifice (200 days after initiation) for all five samples is given in Table 23.

The two NTSL process materials and the ITSL HTR feed had the highest activities when expressed either as incidence (percent of mice with tumors) or tumors per group. The ITSL HTR bottoms and the PDU <650°F distillate displayed approximately equivalent activity. This is particularly noteworthy since the pilot plant HTR bottoms had a higher nominal boiling point range (450-850°F; ~60% > 650°F) than the PDU process distillate. Thus, if tumor initiating activity is considered a measure of product quality, the pilot plant end-product with its lower toxicity seems to be of better quality than the bench-scale PDU <650°F TLP distillate.

In both the NTSL and ITSL modes, a significant reduction in tumorigenic activity resulted from second-stage catalytic hydrotreatment. For example, more than a 40% reduction in both incidence and total tumors was observed when comparing the first-stage ITSL HTR feed to the second-stage HTR distillate column bottoms. A much greater reduction in tumorigenicity was observed for process materials from the coupled or ITSL operating mode versus the non-coupled or NTSL operating mode, even though the HTR feed in both cases was of comparable activity. Presumably, this is due to the higher quality recycle process solvent used in the ITSL mode of operation, which results in more efficient hydrogen incorporation during both the first- and second-stage liquefaction processes. This hypothesis is supported by the observed higher H/C ratios of the ITSL versus the NTSL process materials, as explained in product composition and sample materials section.

FIGURE 7. Tumor Initiating Activity of NTSL HTR Feed and HTR Distillate Column Bottoms: (A) Percent Incidence and (B) Total Adjusted Tumors

FIGURE 8. Tumor Initiating Activity of Pilot Plant ITSL HTR Feed and HTR Distillate Column Bottoms and PDU ITSL <650°F Distillate of the TLP: (A) Percent Incidence and (B) Total Adjusted Tumors

TABLE 23. Summary of Tumor Initiating Activity of NTSL/ITSL Process Materials

Process Materials	PNL #	Percent Tumor Incidence	Total Adjusted Tumors
NTSL: HTR feed	5226-021	86	67
NTSL: HTR distillation column bottoms	5226-022	73	39
ITSL: HTR feed	5226-061	93	96
ITSL: HTR distillation column bottoms	5226-059	50	31
ITSL (PDU) TLP (<650°F)	3399-135	50	31
Controls	---	14	7

Table 24 provides comparative I/P assay data for process materials of nearly equivalent boiling point range from different direct coal liquefaction technologies. The least tumorigenic material in mouse skin was the pilot plant ITSL HTR product, with the analogous NTSL materials being next least active. The EDS pilot plant process material was more active than the ITSL pilot plant material, but less active than the SRC pilot plant materials. Materials produced in the absence of process hydrotreatment had higher potencies than similar materials processed with "on-line" catalytic hydrogenation. These data verify initial investigations, which showed that the biological activity of SRC II fuel oil blend was significantly reduced by mild and severe postproduction catalytic hydrogenation. It was also proposed, based upon these findings, that similar trends would be observed for coal liquefaction process materials produced by "on-line" hydrogenation techniques (Mahlum et al., 1983; Wilson et al., 1981).

Table 25 reports preliminary data for the I/P tumorigenic activity of benzo[a]pyrene, two hydrobenzo[a]pyrenes, and a complex mixture resulting from a mild hydrogenation of benzo[a]pyrene. As discussed in the microbial mutagenicity section, the mutagenicity and tumorigenicity assays have been conducted in an effort to elucidate the biologically related effects of catalytic hydrogenation on genotoxic agents found in coal liquefaction materials. A reduction in tumorigenic potency (Table 25) was observed that correlated with increased hydro-substitution. The 4,5-dihydrobenzo[a]pyrene possessed significant tumor initiating activity: approximately 80% of the activity of an equivalent dose of benzo[a]pyrene. However, the tumorigenicity of 7,8,9,10-tetrahydrobenzo[a]pyrene, as determined by percent incidence and tumor yield, was reduced 7-fold and 14-fold, respectively, as compared to the parent benzo[a]pyrene. The tumorigenic activity for equivalent doses of the mild hydrogenate of benzo[a]pyrene was intermediate in potency between the dihydro and tetrahydro isomers tested. Figure 9 is a gas chromatogram of this material; Table 26 provides the corresponding peak identifications and relative concentrations for the sample constituents, as determined by GC, GC/MS and NMR.

A reduction in the mutagenic and tumorigenic biological potency was observed in the bioassay data presented for benzo[a]pyrene and its hydroaromatic derivatives. Although other PAH compounds have not been as thoroughly inves-

TABLE 24. Comparative Tumor Initiating Activity of Selected Process Materials from Different Pilot Plant Direct Coal Liquefaction Technologies

Process Material	Boiling Point Range (°F)	Percent Tumor Incidence ^{a,b}	Number of Tumors per Mouse (±SE) ^b
NTSL HTR bottoms	450-850	73*	1.3 ± 1.2 [†]
ITSL HTR bottoms	450-850	50**	1.1 ± 1.4 [†]
EDS bottoms recycle process solvent	400-1000	73*	1.7 ± 1.6 ^{††}
SRC I process solvent	450-850+	83*	2.1 ± 1.3 ^{†††}
SRC II heavy distillate	500-850	92***	2.1 ± 1.5 ^{†††}

^aPercentage of mice with tumors produced with a 25-mg initiating dose of crude process material in a population of 30 mice.

^bValues that are not significantly different ($P < 0.05$) from each other have the same number of asterisks or daggers.

TABLE 25. I/P Tumorigenicity of Benzo[a]pyrene and Selected Hydroaromatic Derivatives^a

Compound	Initiating Dose (µg)	Percent Incidence	Total Tumors
Benzo[a]pyrene	25	70	43
4,5-Dihydrobenzo[a]pyrene	25 125	57 70	31 76
7,8,9,10-Tetrahydrobenzo[a]pyrene	25 125	10 3	3 1
Mildly hydrotreated benzo[a]pyrene ^b	125	47	22
Blank: Solvent control	--	3	1

^aPreliminary I/P data at 90 days after initiation of a 200-day study

^bBenzo[a]pyrene (~200 mg) reacted in an autoclave at 80°C under 800 psi H₂ for 30 hours with a Pd/PtO₂ catalyst (100 mg 10% on carbon/60 mg) in 50 ml of cyclohexane solvent.

FIGURE 9. Capillary Column Gas Chromatogram of the Mild Hydrogenate of Benzo-[a]pyrene. See Table 26 for peak identifications.

TABLE 26. Peak Identifications of Components in the Mild Hydrogenate of Benzo[a]pyrene

Peak Number	Mass	Compound Identification	Relative Concentration (%) ^a
1	266	1,2,3,3a,4,5,7,8,9,10,11,12,12a,12b-Tetradecahydrobenzo[a]pyrene	1.5
2	260	4,5,7,8,9,10,11,12-Octahydrobenzo[a]pyrene	13.1
3	256	Unidentified tetrahydrobenzo[a]pyrene	4.6
4	256	4,5,11,12-Tetrahydrobenzo[a]pyrene	10.8
5	258	Unidentified hexahydrobenzo[a]pyrene	4.2
6	258	4,5,7,8,9,10-Hexahydrobenzo[a]pyrene	9.4
7	258	7,8,9,10,11,12-Hexahydrobenzo[a]pyrene	2.9
8	254	4,5-Dihydrobenzo[a]pyrene	27.3
9	256	7,8,9,10-Tetrahydrobenzo[a]pyrene	12.8
10	252	Benzo[a]pyrene	10.2
Total			96.8

^aRelative concentration, determined using GC peak heights

tigated in this laboratory to date, similar work reported in the literature supports the hypothesis that tumorigenicity generally decreases with increasing hydro-substitution (Kotin et al., 1956; Lijinsky et al., 1970; Lijinski, Cefis et al., 1965; Lijinski, Garcia et al., 1965). If the trends observed for benzo[a]pyrene are applicable to other PAH constituents found in coal liquefaction process materials, an overall reduction of biological activity would be anticipated for catalytically hydrotreated coal liquefaction materials. This assumption is certainly supported by the data presented in this report for the comparative biological activity of "on-line" hydrotreated versus non-hydrotreated liquefaction process materials (see Tables 22 and 24). Results of the chemical characterization of those NTSL/ITSL process materials tested for tumorigenicity are given in a following section.

Aquatic Toxicity Assay

The acute toxicity of the WSF of the SRC and HTR distillation column overheads were determined in a static aquatic system with D. magna. The LC_{50} for these materials in D. magna ranged from 0.5 to 2.5% WSF for the four materials tested. Based on percent dilution of the WSF, first-stage products from both the NTSL and ITSL processes were more toxic than second-stage products (Table 27). However, when toxicity comparisons were made relative to TC in solution, WSF generated from second-stage products appeared more toxic. This discrepancy can be explained by the relative solubility of the parent materials and WSF concentrations. For example, WSF from the NTSL first-stage product were greater than 2000 mg/L TC. Thus, toxic concentrations could be achieved at about 20% of the dilution observed for the WSF from the ITSL second-stage product, which was only 260 mg/L TC.

No difference was observed in the toxicity of first-stage products with respect to process modes. However, based on the presence of equal amounts of toxic constituents in solution, second-stage products produced in the NTSL mode were significantly ($\alpha = 0.05$) more toxic to daphnids than second-stage products produced in the ITSL mode. The acutely toxic range of the four materials tested was similar to that observed in previous studies with other coal liquids, ranging from 1.5 to 9.6 mg/L TC.

TABLE 27. Acute Toxicity of WSF Derived from Selected NTSL and ITSL Materials to D. Magna^a

Process	Material	WSF TC (mg/L)	48 Hour LC ₅₀	
			% WSF	TC (mg/L)
NTSL	T-104, 1st-stage SRC overhead product	2035 ± 247	0.5	9.6
	T-105, 2nd-stage HTR overhead product	150 ± 26	1.0	1.5 ^b
ITSL	T-104, 1st-stage SRC overhead product	1208 ± 284	0.7	8.2
	T-105, 2nd-stage HTR overhead product	260 ± 39	2.5	6.4

^aWSF concentrations given as mean ± 1 standard deviation.

^bSignificantly different at $\alpha = 0.05$

Previous studies with several coal liquids have shown that phenols typically constituted more than 90% of the TC in WSF and that other relatively insoluble chemical classes probably contributed little to their observed toxicity. Therefore, for the present studies, detailed chemical characterization was conducted for phenols only. Total phenol concentrations were highest for WSF derived from first-stage products and ranged from 129 to 2590 mg/L for the four materials tested (Table 28). Concentrations of phenols in WSF derived from the NTSL second-stage product were about half those noted for the second-stage product from the ITSL process.

Phenol composition of the WSF varied somewhat according to both process modes and product stage. For example, phenols, cresols, and C_2 -phenols collectively comprised >90% of the phenols measured in the NTSL distillation overheads. This same chemical group contributed, respectively, about 85% and 68% of the total phenols in WSF from comparable distillation overheads produced in the ITSL process mode. Percent contribution of C_3 -phenols in WSF derived from the second-stage NTSL product were 3 to 15 times less than those noted in the other three WSF.

The four NTSL/ITSL materials tested were more soluble in water (i.e., higher WSF concentrations) than three ITSL (New Brunswick) materials previously tested (Dauble et al., 1983). The difference may be attributable to the greater predominance of lower-molecular-weight compounds, mainly phenol and cresol, in the pilot plant NTSL/ITSL process materials.

CHEMICAL ANALYSES

Detailed chemical characterization of the NTSL/ITSL process materials was performed to enable correlation of chemical composition with observed biological response. Although these data have been generated as a component of toxicological studies, they also offer insights into the differences in chemical composition of coal liquefaction materials obtained from different process technologies. In this section and the corresponding appendices, the results of the chemical analyses for the NTSL/ITSL process materials are presented and discussed.

TABLE 28. Phenol Concentrations (mg/L) in WSF Derived from NTSL/ITSL Process Materials^a

Compound	NTSL Mode ^a		ITSL Mode ^a	
	SRC 1st-Stage Overhead Product	HTR 2nd-Stage Overhead Product	SRC 1st-Stage Overhead Product	HTR 2nd-Stage Overhead Product
Phenol	619	.28	187	32
Cresols	1300	57	404	66
C ₂ -phenols	501	31	426	98
C ₃ -phenols	49	10	116	80
C ₄ -phenols	6	1	12	5
C ₅ -phenols	2	<1	10	1
Indanols	10	1	39	5
C ₁ -indanols	<u>4</u>	<u><1</u>	<u>11</u>	<u>1</u>
Total phenols ^b	2590	129	1200	288

^aConcentrations (mg/L) expressed as means of duplicate samples.^bTotals are rounded to three significant figures

Gross Chemical Composition of NTSL/ITSL Process Materials

The relative chemical composition of those NTSL/ITSL materials fractionated by alumina adsorption chromatography are shown in Table 29. The aliphatic hydrocarbon (A_1) and neutral PAH (A_2) chemical fractions were typically responsible for more than 50% of the total mass of the SRC and HTR distilled materials from both the NTSL and ITSL operating modes. In general, the distilled products contained relatively less N-PAC than either the undistilled NTSL/ITSL materials or the other direct coal liquefaction process materials studied to date. However, the undistilled process materials, such as the deashed SRC product, CSD ash concentrate extract, NTSL vacuum flash bottoms and ITSL recycle process solvent, contained relatively low levels of aliphatic hydrocarbons and neutral PAH and were composed primarily of N-PAC and hydroxy-PAH. Except for the distilled products from the HTR unit, all of the NTSL/ITSL crude process materials had levels of hydroxy-PAH greater than 20% by weight. The HTR distillation products were nominally composed of less than 10-15% hydroxy-PAH and N-PAC. These results indicate efficient removal of oxygen and nitrogen heteroatoms from the deashed SRC product during processing in the second-stage catalytic HTR unit. For samples collected during Run 242-720°B, for example, the sum of the weight contribution of the N-PAC and hydroxy-PAH fractions to the deashed SRC product and HTR feed was in excess of 50%, but it was only approximately 15% of the HTR distillation column overheads and bottoms. This trend was also observed for NTSL Run 241 and ITSL Run 242-740°F process materials.

The most noticeable differences in gross chemical composition between the process materials of the NTSL and ITSL operating modes were observed for the first-stage deashed SRC product. In the NTSL mode, only ~10% of the deashed SRC product was aliphatic hydrocarbons (A_1) and/or neutral PAH (A_2); more than 60% of the crude material was N-PAC and hydroxy-PAH. The low recovery of this material from the alumina column (~80%) is also indicative of its highly polar nature and/or low solubility. However, in the ITSL mode, the chemical composition is redistributed: Fractions A_1 and A_2 account for approximately 30-40% of the deashed SRC product, with a reduction in the concentration of hydroxy-PAH (A_4).

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
SP: T-102, Tray 8	A ₂	---	49	46
	A ₃	---	6	9
	A ₄	---	13	18
	Total	---	102%	111%
		(5226-019)	(5226-057)	
SRC: 1st-stage product distillate	A ₁	34	44	---
SP: T-102, Tray 3	A ₂	30	29	---
	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-105 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

This compositional redistribution cannot be wholly explained by "dilution" effects due to differences in process configuration. It must also be the result of improved coal dissolution and hydrogenation in the higher-quality liquefaction process solvent used in the ITSL operating mode. The hydrogenated heavy-end process solvent used to slurry the feed coal during ITSL operations allows the coal to be solvated more readily and efficiently and minimizes the possibility of retrograde reactions that lead to coking, polymerization and the formation of polar materials. These factors, coupled with the operation of the SRC unit in the SCT mode, result in improved liquefaction in the first-stage and a correspondingly less aromatic second-stage product. The higher content of aliphatic hydrocarbons (A_1) in the ITSL versus the NTSL distillation column bottoms, by nearly 20% (see Table 29), also supports this view.

Since the chemical composition of the first-stage deashed SRC product was different for the NTSL and ITSL operating modes, it was of interest to investigate the gross chemical composition of this material and of the HTR feed as a function of the HTR unit operating temperature. This was done in an effort to determine if this process parameter affected the product composition of the first-stage material used for feed to the second-stage HTR unit. HTR operating temperature had an observable effect on the microbial mutagenic activity of the deashed SRC product (Figure 6). It was therefore of interest to determine if differences in chemical composition could be observed and correlated with the biological observation.

The results from the alumina adsorption class fractionation of the deashed SRC product and the HTR feed (an ~50/50 blend of deashed SRC product and SRC distillate process solvent from T-102, Tray 8), sampled with the HTR unit operating at different temperatures, are reported in Table 30. The chemical compositions of these materials were fairly similar, with no major or definitive changes in the contribution of any chemical classes to the gross composition. More subtle changes were, however, observed. For example, the aliphatic hydrocarbon weight percent appeared to decrease with increasing HTR temperature, while the PAH weight percent seemed to increase. The N-PAC and hydroxy-PAH fractions fluctuated at around 25-35% for the deashed SRC product and 20-25% for the HTR feed, with no indication of a definite trend with re-

TABLE 30. Chemical Composition of Deashed SRC Product and HTR Feed as a Function of HTR Reactor Temperature

Chemical Fraction	Weight Percent Distribution (%)					
	Start-Up	242-680°	242-700°	242-720°A	242-720°B	242-740°
HTR Feed:	(5226-098)	(5226-081)	(5226-103)	(5226-053)	(5226-061)	(5226-070)
A ₁ Aliphatic hydrocarbons	19	20	21	15	14	16
A ₂ Neutral PAH	32	33	33	34	38	41
A ₃ N-PAC	17	24	22	26	27	24
A ₄ Hydroxy-PAH	<u>22</u>	<u>23</u>	<u>21</u>	<u>24</u>	<u>23</u>	<u>20</u>
<u>Total:</u>	90%	100%	97%	99%	102%	101%
Deashed SRC Product:	(5226-074)	(5226-080)	(5226-102)	(5226-050)	(5226-063)	(5226-066)
A ₁ Aliphatic hydrocarbons	5	3	3	3	3	4
A ₂ Neutral PAH	25	28	31	27	34	40
A ₃ N-PAC	29	32	33	36	34	34
A ₄ Hydroxy-PAH	<u>27</u>	<u>26</u>	<u>23</u>	<u>27</u>	<u>22</u>	<u>22</u>
<u>Total:</u>	86%	89%	90%	93%	93%	100%

spect to HTR temperature. No trends in the gross chemical composition of these materials that could be correlated with the variations noted for the mutagenic activities were obvious at this level of chemical analysis.

Hydroaromatic Compounds

Hydrogen incorporation is a key aspect of converting solid coal to liquid products via liquefaction processes. Hydroaromatic compounds are partially saturated PAH that are intermediate products in the hydrogenative reduction of aromatic moieties which are major components of coal macerals, to aliphatic hydrocarbons. The quantitative determination of overall hydroaromatic content of coal liquefaction process materials can, therefore, be used to measure the efficiency of hydrogen incorporation via different process approaches. Recently, Wozniak and Hites (1983) developed and reported a method, similar to the alumina adsorption column chromatography used in this laboratory, for the class separation of aliphatic hydrocarbons, hydroaromatic compounds and PAH (see Figure 5). In collaboration with these investigators, selected NTSL and ITSL process materials were fractionated by this method to determine the contribution of the hydroaromatic compounds to the overall composition of these materials. The levels of hydroaromatic and aliphatic hydrocarbons can be used to compare the degree of hydrogen incorporation between the NTSL and ITSL operating modes. Table 31 presents the results of the hydroaromatic class separation done for the deashed SRC product, HTR feed and HTR distillation column bottoms from both the NTSL and ITSL operating modes.

The levels of aliphatic hydrocarbons, as expected, were highest in the HTR distillate column bottoms material: the ITSL material was ~15% higher in aliphatic hydrocarbon content than the corresponding NTSL sample. This is an indication that hydrogen was more effectively incorporated in the ITSL mode, which was primarily a result of the higher-quality recycle solvent used in the ITSL process. The 15% difference appeared to be distributed in the PA₂ (10% difference) and PA₃ (6% difference) fractions of the NTSL distillation column bottoms; the levels of hydroaromatics and dihydro-PAH and <three-ring PAH were correspondingly higher in the NTSL HTR bottoms. The >three-ring PAH and polar compounds were approximately equivalent in both materials. Also, in both materials, the weight percentage sum of the compounds eluted from the picric

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.

acid/alumina column accounted for almost 100% of the sample material and closely matched the sum of the aliphatic hydrocarbon and PAH fraction of the alumina column separation (see Table 31).

The picric acid/alumina separation allowed a differentiation between the aliphatic hydrocarbons and hydroaromatic compounds that was not achievable with the alumina separation. This enabled a more precise assessment of the chemical composition of these liquefaction materials with regard to fully saturated, partially saturated and fully aromatic hydrocarbon compounds. The deashed SRC product (a first-stage product) contained only low levels of hydroaromatic compounds relative to the PAH and heteroatomic PAH. This observation indicates that hydrogen incorporation in the thermal, noncatalytic SRC unit is not as extensive as in the catalytic HTR stage. A possible explanation for this observation may be that first-stage hydrogen serves primarily to cap free radicals and excised intramolecular bonds resulting from dissociation of the coal macrostructure, with very little hydrogen going to saturate aromatic ring structures.

Another observation that can be made from Table 31 is that the NTSL HTR feed contained higher levels of hydroaromatic compounds and lower levels of other PAH than the corresponding ITSL HTR feed. The explanation for this observation is process-related. The HTR feed in the NTSL mode was a blend of deashed SRC product from the first stage and the >450°F distillation bottoms from the HTR stage. Hence, the NTSL HTR feed was composed partially of catalytically hydrotreated material. The ITSL HTR feed was composed entirely of first-stage products: ~50:50 blend of deashed SRC product and depleted SRC solvent (T-102, Tray 8). Nonetheless, the ITSL HTR feed contained ~20% more hydrocarbon-type compounds (sum of picric acid fractions; Table 31) than the NTSL material, probably the result of a more effective hydrogen donating process solvent used in the ITSL mode.

Detailed chemical analyses for the picric acid/alumina column fractions were conducted by capillary column GC and GC/MS. Figures 10 and 11 show chromatograms for the hydroaromatic fractions, PA₂, of the HTR distillate column bottoms from the NTSL and ITSL operating modes, respectively. Peak identifications are given in Table 32. The ITSL HTR distillation column bottoms

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.

TABLE 32. Peak Identifications (Figures 10 and 11) for Hydroaromatic Compounds in Fraction PA₂ of the NTSL and ITSL HTR Distillation Column Bottoms (PNL #5226-022 and #5226-059)

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 32. (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.

(Figure 11) appeared to be of slightly higher boiling range and somewhat more complex than the corresponding NTSL material (Figure 10). However, for the most part, the same compounds were identified in both the NTSL and ITSL HTR bottoms, although variations in relative concentrations of some hydroaromatic compounds were observed. Specific compound identifications were based on GC retention information and MS fragmentation patterns of authentic standard compounds. Most identifications, however, were not specific, and isomers other than those listed in Table 32 cannot be ruled out at this point. For the most part, compounds in these fractions had a high degree of alkylation in conjunction with varying degrees of hydro-substitution. Nonalkylated parent compounds were typically less concentrated than their alkylated counterparts.

Figure 12 is a capillary column gas chromatogram of the ITSL HTR feed, which is a blend of first-stage SRC unit materials. Overall, this material was highly complex, with less hydro-substitution of the PAH systems than HTR products. However, significant levels of hydroaromatic compounds were present in this material even though it had not undergone second-stage catalytic hydrogenation. Comparison of the ITSL HTR feed (Figure 12) and HTR distillation column bottoms product (Figure 11) indicates that further hydrogen-incorporation occurred as a result of catalytic hydrotreatment in the second liquefaction stage. Higher degrees of alkylation and hydro-substitution are present in the HTR product than in the HTR feed. Coupled with the data in Table 31, which show an increase from 24% aliphatic/hydroaromatic hydrocarbons to 81%, for HTR feed to HTR product, it can be concluded that the ITSL process favors high yields of aliphatic hydrocarbons and hydroaromatic compounds.

It was also of interest in this study to determine if scale-up effects were observable, with regard to chemical composition, in going from ITSL processing at the bench-scale to pilot-plant-level operation. A GC trace of the hydroaromatic fraction PA_2 of the Lummus PDU TLP is shown in Figure 13 and can be compared with Figures 10 and 11 of the pilot plant samples. Overall, alkylation was not as extensive in the bench-scale product compared with the pilot plant materials. The PDU material was mostly hydro-substituted parent PAH with relatively little alkylation, particularly above C_2 . Apparently, hydrogenation in the pilot plant resulted in a greater degree of aromatic ring scission than in the PDU reactor.

FIGURE 12. Capillary Column Gas Chromatogram of the Hydroaromatic Fraction, PA₂, of the ITSL HTR Feed (PNL Sample #5226-061)

FIGURE 13. Capillary Column Gas Chromatogram of the Hydroaromatic Fraction, PA₂, of the Lummus PDU ITSL TLP

Detailed Chemical Composition of NTSL/ITSL Process Materials

Detailed chemical analysis of the chemical class fraction for each of the samples collected for NTSL Run 241 and ITSL Run 242-720°B were performed by capillary column GC, GC/MS and direct probe MS. Of the several sample suites collected during Run 242, when the HTR unit was operated at various temperatures, the set collected during lined-out operation with the HTR at 720°F was considered the most representative because the HTR was operated longer at this temperature than at any other. The most extensive analyses were therefore performed using this sample set for the ITSL operating mode.

NTSL/ITSL SRC Unit Process Materials. Figure 14 shows capillary gas chromatograms of the PAH fractions of the first-stage SRC unit distillation products from NTSL Run 241. The PAH fraction constitutes 16% of the unfractonated materials for the light fuel oil and 30% for the first-stage product distillate (see Table 29). The major components of the light fuel oil were naphthalene and its C₁, C₂, and C₃ alkyl analogs. Relative concentrations of parent PAH and their hydro-substituted derivative species indicate the extent of hydrogen incorporation. For example, fluorene and the dihydrofluorenes are of comparable concentration levels in this distilled product, indicating a moderate level of hydrogen incorporation. Phenanthrene and its alkyl analogs were also present in the NTSL SRC unit light fuel oil. As anticipated, the first-stage product distillate (Figure 14) was of somewhat higher boiling range (see Table 5) than the light fuel oil. Correspondingly, the three-ring PAH, such as fluorene, dihydrofluorenes, and phenanthrene, as well as the C₂- and C₃-naphthalenes, were the major constituents of the NTSL first-stage product distillate. The ratio of 1,4-dihydrofluorene (major peak in Group #20; m/z = 168 by GC/MS) to fluorene (Peak #19) was significantly different from that in the light fuel oil: the dihydro species was more concentrated than the parent compound. GC retention measurements with standard reference compounds revealed that the major peak of Group #20 had the same retention time and index as 1,4-dihydrofluorene. Several components of 182 m/z, which correspond to C₁-dihydrofluorenes, were also present in the NTSL SRC unit first-stage product distillate. The high levels of both alkylation and hydro-substitution observed indicate the effectiveness of hydrogen incorporation in this two-stage liquefaction process. The "cut-off" boiling point for both

FIGURE 14. Capillary Chromatograms of the PAH Fractions of (Top) the Light Fuel Oil (PNL #5226-018) and (Bottom) the First-Stage Product Distillate (PNL #5226-019) Process Materials from the First-Stage SRC Unit of NTSL Run 241. (See Table 33 for peak identifications.)

TABLE 33. Identifications of Compounds in PAH Fractions Isolated from Selected NTSL and ITSL Products as Determined by GC/MS and Capillary Gas Chromatographic Retention Times

Peak Number ^a	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

^aRefers to peaks labeled in Figures 14, 16, 19 and 20.

TABLE 33. (continued)

Peak Number ^a	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

^aRefers to peaks labeled in Figures 14, 16, 19 and 20

NTSL SRC unit materials was approximately at the C₁-phenanthrene range. Detailed quantitation of the constituents in these process materials is provided in Appendix B, Table B1.

Figure 14, which shows the PAH fractions of the NTSL SRC unit distilled products, can be compared with Figure 15, which shows capillary gas chromatograms of the PAH fraction of the ITSL SRC unit light fuel oil and first-stage product distillate as well as the SRC distillate process solvent. The ITSL SRC light fuel oil is composed of naphthalenes and C₁-, C₂-, and C₃-naphthalenes, like the NTSL SRC light fuel oil, but an increased proportion of three-ring PAH were also present as compared to the NTSL material. The ratio of fluorene to dihydrofluorenes in the two materials was also comparable. The first-stage product distillate from the ITSL SRC unit was also chemically similar to the corresponding NTSL material; however, as noted for the light fuel oils, higher molecular weight materials were observed in the ITSL sample. For example, pyrene and its methyl analogs were detected in the ITSL but not in the NTSL SRC unit first-stage product distillate. As with the NTSL first-stage product distillate, the levels of fluorene (Peak #19) were much lower than the dihydrofluorenes (Peak Group #20), and several C₁-dihydrofluorene isomers (182 m/z) were also detected. Detailed quantitation of the compounds identified in these isolates is given in Table B3 of Appendix B.

The SRC distillate process solvent (bottom chromatogram, Figure 15) was a wider boiling range material (450+°F) than either of the materials just discussed. This crude SRC unit product was blended in approximately a 1:1 ratio with the deashed SRC product in the ITSL mode to make the second-stage HTR feed. The PAH isolate constitutes ~36% of the crude material. A broad range of two- to five-ring PAH, as well as hydro-, alkyl- and hydro/alkyl-substituted PAH, were detected in this process material. Pyrene, which has been considered an important hydrogen shuttle molecule (Wilson et al., 1983), was the most abundant compound in this sample. Table B3 of Appendix B provides further quantitative results for the PAH isolate of this process material.

Chromatograms for the PAH isolates of the NTSL and ITSL deashed SRC unit product are shown in Figure 16. Detailed quantitative results for these pro-

FIGURE 15. Capillary Chromatograms of the PAH Fractions of the First-Stage Unit Process Materials from ITSL Run 242-720°B. Key: (A) Light Fuel Oil (PNL #5226-055), (B) First-Stage Product Distillate (PNL #5226-057), and (C) SRC Distillate Process Solvent (PNL #5226-056). (See Table 33 for peak identifications.)

FIGURE 16. Capillary Column Gas Chromatogram of the PAH Fraction, A₂, of the Deashed SRC Product from the NTSL (Top), and ITSL (Bottom) Process

cess materials are given in Tables B1 and B3 of Appendix B. Although the deashed SRC materials from the NTSL and ITSL process modes are of comparable boiling point ranges (450-1000°F), the difference in the individual components of these two materials is marked. The neutral PAH isolate of the ITSL deashed SRC product is composed primarily of parent PAH compounds; the corresponding NTSL material has levels of alkylated PAH equivalent to those of the respective parent compound (see Figure 16). This difference is also believed to be due to the different qualities of the NTSL and ITSL process solvents. The major components of the first-stage SRC product from both the NTSL and ITSL modes were the three- to six-ring PAH, such as phenanthrenes, pyrenes, chrysenes, benz[o]pyrenes, benzo[ghi]perylene, etc. Again, the C₁- and C₂-alkyl analogs were more abundant in the NTSL SRC product.

As manifested by the rising baseline in the chromatograms of Figure 16, there were numerous unresolved, high molecular weight PAH in the NTSL/ITSL deashed SRC products. Probe inlet, low voltage MS of these materials provided insights into their qualitative and quantitative differences that were not readily apparent from the GC and GC/MS analysis. Figure 17 shows the 12-eV MS for the PAH fraction of the NTSL and ITSL deashed SRC product. High molecular weight PAH up to m/z 500 were present in both the NTSL and ITSL materials. However, the average molecular weight for the NTSL deashed SRC product was ~300 m/z, which was much lower than the ITSL/NTSL material, which had an average molecular weight between 350 and 375 m/z. Again, extensive alkylation was observed in the NTSL deashed SRC product. For example, the series starting at m/z 228, chrysene and/or benzanthracene, had corresponding alkylated representatives with parent ions at m/z 242, 256, 270, 284, 298, 310, 324, 338, etc., representing C₁ to C₈ alkylation. Low voltage MS of the other alumina column chemical fractions of these materials are provided in Appendix C.

In general, the levels of N-PAC were lower in the ITSL versus the NTSL SRC unit materials. Figure 18 shows high resolution gas chromatograms of the N-PAC isolate Fraction A₃ of the NTSL/ITSL SRC unit first-stage product distillate. Accompanying peak identifications are found in Table 34. Detailed quantitative information for the N-PAC constituents of the NTSL/ITSL SRC unit products is given in Appendix B, Tables B5 and B7. The main constituents of the NTSL SRC first-stage product distillate are the quinolines, indoles and

FIGURE 17. 12-eV Mass Spectra of the PAH Fraction, A₂, of the Deashed SRC Product from (A) the ITSL and (B) the NTSL Operating Modes

FIGURE 18. Capillary Chromatograms of the N-PAC Fraction, A₃, of the SRC Unit First-Stage Product Distillate: (Top) ITSL Run 242-720°B (PNL #5226-056) and (Bottom) NTSL Run 241 (PNL #5226-019)

TABLE 34. Identifications of Components in N-PAC Fractions Isolated from Selected ITSL and NTSL Products as Determined by GC/MS and High Resolution GC Retention Time

Peak Number ^a	Molecular Weight	Tentative Identification
1	136	C ₃ -Phenols
2	133	Tetrahydroquinoline
3	129	Quinoline
4	129	Isoquinoline
5	135	C ₄ -Pyridines
6	147	C ₁ -Tetrahydroquinolines
7	150	C ₄ -Phenols
8	117	Indole
9	143	C ₁ -Quinolines
10	164	C ₅ -Phenols
11	131	C ₁ -Indoles
12	148	Tetrahydronaphthol
13	157	C ₂ -Quinolines
14	162	C ₁ -Tetrahydroanaphthols
15	178	C ₆ -Phenols
16	145	C ₂ -Indoles
17	176	C ₂ -Tetrahydronaphthols
18	171	C ₃ -Quinolines
19	190	C ₃ -Tetrahydronaphthols
20	159	C ₃ -Indoles
21	185	C ₄ -Quinolines
22	204	C ₄ -Tetrahydronaphthols
23	187	Octahydrobenzoquinoline
24	201	C ₁ -Octahydrobenzoquinoline
25	179	Benzo[h]quinoline
26	171	Tetrahydrocarbazole
27	179	Benzo[f]quinoline, phenanthridine
28	187	Octahydrobenzoquinoline
29	167	Carbazole
30	193	2- or 3-methylbenzo[f]quinoline
31	181	1-Methylcarbazole
32	181	3-Methylcarbazole
33	181	2-Methylcarbazole
34	181	4-Methylcarbazole
35	212	2-Chloroanthracene, ISTD
36	195	C ₂ -Carbazoles
37	209	Hexahydroazafluoranthene
38	203	Azapyrene
39	223	C ₁ -Hexahydroazafluoranthene

^aRefers to peaks labeled in Figures 18 and 21.

TABLE 34. (continued)

Peak Number ^a	Molecular Weight	Tentative Identification
40	217	C ₁ -Azapyrenes
41	231	C ₂ -Azapyrenes
42	221	Tetrahydrobenzocarbazoles
43	217	Benzo[a]carbazole
44	229	Azachrysene
45	217	Benzo[a]carbazole
46	217	Benzo[c]carbazole
47	243	C ₁ -Azapyrenes
48	253	Azabenzopyrenes, azabenzofluoranthenes

^aRefers to peaks labeled in Figures 18 and 21.

carbazoles. Both hydro- and alkyl-substituted derivatives of these compounds were detected by GC/MS in this sample. As with the PAH fraction, the boiling point range of these materials ends at the three-ring compounds, i.e., carbazole and methylcarbazoles. The contribution of the N-PAC to the overall crude first-stage product distillate material was approximately 13% by weight (see Table 29).

Although several N-PAC constituents were detected in the ITSL SRC unit first-stage product distillate Fraction A₃, the major components were the highly alkylated phenols and hydrogenated naphthols (1,2,3,4-tetrahydronaphthol was identified, for example). The reduced concentration of the N-PAC and the presence of the highly alkylated/hydrogenated hydroxy-PAH in this fraction are indications that denitrogenation and hydrogen incorporation occurred to a greater extent in the ITSL than in the NTSL mode, even in the first stage of liquefaction. Carbazole and its four methyl analogs were the most concentrated N-PAC in that fraction of the ITSL SRC unit first-stage product distillate, suggesting that the carbazole-type compounds are the N-PAC species most resistant to deamination via hydrogenation. Again, the ITSL material was of higher boiling point range than the NTSL sample (see Figure 18).

The observations that hydroxy-PAH eluted in the alumina column A₃ or N-PAC fraction of the ITSL first-stage product distillate deserves further comment. The alumina adsorption procedure separates compounds according to their polarity: the more polar compounds are retained more strongly. Evidently, hydrogenation of the hydroxy-functional PAH reduced their polarity sufficiently to permit their premature elution in the N-PAC fraction. The overall implication is that the ITSL SRC unit first-stage product distillate is generally less polar in nature than the same NTSL process material. The polar compounds are generally accepted as the source of retrograde reactions that lead to coking and polymerization in coal liquefaction process materials. Hence, a reduction in the polarity of constituents in process materials is advantageous and appeared to occur in the ITSL operating mode to a greater extent than in the NTSL mode.

In summary, there are some similarities in the chemical composition of the NTSL and ITSL SRC unit distilled and deashed products. In general,

though, the ITSL process materials from the SRC unit were of higher molecular weight. The N-PAC were in lower concentration in the ITSL materials as compared to corresponding NTSL samples. Finally, NTSL SRC unit products had concentrations of alkylated PAH more equivalent to those of the parent PAH than did comparable ITSL materials.

NTSL/ITSL HTR Unit Process Materials. Figures 19 and 20 are capillary chromatograms of the <450°F and >450°F distillate fractions of the NTSL and ITSL HTR products, respectively. Qualitative peak identifications are given in Table 33; detailed quantitative data are provided in Tables B2 and B4 of Appendix B. In general, the ITSL HTR products are chemically more complex than the corresponding NTSL materials, with proportionally more hydro-substituted PAH. Comparatively, the ITSL HTR light fuel oil had a plethora of low molecular weight PAH (below that of naphthalene) that were not present at as high concentrations in the NTSL HTR light fuel oil (compare top chromatograms of Figures 19 and 20). Furthermore, the PAH fraction of the HTR distillate column bottoms (>450°F) from the NTSL mode had a less complex capillary chromatogram than the corresponding ITSL product (compare bottom chromatograms of Figures 19 and 20). This is mainly the result of a wider range of a greater number of hydroaromatic species in the ITSL as compared to the NTSL HTR bottoms. Furthermore, while the NTSL HTR >450°F PAH fraction was composed mostly of a few major species, such as fluorene, phenanthrene, pyrene and benzofluorene, relatively equal concentrations of these compounds, along with numerous hydroaromatic compounds such as hydrofluorenes, hydrophenanthrenes, hydrofluoranthenes and hydropyrenes, were present in the ITSL HTR >450°F PAH fraction.

Characterization of the hydroaromatic compounds was discussed and the data were presented in Figures 10 through 12 and Table 32. Table 35 compares the concentration of selected parent, alkylated and hydro-substituted PAH in three process materials from the NTSL and ITSL pilot plant runs. Alkylation tended to be greater in the NTSL SRC unit materials; however, in the HTR unit products, the ITSL samples contained alkylated products at comparable concentration levels. Parent PAH were relatively more concentrated in the NTSL samples. The hydro-substituted PAH were more concentrated in the ITSL light fuel oil, of equivalent concentrations in the HTR distillation column bottoms, and

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.)

FIGURE 20. Capillary Chromatograms of the PAH Fractions of the Second-Stage HTR Unit Process Materials from ITSL Run 242-720°B: (Top) Light Fuel Oil (PNL #5226-062) and (Bottom) Distillation Column Bottoms (PNL #5226-059). (See Table 33 for peak identifications.)

TABLE 35. Concentrations of Selected PAH in Selected NTSL/ITSL Process Materials (from Appendix B).

Compounds	Concentration ($\mu\text{g/g}$)					
	Light Fuel Oils ($\mu\text{g/g}$)		HTR Feeds ($\mu\text{g/g}$)		HTR Distillation Column Bottoms ($\mu\text{g/g}$)	
	NTSL	ITSL	NTSL	ITSL	NTSL	ITSL
Fluorene	1710 $\pm$ 80	5420 $\pm$ 270	1800 $\pm$ 80	404 $\pm$ 78	1490 $\pm$ 100	2590 $\pm$ 150
Dihydrofluorenes (m/z = 168)	2450 $\pm$ 130	10800 $\pm$ 700	10200 $\pm$ 300	3430 $\pm$ 110	8450 $\pm$ 1500	9150 $\pm$ 370
2-Methylfluorene	1040 $\pm$ 30	5220 $\pm$ 420	2180 $\pm$ 420	319 $\pm$ 170	2200 $\pm$ 230	1290 $\pm$ 100
Dihydromethylfluorenes (m/z = 182)	2370 $\pm$ 90	12700 $\pm$ 1000	7790 $\pm$ 220	3020 $\pm$ 390	7740 $\pm$ 670	10200 $\pm$ 300
Fluoranthene	800 $\pm$ 200	4120 $\pm$ 210	597 $\pm$ 64	872 $\pm$ 46	752 $\pm$ 6	1020 $\pm$ 80
Pyrene	461 $\pm$ 59	4290 $\pm$ 1040	8260 $\pm$ 190	4210 $\pm$ 120	13300 $\pm$ 160	5320 $\pm$ 210
Dihdropyrene (m/z = 204)	---	1960 $\pm$ 670	1210 $\pm$ 230	694 $\pm$ 170	1640 $\pm$ 200	1130 $\pm$ 110
1-Methylpyrene	---	713 $\pm$ 200	530 $\pm$ 387	878 $\pm$ 186	1020 $\pm$ 640	961 $\pm$ 78
Fluorene: 2-Methylfluorene ratio	1.6	1.0	0.8	1.3	0.7	2.0
Pyrene: 1-Methylpyrene ratio	---	6.0	15.6	4.8	13.0	5.5
Dihydrofluorene: Fluorene ratio	1.4	2.0	5.7	8.5	5.7	3.5

more concentrated in the NTSL HTR feed. The NTSL HTR feed was a 1:1 blend of SRC product and >450°F HTR product.

In the NTSL mode, the first-stage process solvent was a first-stage distillation product and was therefore not hydrogenated. However, hydrogenated heavy-end materials from the high pressure separator following the HTR reaction vessel were recycled from the second to the first stage as the process solvent in the ITSL operating mode. The generally increased relative levels of hydroaromatics, as well as the increased complexity of the ITSL versus the NTSL HTR products (compare Figures 19 and 20), was the result of integrally coupling the two liquefaction stages. In the ITSL mode, hydrogenation and/or hydrocracking of coal constituents were initiated more effectively in the presence of a high-quality hydrogen donating process solvent under low severity thermal conditions in the first stage. The intermediate product is thus more susceptible to catalytic hydrogenation in the second stage. The overall result is the production of more hydrogen-rich end-products, which are composed of higher levels of aliphatic hydrocarbons and isomeric hydro-substituted PAH. This enhances the quality of the end-products and renders them more suitable for upgrading and refining into commercially usable final products.

Another measure of product quality is the heteroatomic PAH content. As discussed previously, the HTR products from both the NTSL and ITSL operating modes contained less than 15% (by weight) N-PAC and hydroxy-PAH. Figure 21 is a capillary gas chromatogram of the N-PAC fraction of the HTR distillation column bottoms for both NTSL and ITSL operating modes. Peak identifications are given in Table 34. Detailed quantitative data are provided in Appendix B, Tables B6 and B8. The major components in the NTSL HTR distillation column bottoms were the pyrrolic-PAH, such as carbazole and benzocarbazole, and related alkylated species of these compounds. The pyridine-type compounds were also present but at relatively lower concentrations than the pyrrolic-PAH. The N-PAC fraction of the ITSL also contained carbazoles and methyl carbazoles. However, as with the SRC unit products, there were also highly alkylated and hydro-substituted phenols and hydrox-PAH present in this fraction. The reasons for the elution of these compounds in the N-PAC Fraction A₃ were discussed earlier.

FIGURE 21. Capillary Chromatograms of the N-PAC Fractions of the HTR Distillation Column Bottoms: (Top) ITSL Run 242-720°B (PNL #5226-059) and (Bottom) NTSL Run 242 (PNL #5226-022).

Table 36 provides comparative quantitative data for selected N-PAC in an SRC unit and two HTR unit NTSL/ITSL process materials. In general, higher concentration levels of N-PAC were found in the SRC unit versus the HTR unit process materials. Furthermore, concentrations of N-PAC were typically lower in ITSL materials than in comparable NTSL samples. Similar observations of reductions of N-PAC concentrations in second-stage as compared to first-stage materials have also been reported for the Lummus PDU ITSL samples (Wilson et al., 1983). From the data in Tables 18, B6 and B8, it is apparent that those N-PAC constituents with the most resistance to thermal or catalytic hydrogenation are the pyrrolic-PAH, particularly carbazole and its methyl analogs. Schmitter and coworkers have similarly reported that the pyrrolic-PAH were among the most persistent N-PAC in hydrotreated coker gas oil (Dorbon et al., 1984; Schmitter et al., 1984). Quinoline and benzologs of quinoline were found in reduced levels in the ITSL and second-stage process samples as compared to NTSL and first-stage products. For example, the levels of benzoquinoline were lower in second-stage compared to first-stage materials. In corresponding samples, the benzoquinolines were present at levels below detection limits in the ITSL and NTSL second-stage process materials.

Several hydro-substituted N-PAC were also detected in these process materials. In general, these hydroaromatic N-PAC were present in higher concentrations in second-stage versus first-stage materials and in ITSL as compared to NTSL samples. Such compounds were identified as isomers of the hydrocarbazoles, hydroazafluoranthene/pyrenes and hydrobenzoquinolines (see Table 34 and Figure 21).

Another indication that levels of N-PAC were reduced in ITSL as compared to NTSL process material was shown in Table 19 and were discussed in conjunction with the microbial mutagenicity assay results. This assay is particularly sensitive to levels of N-PAC; in particular the amino-PAH. Results for the HTR distillation column bottoms showed that reduced levels of TA98 mutagenicity were observed in the ITSL A₃ fractions (241-742-720°B: 3 rev/μg; 242-740°F: 14 rev/μg) versus the same NTSL material N-PAC isolate (65 rev/μg). Similar observations held for the mutagenic activity of the crude unfractionated HTR distillate column bottoms; NTSL HTR bottoms: 6 rev/μg, ITSL 242-720°B, and 242-740°F HTR bottoms: no activity detected at comparable dose

TABLE 36. Comparative Concentrations of Selected N-PAC Components Determined by HRGC A₃ Fractions Isolated from Products of NTSL Run #241 and ITSL Run #242-720°B.

Compound	Concentration (µg/g)					
	SRC		HTR Feed		HTR Distillation	
	1st-Stage Product Distillate				Column Bottoms	
	NTSL (5226-019)	ITSL (5226-057)	NTSL (5226-021)	ITSL (5226-061)	NTSL (5226-022)	ITSL (5226-059)
Quinoline	13200 ± 1710	1350 ± 80	---	---	---	---
Indole	22500 ± 3800	<20	<20	17 ± 2	---	---
8-Methylquinoline	3570 ± 1350	2970 ± 570	<20	12 ± 1	---	---
Benzo[h]quinoline	850 ± 185	252 ± 21	208 ± 40	37 ± 16	---	---
Carbazole	7940 ± 170	967 ± 75	254 ± 63	49 ± 9	1950 ± 270	2550 ± 330
3-Methylcarbazole	1490 ± 80	1320 ± 120	258 ± 3	90 ± 25	1570 ± 320	1540 ± 100
4-Azapyrene	---	---	250 ± 23	69 ± 14	1030 ± 540	838 ± 160
Benzo[a]carbazole	---	---	181 ± 89	33 ± 17	669 ± 97	<200

levels. From these data, a reduction in the actual concentrations of mutagenic N-PAC in the second-stage and ITSL process material would be anticipated. The analytical data reported for the A₃ fractions in Tables 29, 36 and B5 through B8 support these conclusions.

Hydroxy-PAH are the fourth major class of PAC isolated by alumina adsorption chromatography from the NTSL/ITSL HTR process materials. These compounds, including phenol, indanol and their alkylated analogs, were the major chemical constituents in the WSF of the NTSL and ITSL HTR distillation overheads used for the aquatic toxicity assays (Table 28). Figure 22 shows the low voltage probe mass spectra of the hydroxy-PAH fraction isolated from the HTR distillation column bottoms of the NTSL and ITSL samples. The main constituents in the ITSL HTR product are the alkyl phenols and alkylindanols. The mass of this chemical fraction for this sample ranged from 108 m/z (creosols) to approximately 350 m/z. The average molecular weight was approximately 180 to 400 m/z. The NTSL HTR distillation column bottoms had a higher mass range than the ITSL material: 122 m/z (C₂-phenol) to more than 500 m/z; and a higher average molecular weight: greater than 300 m/z. Both ITSL and NTSL A₄ fractions contained parent and alkylated two-, three-, four-, and five-ring hydroxy-PAH. Alkylation appeared to exceed C₆. Furthermore, the NTSL hydroxy-PAH fraction appeared to be much more complex than the same ITSL isolate, presumably because of the hydro-substituted hydroxy-PAH.

In summary, the two ITSL HTR products were generally more complex materials than the equivalent NTSL samples. Unlike the SRC unit products, the PAH and N-PAC chemical fractions of the NTSL HTR products were of higher molecular weight and boiling point range than the ITSL HTR products. Likewise, the NTSL hydroxy-PAH isolate of the HTR distillation column bottoms (>450°F) was of higher molecular weight and boiling point range than the corresponding ITSL material. Additional direct probe low voltage mass spectra of the chemical fractions of the NTSL/ITSL HTR distillation column bottoms are included in Appendix C. Complete quantitative data for the PAH and N-PAC constituents are provided in Appendix B.

Comparative Chemical Analysis of the ITSL Process Solvent. The recycle solvent is the internal stream in direct coal liquefaction processes

FIGURE 22. 12-eV Mass Spectra of the Hydroxy-PAH Fraction, A₄, of the HTR Distillation Column Bottoms from (A) the ITSL and (B) the NTSL Operations Modes

that has the greatest impact on end-product yield and quality. An important feature of two-stage liquefaction processes is the increased flexibility offered in producing process solvents of differing physical and chemical properties. For example, the process solvent may be taken from distillation of first-stage products, or it may be recycled from the products of the second-stage hydrogenation unit. These two process materials may be blended or some other option can be selected. The process solvent in TSL, regardless of its source, generally constitutes a major portion of the process feed material. Obviously, one of the most critical properties of a process solvent is its hydrogen donating activity.

Low voltage (12-eV) direct probe mass spectra of the PAH and N-PAC chemical fraction of the ITSL Run 242 recycle process solvent (PNL#5226-058) are shown in Figure 23. From these spectra, it is obvious that this extremely complex material is composed of high molecular weight PAH and N-PAC, many of which would not be amenable to GC or GC/MS analysis. The molecular weight range of the PAH fraction started below 150 m/z and extended beyond mass 500. The N-PAC isolate showed the presence of odd molecular weight nitrogen species from ~181-303 but also included even molecular weight constituents, most probably PAH that eluted in the A₃ fraction, starting at mass 300 and exceeding 600 m/z. Hence, the combined molecular weight range for PAH components was approximately 150 to >600 m/z.

In the historical development of effective process solvents, certain trends have evolved in terms of chemical properties and composition. Recycle process solvents have progressively become higher molecular weight materials and chemically more complex, presumably due to hydrogenation. Typical single-stage process solvents have had boiling point ranges between ~500°F and >850°F, whereas these two-stage process solvents have boiling ranges starting at 650°F and usually extending beyond 1000°F.

There are also differences in gross and specific chemical composition between the early and more recently developed process solvents that are noteworthy. Table 37 compares the relative concentrations of aliphatic hydrocarbons, PAH, N-PAC and hydroxy-PAH of several single- and two-stage liquefaction materials. In general, the pilot plant ITSL recycle process solvent contained

FIGURE 23. 12-eV Mass Spectra of (A) PAH Fraction, A₂, and (B) N-PAC Fraction, A₃, of the ITSL Recycle Solvent from Run 242-720°B

TABLE 37. Comparative Chemical Class Composition of Process Solvents from Different Direct Coal Liquefaction Technologies

Process Solvent	Chemical Class Composition (% by Weight) ^a			
	AH	PAH	N-PAC	Hydroxy-PAH
SRC I	14	47	14	25
EDS Bottoms Recycle	45	36	7	12
EDS Once Through	55	31	7	13
ITSL; Lummus PDU	31	34	12	23
NTSL Pilot Plant (2nd Stage only)	44	34	7	15
ITSL Pilot Plant	19	45	20	16

^aAll weight percentages normalized to 100% recovery

the lowest levels of aliphatic hydrocarbons and the highest levels of PAH and polar N-PAC and hydroxy-PAH. The presence of fairly significant levels of polar constituents, such as the N-PAC, which are known to solvate coal to a greater extent than nonfunctional PAH, probably enhances the solubility of coal in the first-stage SCT reactor. As previously mentioned, hydro-substituted N-PAC and hydroxy-PAH were also found in the ITSL process solvent and other process materials. In addition to providing enhanced solubility, the hydro-substituted heteroatomic PAH probably contribute significantly to the hydrogen donating activity of the process solvent, as do the peri-condensed PAH, such as pyrene, which are known to be effective hydrogen-shuttling compounds.

Figures 24 and 25 compare the specific chemical composition differences of various coal liquefaction process solvents, using capillary column GC. Figure 24 shows the PAH fractions isolated from an SRC I process solvent obtained from the Fort Lewis pilot plant and from the recycle solvent from the Lummus PDU ITSL process. Figure 25 shows similar chromatograms of the same chemical fraction from two process solvents collected from the EDS pilot plant. These chromatograms illustrate the differences in chemical composition arising from different operating conditions and/or process unit configurations. The most apparent difference is the increased molecular weight of the ITSL as compared to the EDS and SRC process solvents. The EDS and SRC process solvents contained PAH with molecular weights below that of pyrene (202 m/z); approximately 50% or more of the PDU ITSL process solvent components had molecular weights equivalent to or greater than that of pyrene. Figure 26 shows the averaged probe inlet mass spectra of the unfractionated Lummus PDU and Wilsonville pilot plant ITSL process solvents. They demonstrate that the pilot plant ITSL process solvent is of much higher molecular weight than even the PDU ITSL recycle solvent.

These factors, along with the difference in gross chemical composition (see Table 37) and the higher boiling point range, differentiate the pilot plant ITSL process solvent from other previously studied coal liquefaction process solvents. The improved quality of the intermediate- and end-products in terms of lower biological activity and higher levels of saturated hydrocarbons are the direct result of liquefaction in the presence of this process

FIGURE 24. High Resolution Gas Chromatogram of (A) SRC I Process Solvent and (B) Lummus PDU ITSL Recycle Solvent

FIGURE 25. Capillary Column Gas Chromatogram of the PAH Fractions from the EDS (A) Once-Through Process Solvent and (B) Bottoms Recycle Process Solvent

FIGURE 26. Low Voltage 12-eV Probe Mass Spectra of (A) the Lummus PDU and (B) the Wilsonville Pilot Plant ITSL Crude Recycle Process Solvents

solvent. Highly effective hydrogen incorporation in the ITSL process is due to the high hydrogen-donating activity of this material which, in turn, is a result of its chemical composition.

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APPENDIX A

THIS APPENDIX PROVIDES THE RAW UNTRANSFORMED DOSE RESPONSE DATA FOR THE MUTAGENICITY OF CRUDES, ALIPHATIC HYDROCARBONS (A₁), NEUTRAL PAH (A₂), N-PAC (A₃) AND HYDROXY-PAH (A₄) FRACTIONS OF THE NTSL/ITSL PROCESS MATERIALS.

TABLE A1. Average Positive and Negative Control Data for *S. typhimurium* TA98

Compound ^a	µg/Plate	S9 (µl)	Average Revertant Colonies/Plate
2-AA	1.0	10	4770 ± 750
BII	5.7	20	2196 ± 590
BaP	10.0	100	299 ± 61
MNNG	1.0	0	79 ± 33
None	0	20	53 ± 14
None	0	100	60 ± 21
None	0	0	33 ± 15

Key: 2-AA = 2-aminoanthracene
 BII = SRC II basic tar
 BaP = benzo[a]pyrene
 MNNG = n-methyl-N'-nitro-N-nitrosoguanidine

TABLE A2. Raw Dose Response Data for the *S. typhimurium* TA98 Mutagenicity Testing of NTSL Run 241 Process Materials

Crude or Fraction	First-Stage SRC Products									CSD Product		
	Light Fuel Oil (5226-018)			1st-Stage Product Distillate (5226-019)			Deashed SRC (5226-020)			Ash Concentrate (5226-025)		
	S9	µg/	Revertant	S9	µg/	Revertant	S9	µg/	Revertant	S9	µg/	Revertant
	(µl)	Plate	Colonies	(µl)	Plate	Colonies	(µl)	Plate	Colonies	(µl)	Plate	Colonies
Crude	20	0		20	0	34 ± 4	20	0	34 ± 4	20	0	
		2	71 ± 1		2	43 ± 10		2			2	71 ± 1
		4	89 ± 7		4	40 ± 3		4	58 ± 10		4	89 ± 7
		8	103 ± 3		8	35 ± 2		8	60 ± 6		8	103 ± 3
		10	92 ± 16		10	20 ± 4		10	72 ± 1		10	92 ± 16
		20	92 ± 6		20	37 ± 1		20	106 ± 4		20	92 ± 6
		50	121 ± 3		50	28 ± 1		50	152 ± 1		50	121 ± 3
A ₁	20	0	47 ± 0	20	0	37 ± 0	20	0	37 ± 0	20	0	70 ± 0
		2	41 ± 9		2	41 ± 9		2	27 ± 3		2	66 ± 1
		4	30 ± 0		4	38 ± 3		4	23 ± 0		4	50 ± 1
		8	33 ± 7		8	37 ± 1		8	24 ± 5		8	54 ± 6
		10	34 ± 6		10	38 ± 4		10	28 ± 2		10	46 ± 4
		20	39 ± 4		20	39 ± 2		20	24 ± 1		20	57 ± 2
		50	37 ± 1		50	41 ± 2		50	8 ± 0		50	8 ± 0
A ₂	100	0	39 ± 0	100	0	48 ± 0	100	0	48 ± 0	100	0	80 ± 0
		2	44 ± 5		2	49 ± 0		2	57 ± 15		2	59 ± 6
		4	42 ± 6		4	42 ± 9		4	62 ± 3		4	56 ± 5
		8	44 ± 9		8	35 ± 2		8	55 ± 3		8	49 ± 0
		10	46 ± 10		10	31 ± 5		10	53 ± 9		10	56 ± 0
		20	34 ± 10		20	39 ± 8		20	67 ± 15		20	47 ± 5
		50	41 ± 5		50	51 ± 8		50	84 ± 12		50	66 ± 8

TABLE A2. (Continued)

Crude or Fraction	First-Stage SRC Products									CSD Product		
	Light Fuel Oil (5226-018)			1st-Stage Product Distillate (5226-019)			Deashed SRC (5226-020)			Ash Concentrate (5226-025)		
	S9	µg/	Revertant	S9	µg/	Revertant	S9	µg/	Revertant	S9	µg/	Revertant
	(µl)	Plate	Colonies	(µl)	Plate	Colonies	(µl)	Plate	Colonies	(µl)	Plate	Colonies
A ₃	20	0	47 ± 0	20	0.0	37 ± 0	20	0	37 ± 0	20	0	70 ± 0
		2	38 ± 5		0.2	34 ± 7		2	41 ± 4		2	68 ± 19
		4	39 ± 11		0.4	29 ± 1		4	70 ± 10		4	61 ± 6
		8	36 ± 1		0.8	32 ± 4		8	99 ± 10		8	90 ± 21
		10	43 ± 0		1.0	30 ± 6		10	116 ± 8		10	91 ± 3
		20	40 ± 4		2.0	36 ± 3		20	129 ± 21		20	138 ± 9
		50	41 ± 7		5.0	42 ± 9		50	155 ± 3		50	172 ± 25
A ₄	20	0	47 ± 0	20	0	37 ± 0	20	0	37 ± 0	100	0	70 ± 0
		2	38 ± 5		2	26 ± 1		2	47 ± 1		2	42 ± 0
		4	39 ± 11		4	37 ± 4		4	46 ± 4		4	45 ± 5
		8	36 ± 1		8	22 ± 3		8	77 ± 16		8	43 ± 6
		10	43 ± 0		10	29 ± 0		10	114 ± 13		10	55 ± 10
		20	40 ± 4		20	28 ± 5		20	119 ± 11		20	81 ± 13
		50	41 ± 7		50	41 ± 13		50	160 ± 38		50	96 ± 1

TABLE A2. (Continued)

Crude or Fraction	Second-Stage HTR Products											
	Feed; Blend of SRC (5226-021)			Light Fuel Oil (5226-023)			Distillation Column Bottoms (5226-022)			Vacuum Flash Bottoms (5226-024)		
	S9 (μ l)	μ g/ Plate	Revertant Colonies	S9 (μ l)	μ g/ Plate	Revertant Colonies	S9 (μ l)	μ g/ Plate	Revertant Colonies	S9 (μ l)	μ g/ Plate	Revertant Colonies
Crude	20	0.0	34 $\pm$ 4	20	0	34 $\pm$ 4	20	0	34 $\pm$ 4	20	0	34 $\pm$ 4
		0.2	35 $\pm$ 3		2	30 $\pm$ 1		2	40 $\pm$ 1		2	36 $\pm$ 3
		0.4	32 $\pm$ 2		4	29 $\pm$ 5		4	58 $\pm$ 3		4	60 $\pm$ 2
		0.8	40 $\pm$ 6		8	38 $\pm$ 1		8	70 $\pm$ 2		8	77 $\pm$ 13
		1.0	50 $\pm$ 3		10	35 $\pm$ 6		10	97 $\pm$ 9		10	96 $\pm$ 6
		2.0	72 $\pm$ 1		20	39 $\pm$ 4		20	146 $\pm$ 17		20	128 $\pm$ 7
		5.0	110 $\pm$ 9		50	39 $\pm$ 5		50	181 $\pm$ 13		50	137 $\pm$ 35
A ₁	20	0	37 $\pm$ 0	20	0	70 $\pm$ 0	20	0	47 $\pm$ 1	20	0	70 $\pm$ 0
		2	39 $\pm$ 4		2	65 $\pm$ 4		2	25 $\pm$ 7		2	61 $\pm$ 1
		4	34 $\pm$ 3		4	73 $\pm$ 3		4	39 $\pm$ 9		4	56 $\pm$ 5
		8	27 $\pm$ 1		8	61 $\pm$ 3		8	36 $\pm$ 2		8	66 $\pm$ 4
		10	33 $\pm$ 3		10	64 $\pm$ 7		10	32 $\pm$ 2		10	51 $\pm$ 12
		20	23 $\pm$ 9		20	84 $\pm$ 1		20	31 $\pm$ 1		20	56 $\pm$ 2
		50	23 $\pm$ 4		50	63 $\pm$ 7		50	32 $\pm$ 6		50	7 $\pm$ 0
A ₂	100	0	48 $\pm$ 0	100	0	80 $\pm$ 0	100	0	39 $\pm$ 0	100	0	80 $\pm$ 0
		2	102 $\pm$ 4		2	67 $\pm$ 1		2	40 $\pm$ 1		2	83 $\pm$ 6
		4	51 $\pm$ 2		4	68 $\pm$ 3		4	30 $\pm$ 5		4	73 $\pm$ 8
		8	71 $\pm$ 10		8	76 $\pm$ 10		8	39 $\pm$ 5		8	79 $\pm$ 10
		10	34 $\pm$ 5		10	68 $\pm$ 13		10	30 $\pm$ 5		10	80 $\pm$ 2
		20	92 $\pm$ 23		20	79 $\pm$ 4		20	44 $\pm$ 6		20	84 $\pm$ 0
		50	96 $\pm$ 23		50	80 $\pm$ 5		50	59 $\pm$ 5		50	75 $\pm$ 13

TABLE A2. (Continued)

Crude or Fraction	Second-Stage HTR Products											
	Feed; Blend of SRC (5226-021)			Light Fuel Oil (5226-023)			Distillation Column Bottoms (5226-022)			Vacuum Flash Bottoms (5226-024)		
	S9 (μ l)	μ g/ Plate	Revertant Colonies	S9 (μ l)	μ g/ Plate	Revertant Colonies	S9 (μ l)	μ g/ Plate	Revertant Colonies	S9 (μ l)	μ g/ Plate	Revertant Colonies
A ₃	20	0	37 $\pm$ 0	20	0	70 $\pm$ 0	20	0.0	47 $\pm$ 0	20	0	70 $\pm$ 0
		2	58 $\pm$ 11		2	57 $\pm$ 7		0.2	44 $\pm$ 1		2	75 $\pm$ 2
		4	74 $\pm$ 16		4	63 $\pm$ 10		0.4	68 $\pm$ 10		4	89 $\pm$ 5
		8	117 $\pm$ 32		8	60 $\pm$ 2		0.8	73 $\pm$ 9		8	92 $\pm$ 4
		10	114 $\pm$ 12		10	43 $\pm$ 8		1.0	109 $\pm$ 4		10	98 $\pm$ 24
		20	140 $\pm$ 36		20	42 $\pm$ 6		2.0	184 $\pm$ 1		20	167 $\pm$ 23
		50	122 $\pm$ 18		50	61 $\pm$ 5		5.0	361 $\pm$ 47		50	183 $\pm$ 23
A ₄	20	0	37 $\pm$ 0	20	0	70 $\pm$ 0	20	0	47 $\pm$ 0	20	0	70 $\pm$ 0
		2	43 $\pm$ 16		2	56 $\pm$ 7		2	39 $\pm$ 1		2	64 $\pm$ 19
		4	38 $\pm$ 7		4	63 $\pm$ 3		4	39 $\pm$ 5		4	57 $\pm$ 14
		8	56 $\pm$ 2		8	59 $\pm$ 5		8	38 $\pm$ 4		8	50 $\pm$ 4
		10	66 $\pm$ 15		10	49 $\pm$ 5		10	41 $\pm$ 9		10	69 $\pm$ 5
		20	67 $\pm$ 4		20	60 $\pm$ 19		20	53 $\pm$ 1		20	99 $\pm$ 3
		50	85 $\pm$ 8		50	51 $\pm$ 16		50	76 $\pm$ 13		50	167 $\pm$ 5

TABLE A3. Raw Dose Response Data for the *S. typhimurium* TA98 Mutagenicity Testing of ITSL Run 242-720°F B Process Materials

Crude or Fraction	First-Stage SRC Products												CSD Product		
	Light Fuel Oil (5226-055)			Distillate Process Solvent (5226-056)			1st-Stage Product Distillate (5226-057)			Deashed SRC (5226-063)			Ash Concentrate (5226-060)		
	S9 (μl)	μg/Plate	Revertant Colonies	S9 (μl)	μg/Plate	Revertant Colonies	S9 (μl)	μg/Plate	Revertant Colonies	S9 (μl)	μg/Plate	Revertant Colonies	S9 (μl)	μg/Plate	Revertant Colonies
Crude	20	0	47 ± 6	20	0	47 ± 6	20	0	47 ± 6	20	0	28 ± 8	20	0	44 ± 1
		2	46 ± 9		2	66 ± 1		2	68 ± 15		2	42 ± 10		2	55 ± 4
		4	49 ± 6		4	67 ± 11		4	81 ± 7		4	46 ± 6		4	56 ± 10
		8	58 ± 2		8	69 ± 3		8	63 ± 9		8	42 ± 1		8	64 ± 11
		10	67 ± 13		10	67 ± 1		10	107 ± 1		10	62 ± 1		10	80 ± 4
		20	84 ± 26		20	78 ± 10		20	86 ± 10		20	57 ± 8		20	67 ± 2
		50	72 ± 1		50	95 ± 13		50	83 ± 8		50	58 ± 3		50	89 ± 11
A ₁	20	0	47 ± 6	20	0	47 ± 6	20	0	47 ± 0	20	0	28 ± 8	20	0	44 ± 1
		2	32 ± 2		2	55 ± 5		0	90 ± 13		0	23 ± 4		2	50 ± 2
		4	41 ± 1		4	37 ± 1		4	87 ± 14		4	22 ± 6		4	56 ± 12
		8	59 ± 5		8	52 ± 6		8	60 ± 8		8	20 ± 4		8	37 ± 1
		10	39 ± 7		10	42 ± 2		10	104 ± 11		10	33 ± 5		10	42 ± 1
		20	61 ± 0		20	44 ± 8		20	95 ± 14		20	22 ± 0		20	48 ± 2
		50	40 ± 2		50	38 ± 6		50	87 ± 8		50	28 ± 3		50	61 ± 4
A ₂	100	0	87 ± 12	100	0	87 ± 12	100	0	87 ± 12	100	0	47 ± 1	100	0	71 ± 8
		2	76 ± 0		2	94 ± 5		2	57 ± 5		2	51 ± 4		2	85 ± 5
		4	63 ± 0		4	81 ± 1		4	71 ± 17		4	63 ± 0		4	75 ± 14
		8	72 ± 15		8	70 ± 3		8	54 ± 12		8	40 ± 5		8	51 ± 0
		10	62 ± 0		10	68 ± 7		10	41 ± 5		10	41 ± 6		10	60 ± 18
		20	61 ± 17		20	82 ± 1		20	57 ± 4		20	69 ± 10		20	94 ± 10
		50	65 ± 4		50	85 ± 11		50	41 ± 8		50	71 ± 2		50	88 ± 0

TABLE A3. (Continued)

Crude or Fraction	First-Stage SRC Products												CSD Product		
	Light Fuel Oil (5226-055)			Distillate Process Solvent (5226-056)			1st-Stage Product Distillate (5226-057)			Deashed SRC (5226-063)			Ash Concentrate (5226-060)		
	S9 (μ l)	μ g/ Plate	Revertant Colonies	S9 (μ l)	μ g/ Plate	Revertant Colonies	S9 (μ l)	μ g/ Plate	Revertant Colonies	S9 (μ l)	μ g/ Plate	Revertant Colonies	S9 (μ l)	μ g/ Plate	Revertant Colonies
A ₃	20	0	47 $\pm$ 6	20	0.0	47 $\pm$ 6	20	0.0	47 $\pm$ 6	20	0	28 $\pm$ 8	20	0.0	44 $\pm$ 1
		2	92 $\pm$ 6		0.2	47 $\pm$ 7		0.2	64 $\pm$ 1		2	48 $\pm$ 3		0.2	46 $\pm$ 14
		4	84 $\pm$ 12		0.4	60 $\pm$ 12		0.4	65 $\pm$ 12		4	27 $\pm$ 5		0.4	47 $\pm$ 6
		8	112 $\pm$ 25		0.8	57 $\pm$ 5		0.8	81 $\pm$ 4		8	41 $\pm$ 7		0.8	35 $\pm$ 2
		10	187 $\pm$ 30		1.0	75 $\pm$ 11		1.0	90 $\pm$ 9		10	36 $\pm$ 1		1.0	48 $\pm$ 5
		20	178 $\pm$ 42		2.0	99 $\pm$ 4		2.0	106 $\pm$ 7		20	50 $\pm$ 6		2.0	46 $\pm$ 10
		50	222 $\pm$ 16		5.0	109 $\pm$ 7		5.0	123 $\pm$ 4		50	66 $\pm$ 1		5.0	58 $\pm$ 6
A ₄	20	0	47 $\pm$ 6	20	0	47 $\pm$ 6	20	0	47 $\pm$ 6	20	0	28 $\pm$ 8	20	0	44 $\pm$ 1
		2	43 $\pm$ 5		2	49 $\pm$ 9		2	87 $\pm$ 5		2	37 $\pm$ 1		2	41 $\pm$ 4
		4	52 $\pm$ 14		4	48 $\pm$ 0		4	55 $\pm$ 5		4	42 $\pm$ 6		4	52 $\pm$ 2
		8	46 $\pm$ 11		8	63 $\pm$ 2		8	64 $\pm$ 10		8	40 $\pm$ 6		8	28 $\pm$ 3
		10	51 $\pm$ 12		10	43 $\pm$ 5		10	42 $\pm$ 6		10	71 $\pm$ 13		10	40 $\pm$ 6
		20	50 $\pm$ 3		20	35 $\pm$ 1		20	66 $\pm$ 2		20	69 $\pm$ 11		20	58 $\pm$ 0
		50	41 $\pm$ 9		50	52 $\pm$ 2		50	45 $\pm$ 8		50	73 $\pm$ 6		50	58 $\pm$ 7

TABLE A3. (Continued)

Crude or Fraction	Second-Stage HTR Products											
	Feed; Blend of SRC (5226-061)			Light Fuel Oil (5226-062)			Distillation Column Bottoms (5226-059)			Recycle Pasting Solvent (5226-058)		
	S9 (μ l)	μ g/ Plate	Revertant Colonies	S9 (μ l)	μ g/ Plate	Revertant Colonies	S9 (μ l)	μ g/ Plate	Revertant Colonies	S9 (μ l)	μ g/ Plate	Revertant Colonies
Crude	20	0	28 $\pm$ 8	20	0	28 $\pm$ 8	20	0	62 $\pm$ 2	20	0	56 $\pm$ 4
		2	30 $\pm$ 4		2	29 $\pm$ 7		2	42 $\pm$ 2		2	49 $\pm$ 3
		4	34 $\pm$ 11		4	27 $\pm$ 4		4	43 $\pm$ 1		4	36 $\pm$ 8
		8	40 $\pm$ 2		8	25 $\pm$ 3		8	69 $\pm$ 2		8	47 $\pm$ 5
		10	51 $\pm$ 7		10	26 $\pm$ 9		10	63 $\pm$ 14		10	51 $\pm$ 8
		20	40 $\pm$ 6		20	28 $\pm$ 6		20	57 $\pm$ 5		20	62 $\pm$ 1
		50	47 $\pm$ 1		50	25 $\pm$ 0		50	92 $\pm$ 3		50	55 $\pm$ 2
A ₁	20	0	56 $\pm$ 4	20	0	28 $\pm$ 8	20	0	56 $\pm$ 4	20	0	56 $\pm$ 4
		2	53 $\pm$ 5		2	34 $\pm$ 4		2	46 $\pm$ 7		2	43 $\pm$ 4
		4	41 $\pm$ 3		4	33 $\pm$ 5		4	37 $\pm$ 5		4	46 $\pm$ 5
		8	55 $\pm$ 2		8	37 $\pm$ 6		8	33 $\pm$ 10		8	36 $\pm$ 1
		10	38 $\pm$ 2		10	30 $\pm$ 3		10	35 $\pm$ 8		10	39 $\pm$ 4
		20	50 $\pm$ 5		20	30 $\pm$ 7		20	45 $\pm$ 1		20	50 $\pm$ 1
		50	50 $\pm$ 5		50	30 $\pm$ 9		50	40 $\pm$ 12		50	36 $\pm$ 3
A ₂	100	0	36 $\pm$ 13	100	0	47 $\pm$ 1	100	0	36 $\pm$ 13	100	0	36 $\pm$ 13
		2	52 $\pm$ 4		2	28 $\pm$ 1		2	46 $\pm$ 0		2	44 $\pm$ 5
		4	47 $\pm$ 6		4	23 $\pm$ 3		4	36 $\pm$ 0		4	51 $\pm$ 5
		8	48 $\pm$ 6		8	32 $\pm$ 6		8	42 $\pm$ 7		8	55 $\pm$ 6
		10	40 $\pm$ 4		10	31 $\pm$ 2		10	45 $\pm$ 4		10	49 $\pm$ 3
		20	55 $\pm$ 7		20	41 $\pm$ 3		20	38 $\pm$ 8		20	55 $\pm$ 8
		50	62 $\pm$ 3		50	41 $\pm$ 3		50	44 $\pm$ 3		50	57 $\pm$ 4

TABLE A3. (Continued)

Crude or Fraction	Second-Stage HTR Products											
	Feed; Blend of SRC (5226-061)			Light Fuel Oil (5226-062)			Distillation Column Bottoms (5226-059)			Recycle Pasting Solvent (5226-058)		
	S9 (μ l)	μ g/ Plate	Revertant Colonies	S9 (μ l)	μ g/ Plate	Revertant Colonies	S9 (μ l)	μ g/ Plate	Revertant Colonies	S9 (μ l)	μ g/ Plate	Revertant Colonies
A ₃	20	0	56 $\pm$ 4	20	0		20	0	56 $\pm$ 4	20	0	56 $\pm$ 4
		2	51 $\pm$ 2		2			2	83 $\pm$ 1		2	59 $\pm$ 4
		4	54 $\pm$ 2		4			4	98 $\pm$ 17		4	50 $\pm$ 2
		8	43 $\pm$ 3		8			8	76 $\pm$ 7		8	31 $\pm$ 3
		10	38 $\pm$ 1		10			10	137 $\pm$ 1		10	64 $\pm$ 0
		20	62 $\pm$ 1		20			20	163 $\pm$ 23		20	71 $\pm$ 16
		50	76 $\pm$ 1		50			50	210 $\pm$ 3		50	99 $\pm$ 9
A ₄	20	0	56 $\pm$ 4	20	0	28 $\pm$ 8	20	0	56 $\pm$ 4	20	0	56 $\pm$ 4
		2	54 $\pm$ 2		2	31 $\pm$ 0		2	57 $\pm$ 9		2	51 $\pm$ 4
		4	45 $\pm$ 11		4	22 $\pm$ 0		4	46 $\pm$ 1		4	51 $\pm$ 2
		8	56 $\pm$ 1		8	26 $\pm$ 6		8	50 $\pm$ 1		8	38 $\pm$ 7
		10	48 $\pm$ 6		10	23 $\pm$ 0		10	44 $\pm$ 3		10	38 $\pm$ 17
		20	51 $\pm$ 5		20	21 $\pm$ 5		20	36 $\pm$ 5		20	50 $\pm$ 18
		50	79 $\pm$ 5		50	24 $\pm$ 0		50	52 $\pm$ 1		50	41 $\pm$ 6

TABLE A4. Raw Dose Response Data for the *S. typhimurium* TA98 Mutagenicity Testing of ITSL Run 242-740°F Process Materials

Crude or Fraction	First-Stage SRC Products									CSD Product		
	Light Fuel Oil (5226-064)			Solvent Distillate Process (5226-065)			Deashed SRC (5226-066)			Ash Concentrate (5226-067)		
	S9	µg/ Plate	Revertant Colonies	S9	µg/ Plate	Revertant Colonies	S9	µg/ Plate	Revertant Colonies	S9	µg/ Plate	Revertant Colonies
	(µl)			(µl)			(µl)			(µl)		
Crude	20	0	41 ± 1	20	0	41 ± 1	20	0	33 ± 2	20	0	44 ± 1
		2	47 ± 5		2	43 ± 2		2	54 ± 6		2	56 ± 6
		4	47 ± 3		4	46 ± 6		4	56 ± 2		4	56 ± 1
		8	44 ± 6		8	44 ± 5		8	73 ± 2		8	43 ± 1
		10	62 ± 6		10	46 ± 4		10	64 ± 6		10	49 ± 1
		20	87 ± 5		20	79 ± 4		20	59 ± 8		20	62 ± 5
		50	107 ± 13		50	114 ± 15		50	128 ± 14		50	81 ± 10
A ₁	20	0	38 ± 5	20	0	38 ± 5	20	0	33 ± 2	20	0	44 ± 1
		2	33 ± 1		2	39 ± 3		2	40 ± 1		2	49 ± 8
		4	38 ± 4		4	40 ± 4		4	43 ± 3		4	54 ± 1
		8	27 ± 2		8	30 ± 3		8	43 ± 8		8	39 ± 1
		10	36 ± 5		10	30 ± 0		10	37 ± 6		10	40 ± 5
		20	41 ± 6		20	40 ± 4		20	47 ± 1		20	50 ± 1
		50	35 ± 6		50	38 ± 1		50	49 ± 7		50	56 ± 1
A ₂	100	0	36 ± 13	100	0	36 ± 13	100	0	40 ± 8	100	0	71 ± 8
		2	44 ± 6		2	45 ± 4		2	55 ± 7		2	66 ± 17
		4	48 ± 1		4	44 ± 3		4	60 ± 7		4	85 ± 6
		8	47 ± 9		8	32 ± 1		8	73 ± 11		8	54 ± 5
		10	38 ± 1		10	42 ± 3		10	75 ± 2		10	74 ± 1
		20	42 ± 3		20	51 ± 7		20	60 ± 1		20	91 ± 4
		50	41 ± 3		50	67 ± 9		50	86 ± 6		50	111 ± 11

TABLE A4. (Continued)

Crude or Fraction	First-Stage SRC Products									CSD Product		
	Light Fuel Oil (5226-064)			Solvent Distillate Process (5226-065)			Deashed SRC (5226-066)			Ash Concentrate (5226-067)		
	S9	µg/	Revertant	S9	µg/	Revertant	S9	µg/	Revertant	S9	µg/	Revertant
	(µl)	Plate	Colonies	(µl)	Plate	Colonies	(µl)	Plate	Colonies	(µl)	Plate	Colonies
A ₃	20	0.0	38 ± 5	20	0.0	38 ± 5	20	0.0	33 ± 2	20	0.0	44 ± 1
		0.2	38 ± 1		0.2	40 ± 5		0.2	60 ± 6		0.2	40 ± 5
		0.4	43 ± 6		0.4	40 ± 1		0.4	41 ± 1		0.4	35 ± 6
		0.8	42 ± 1		0.8	52 ± 8		0.8	51 ± 6		0.8	42 ± 4
		1.0	54 ± 7		1.0	52 ± 3		1.0	48 ± 4		1.0	29 ± 7
		2.0	65 ± 0		2.0	65 ± 0		2.0	49 ± 4		2.0	35 ± 2
		5.0	93 ± 7		5.0	94 ± 18		5.0	41 ± 1		5.0	43 ± 8
A ₄	20	0	38 ± 5	20	0	38 ± 5	20	0	33 ± 2	20	0	44 ± 1
		2	32 ± 1		2	41 ± 3		2	46 ± 1		2	56 ± 8
		4	41 ± 2		4	41 ± 5		4	48 ± 1		4	62 ± 4
		8	25 ± 4		8	36 ± 1		8	59 ± 2		8	40 ± 1
		10	33 ± 1		10	25 ± 1		10	44 ± 5		10	39 ± 1
		20	38 ± 1		20	37 ± 5		20	52 ± 2		20	63 ± 6
		50	43 ± 1		50	42 ± 4		50	59 ± 4		50	83 ± 12

TABLE A4. (Continued)

Crude or Fraction	Second-Stage HTR Products								
	Feed; Blend of SRC (5226-070)			Light Fuel Oil (5226-068)			Distillation Column Bottoms (5226-069)		
	S9 (μ l)	μ g/ Plate	Revertant Colonies	S9 (μ l)	μ g/ Plate	Revertant Colonies	S9 (μ l)	μ g/ Plate	Revertant Colonies
Crude	20	0	41 $\pm$ 1	20	0	33 $\pm$ 2	20	0	33 $\pm$ 2
		2	27 $\pm$ 1		2	47 $\pm$ 1		2	52 $\pm$ 5
		4	31 $\pm$ 5		4	54 $\pm$ 3		4	50 $\pm$ 5
		8	60 $\pm$ 10		8	51 $\pm$ 1		8	48 $\pm$ 9
		10	78 $\pm$ 5		10	39 $\pm$ 1		10	67 $\pm$ 8
		20	67 $\pm$ 1		20	49 $\pm$ 1		20	84 $\pm$ 3
		50	72 $\pm$ 9		50	43 $\pm$ 2		50	93 $\pm$ 1
A ₁	20	0	33 $\pm$ 2	20	0	33 $\pm$ 2	20	0	33 $\pm$ 2
		2	45 $\pm$ 1		2	37 $\pm$ 0		2	50 $\pm$ 3
		4	30 $\pm$ 2		4	45 $\pm$ 1		4	46 $\pm$ 3
		8	47 $\pm$ 4		8	43 $\pm$ 7		8	45 $\pm$ 6
		10	51 $\pm$ 2		10	30 $\pm$ 2		10	43 $\pm$ 0
		20	42 $\pm$ 2		20	56 $\pm$ 1		20	40 $\pm$ 0
		50			50	54 $\pm$ 8		50	36 $\pm$ 4
A ₂	100	0	40 $\pm$ 8	100	0	40 $\pm$ 8	100	0	40 $\pm$ 8
		2	53 $\pm$ 9		2	57 $\pm$ 5		2	71 $\pm$ 2
		4	73 $\pm$ 3		4	59 $\pm$ 0		4	48 $\pm$ 6
		8	60 $\pm$ 8		8	61 $\pm$ 5		8	58 $\pm$ 1
		10	66 $\pm$ 6		10	56 $\pm$ 3		10	39 $\pm$ 9
		20	66 $\pm$ 5		20	73 $\pm$ 4		20	56 $\pm$ 4
		50	84 $\pm$ 4		50	59 $\pm$ 5		50	61 $\pm$ 7

TABLE A4. (Continued)

Crude or Fraction	Second-Stage HTR Products								
	Feed; Blend of SRC (5226-070)			Light Fuel Oil (5226-068)			Distillation Column Bottoms (5226-069)		
	S9 (μ l)	μ g/ Plate	Revertant Colonies	S9 (μ l)	μ g/ Plate	Revertant Colonies	S9 (μ l)	μ g/ Plate	Revertant Colonies
A ₃	20	0.0	33 $\pm$ 2	20	0.0	33 $\pm$ 2	20	0	33 $\pm$ 2
		0.2	47 $\pm$ 2		0.2	43 $\pm$ 5		2	44 $\pm$ 3
		0.4	52 $\pm$ 1		0.4	40 $\pm$ 5		4	56 $\pm$ 6
		0.8	36 $\pm$ 2		0.8	41 $\pm$ 1		8	60 $\pm$ 9
		1.0	36 $\pm$ 1		1.0	37 $\pm$ 2		10	55 $\pm$ 2
		2.0	37 $\pm$ 1		2.0	41 $\pm$ 3		20	52 $\pm$ 7
		5.0	38 $\pm$ 2		5.0	49 $\pm$ 9		50	114 $\pm$ 11
A ₄	20	0	39 $\pm$ 9	20	0	33 $\pm$ 2	20	0	33 $\pm$ 2
		2	36 $\pm$ 5		2	47 $\pm$ 8		2	45 $\pm$ 1
		4	40 $\pm$ 5		4	44 $\pm$ 0		4	47 $\pm$ 2
		8	25 $\pm$ 5		8	37 $\pm$ 2		8	40 $\pm$ 5
		10	29 $\pm$ 1		10	51 $\pm$ 4		10	41 $\pm$ 1
		20	37 $\pm$ 1		20	44 $\pm$ 3		20	44 $\pm$ 6
		50	36 $\pm$ 4		50	56 $\pm$ 2		50	45 $\pm$ 5

TABLE A5. Raw Dose Response Data for the *S. typhimurium* TA98 Mutagenicity Testing of Crude ITSL Deashed SRC Feeds

Start-Up (5226-074)				680°F (5226-080)				700°F (5226-102)			
S9 (μl)	μg/ Plate	Revertant Colonies		S9 (μl)	μg/ Plate	Revertant Colonies		S9 (μl)	μg/ Plate	Revertant Colonies	
		Experiment				Experiment				Experiment	
		A	B			A	B			A	B
20	0	77 ± 0	48 ± 4	20	0	39 ± 1	35 ± 2	20	0	33 ± 1	53 ± 3
	2	75 ± 8	61 ± 11		2	41 ± 3	43 ± 3		2	---	81 ± 10
	4	84 ± 1	62 ± 7		4	48 ± 5	31 ± 8		4	---	54 ± 4
	8	85 ± 2	53 ± 13		8	92 ± 22	56 ± 6		8	---	58 ± 15
	10	87 ± 7	69 ± 11		10	104 ± 5	50 ± 9		10	31 ± 2	68 ± 10
	20	103 ± 5	67 ± 12		20	179 ± 15	91 ± 2		20	40 ± 5	91 ± 17
	50	107 ± 4	105 ± 1		50	239 ± 1	114 ± 15		50	43 ± 2	105 ± 0
								100			
720°B (5226-063)				740-750°F (5226-066)							
S9 (μl)	μg/ Plate	Revertant Colonies		S9 (μl)	μg/ Plate	Revertant Colonies					
		Experiment				Experiment					
		A ^a	B			A ^a	B				
20	0		39 ± 6	20	0		65 ± 19				
	2		43 ± 7		2		60 ± 13				
	4		47 ± 7		4		52 ± 9				
	8		54 ± 0		8		90 ± 4				
	10		59 ± 2		10		79 ± 17				
	20		81 ± 1		20		127 ± 1				
	50		109 ± 7		50		106 ± 19				

^aSee Tables A3 and A4 for Experiment A data for 720°B (5226-063) and 740° (5226-066) materials.

APPENDIX B

QUANTITATIVE DATA FOR THE PAH AND N-PAC COMPOUNDS IDENTIFIED IN EACH SAMPLE COLLECTED DURING NTSL RUN 241 AND ITSL RUN 242-720°B ARE CONTAINED IN THIS APPENDIX. IDENTIFICATIONS ARE BASED ON GC RETENTION DATA AND GC/MS INFORMATION. TABLES B1 TO B4 PRESENT QUANTITATIVE DATA FOR THE PAH FRACTIONS, A_2 , OF PROCESS MATERIALS FROM THE SRC AND HTR UNITS. TABLES B5 TO B8 PRESENT DATA FOR THE N-PAC, A_3 , FOR THE SAME SAMPLES.

TABLE B1. Concentrations of Selected Compounds Determined by HRGC in PAH Fractions Isolated from SRC Reactor Products in the NTSI Mode Run #241

Compound	SRC Products (Concentration, $\mu\text{g/g}$)			
	Light Fuel Oil (5226-018)	1st-Stage Product Distillate (5226-019)	Deashed SRC (5226-020)	Ash Concentrate (5226-025)
Naphthalene	38000 $\pm$ 1500			
2-Methylnaphthalene	33300 $\pm$ 6200	18700 $\pm$ 700		
1-Methylnaphthalene	5400 $\pm$ 260	6020 $\pm$ 230		
Biphenyl	5280 $\pm$ 190	5420 $\pm$ 480		
2-Ethylnaphthalene	8200 $\pm$ 280	21400 $\pm$ 1000		
2,6- or 2,7-Dimethylnaphthalene	11500 $\pm$ 1200	41600 $\pm$ 2100		
1,7-Dimethylnaphthalene	3580 $\pm$ 150	19100 $\pm$ 600		
1,6- or 1,3-Dimethylnaphthalene	1730 $\pm$ 120	10200 $\pm$ 1200		
2,3- or 1,4-Dimethylnaphthalene	3160 $\pm$ 110	19900 $\pm$ 1500		
1,2-Dimethylnaphthalene	334 $\pm$ 20	3050 $\pm$ 170		
Acenaphthene	1780 $\pm$ 80	14300 $\pm$ 600		
Dibenzofuran	1710 $\pm$ 90	13200 $\pm$ 1300		
2,3,6-Trimethylnaphthalene	639 $\pm$ 39	8170 $\pm$ 600		
Fluorene	1710 $\pm$ 80	24000 $\pm$ 1200		
Dihydrofluorene (m/z 168)	2450 $\pm$ 130	40300 $\pm$ 1100		
2-Methylfluorene	1040 $\pm$ 30	14700 $\pm$ 500		
Methyldihydrofluorene ^a (m/z 182)	2370 $\pm$ 90	31300 $\pm$ 2000	154	
Dibenzothiophene	1290 $\pm$ 40	18800 $\pm$ 900	141	
Phenanthrene	3820 $\pm$ 130	44800 $\pm$ 1200	1550 $\pm$ 205	2270 $\pm$ 400
Anthracene		3290 $\pm$ 580		
3-Methylphenanthrene	942 $\pm$ 7	6540 $\pm$ 280	877 $\pm$ 56	965 $\pm$ 90
2-Methylphenanthrene	1090 $\pm$ 40	6300 $\pm$ 340	1310 $\pm$ 171	1500 $\pm$ 250
9- or 4-Methylphenanthrene	187 $\pm$ 33	1970 $\pm$ 40	223	273
1-Methylphenanthrene	544 $\pm$ 75	2110 $\pm$ 50	257 $\pm$ 39	299
Dihydrofluoranthene (m/z 204)			164	

^aCo-elutes with 1-methylfluorene

TABLE B1. (Continued)

Compound	SRC Products (Concentration, µg/g)			
	Light Fuel Oil (5226-018)	1st-Stage Product Distillate (5226-019)	Deashed SRC (5226-020)	Ash Concentrate (5226-025)
Fluoranthene	800 ± 200	324	1570 ± 50	1720 ± 40
Pyrene	461 ± 59	231	3450 ± 207	4020 ± 160
Dihdropyrene ^b (m/z 204)			887 ± 36	750 ± 50
Benzo[a]fluorene			1860 ± 418	1170 ± 360
Benzo[b]fluorene, 2- or 4-methylpyrene			5230 ± 333	4360 ± 130
m/z 218 ^c			3620 ± 641	2720 ± 420
1-Methylpyrene			1050 ± 263	878 ± 167
Benzo[b]naphtho[2,1,d]thiophene				909 ± 250
Benz[a]anthracene			3840 ± 263	3630 ± 510
Chrysene			5960 ± 453	5270 ± 770
3-Methylchrysene			5270 ± 772	4550 ± 940
2-Methylchrysene			2790 ± 454	2570 ± 460
6- or 4-Methylchrysene			4860 ± 955	3350 ± 580
1-Methylchrysene			1280 ± 149	895 ± 134
Benzo[j or b]fluoranthene			4440 ± 783	4180 ± 1100
Benzo[k]fluoranthene			3110 ± 630	2730 ± 650
Benzo[e]pyrene			1550 ± 351	2500 ± 790
Benzo[a]pyrene			5950 ± 1160	5920 ± 1710
Perylene			601 ± 120	
Indeno[1,2,3-cd]pyrene			990 ± 252	2570 ± 1010
Dibenz[a,h, or a,c]anthracene			667 ± 188	1140
Benzo[g,h,i]perylene			2000 ± 557	3330 ± 1070

^bOr phenylnaphthalene^cPossibly methylphenylnaphthalene

TABLE B2. Concentrations of Selected Compounds Determined by HRGC in PAH Fractions Isolated from HTR Products in the NTSL Mode Run #241

Compound	HTR Products (Concentration, $\mu\text{g/g}$)			
	Feed (5226-021)	Light Fuel Oil (5226-023)	Distillation Column Bottoms (5226-022)	Vacuum Flash Bottoms (5226-024)
Naphthalene	476 $\pm$ 37		1010 $\pm$ 50	
2-Methylnaphthalene	5160 $\pm$ 130	4580 $\pm$ 160	4290 $\pm$ 150	
1-Methylnaphthalene	923 $\pm$ 55	656 $\pm$ 57	905 $\pm$ 30	
Biphenyl	1620 $\pm$ 100	2990 $\pm$ 200	970 $\pm$ 60	
2-Ethylnaphthalene	2300 $\pm$ 50	5790 $\pm$ 240	1340 $\pm$ 50	
2,6- or 2,7-Dimethylnaphthalene	2640 $\pm$ 120	3200 $\pm$ 160	2000 $\pm$ 70	
1,7-Dimethylnaphthalene	1380 $\pm$ 260	1560 $\pm$ 90	963 $\pm$ 21	
1,6- or 1,3-Dimethylnaphthalene	1450 $\pm$ 250		783 $\pm$ 54	
2,3- or 1,4-Dimethylnaphthalene	1690 $\pm$ 210	3150 $\pm$ 160	965 $\pm$ 28	
1,2-Dimethylnaphthalene	332			
Acenaphthene	1460 $\pm$ 240	1130 $\pm$ 160	723 $\pm$ 71	
Dibenzofuran	706 $\pm$ 65	955 $\pm$ 176	438 $\pm$ 35	
2,3,6-Trimethylnaphthalene	378	637 $\pm$ 133	287 $\pm$ 24	
Fluorene	1800 $\pm$ 80	470 $\pm$ 95	1490 $\pm$ 100	
Dihydrofluorene (m/z 168)	10200 $\pm$ 300	2260 $\pm$ 10	8450 $\pm$ 1500	
2-Methylfluorene	2180 $\pm$ 420	93	2200 $\pm$ 230	
Methyldihydrofluorene ^a (m/z 182)	7790 $\pm$ 220	437 $\pm$ 53	7740 $\pm$ 670	
Phenanthrene	3820 $\pm$ 60	141	3160 $\pm$ 320	
Anthracene	1410 $\pm$ 30		1160 $\pm$ 170	
3-Methylphenanthrene	1080 $\pm$ 30		1500 $\pm$ 100	
2-Methylphenanthrene	2100 $\pm$ 190		2660 $\pm$ 50	
9- or 4-Methylphenanthrene	1090 $\pm$ 590		1110 $\pm$ 340	
1-Methylphenanthrene	1200 $\pm$ 440		1680 $\pm$ 500	
Dihydrofluoranthene (m/z 204)	2960 $\pm$ 60		4880 $\pm$ 500	

^aCo-elutes with 1-methylfluorene

TABLE B2. (Continued)

Compound	HTR Products (Concentration, $\mu\text{g/g}$)			
	Feed (5226-021)	Light Fuel Oil (5226-023)	Distillation Column Bottoms (5226-022)	Vacuum Flash Bottoms (5226-024)
Fluoranthene	597 $\pm$ 64		752 $\pm$ 6	
Pyrene	8260 $\pm$ 190		13300 $\pm$ 160	732 $\pm$ 18
Dihdropyrene ^b (m/z 204)	1210 $\pm$ 230		1640 $\pm$ 200	
Benzo[a]fluorene	832 $\pm$ 152		1770 $\pm$ 170	
Benzo[b]fluorene, 2- or 4-methylpyrene	7150 $\pm$ 120		11400 $\pm$ 900	880 $\pm$ 51
m/z 218 ^c	3090 $\pm$ 740		4400 $\pm$ 1650	146
1-Methylpyrene	530 $\pm$ 387		1020 $\pm$ 640	47
Benz[a]anthracene	338 $\pm$ 72		1040 $\pm$ 440	83
Chrysene	1700 $\pm$ 600		2570 $\pm$ 420	334 $\pm$ 35
3-Methylchrysene	1050 $\pm$ 308		786 $\pm$ 172	252
2-Methylchrysene	754 $\pm$ 605		64	26
6- or 4-Methylchrysene	4480 $\pm$ 395		7170 $\pm$ 160	3200 $\pm$ 170
1-Methylchrysene				346 $\pm$ 70
Tetrahydrobenzofluoranthene (m/z 256)				1330 $\pm$ 80
Benzo[j or b]fluoranthene	554 $\pm$ 307		505 $\pm$ 168	307 $\pm$ 78
Benzo[k]fluoranthene				434 $\pm$ 35
Tetrahydrobenzopyrene (m/z 256)				1090 $\pm$ 50
Benzo[e]pyrene	661		828 $\pm$ 34	850 $\pm$ 10
Benzo[a]pyrene	868 $\pm$ 285		233 $\pm$ 51	771 $\pm$ 214
Indeno[1,2,3-cd]pyrene	273		305	1530 $\pm$ 370
Dibenz[a,h, or a,c]anthracene				396 $\pm$ 212
Benzo[g,h,i]perylene	594 $\pm$ 35		608 $\pm$ 40	4920 $\pm$ 660
Coronene				1610

^bOr phenylnaphthalene^cPossibly methylphenylnaphthalene

TABLE B3. Concentrations of Selected Compounds Determined by HRGC in PAH Fractions Isolated from SRC Reactor Products in the ITSL Mode Run #242-720°B

Compound	SRC Products (Concentration, µg/g)				Ash Concentrate (5226-060)
	Light Fuel Oil (5226-055)	Distillate Process Solvent (5226-056)	1st-Stage Product Distillate (5226-057)	Deashed SRC (5226-063)	
Naphthalene	45000 ± 1700		1130 ± 60		
2-Methylnaphthalene	64600 ± 2800	2500 ± 100	25200 ± 400		
1-Methylnaphthalene	15300 ± 600	923 ± 39	8540 ± 850		
Biphenyl	9100 ± 200	233 ± 11	2430 ± 290		
2-Ethyl naphthalene	13400 ± 400	1290 ± 60	11300 ± 600		
2,6- or 2,7-Dimethylnaphthalene	21700 ± 3300	1240 ± 190	10300 ± 500		
1,7-Dimethylnaphthalene	9140 ± 330	1250 ± 90	9800 ± 520		
1,6- or 1,3-Dimethylnaphthalene	4950 ± 530	944 ± 40	7810 ± 290		
2,3- or 1,4-Dimethylnaphthalene	8110 ± 830	1310 ± 60	8540 ± 420		
1,2-Dimethylnaphthalene	1110 ± 10	308	2200 ± 110		
Acenaphthene	4320 ± 170	832 ± 53	5500 ± 450		
Dibenzofuran	3550 ± 140	769 ± 300	5490 ± 1080		
2,3,6-Trimethylnaphthalene	2330 ± 190	354 ± 180	2760 ± 140		
Fluorene	5420 ± 270	439 ± 159	2990 ± 500		
Dihydrofluorene (m/z 168)	10800 ± 700	4800 ± 240	24200 ± 3600		
Dihydrofluorene (m/z 168)	12300 ± 400	4210 ± 260	21100 ± 1700		
2-Methylfluorene	5220 ± 420	1430 ± 90	1770 ± 150		
Methyldihydrofluorene ^a (m/z 182)	12700 ± 1000	4560 ± 400	14500 ± 600		
Dibenzothiophene	8800 ± 1110				
Phenanthrene	27500 ± 2500	3510 ± 170	8260 ± 330		24
Anthracene	1780 ± 710				
3-Methylphenanthrene	10300 ± 700	1700 ± 180	2800 ± 170		105 ± 13
2-Methylphenanthrene	10500 ± 600	2370 ± 130	3960 ± 90		93 ± 3
9- or 4-Methylphenanthrene	3400 ± 40	2360 ± 190	3590 ± 120		

^a Co-elutes with 1-methylfluorene

TABLE B3. (Continued)

Compound	SRC Products (Concentration, µg/g)				
	Light Fuel Oil (5226-055)	Distillate Process Solvent (5226-056)	1st-Stage Product Distillate (5226-057)	Deashed SRC (5226-063)	Ash Concentrate (5226-060)
1-Methylphenanthrene	4060 ± 160	1890 ± 110	2850 ± 130		10
Dihydrofluoranthene (m/z 204)	1740 ± 250	2500 ± 370	1920 ± 250		
Fluoranthene	4120 ± 210	1570 ± 130	1680 ± 300		81 ± 8
Pyrene	4290 ± 1040	7850 ± 190	6270 ± 180	1180 ± 60	642 ± 22
Dihdropyrene ^b (m/z 204)	1960 ± 670	1270 ± 130	1050 ± 90	97	
Benzo[a]fluorene	2130 ± 120				76 ± 32
Benzo[b]fluorene, 2- or 4- methylpyrene	3760 ± 260	8290 ± 420	4810 ± 260	1360 ± 160	652 ± 91
m/z 218 ^c	3880 ± 400	5300 ± 800	3450 ± 230	677 ± 73	282 ± 23
1-Methylpyrene	713 ± 200	1690 ± 470	993 ± 62	287 ± 13	97 ± 22
Benz[a]anthracene				315 ± 37	184 ± 33
Chrysene				342 ± 125	258 ± 25
3-Methylchrysene					267 ± 21
2-Methylchrysene				159 ± 13	85 ± 25
6- or 4-Methylchrysene	296	5310 ± 120	1760 ± 350	2930 ± 280	1310 ± 100
1-Methylchrysene				288 ± 136	241 ± 55
Benzo[j or b]fluoranthene		758 ± 102	325	1050 ± 150	498 ± 50
Benzo[k]fluoranthene		658		784	458 ± 131
Benzo[e]pyrene		628 ± 131	300	879 ± 22	818 ± 114
Benzo[a]pyrene		1170 ± 160	626 ± 113	2250 ± 190	1350 ± 200
Perylene					427 ± 157
Indeno[1,2,3-cd]pyrene		631 ± 71		500	855 ± 164
Dibenz[a,h, or a,c]anthracene					160 ± 95
Benzo[g,h,i]perylene		572 ± 10		2530 ± 570	2340 ± 310
Coronene					403 ± 78

^bor phenylnaphthalene^cPossibly methylphenylnaphthalene

TABLE B4. Concentrations of Selected Compounds Determined by HRGC in PAH Fractions Isolated from HTR Products in the ITSL Mode Run #242-720°B

Compound	HTR Products (Concentration, µg/g)			
	Feed (5226-061)	Light Fuel Oil (5226-062)	Distillation Column Bottoms (5226-059)	Recycle Pasting Solvent (5226-058)
Naphthalene		22300 ± 5800	293 ± 31	
2-Methylnaphthalene	1760 ± 30	20400 ± 4800	6580 ± 320	307 ± 39
1-Methylnaphthalene	547 ± 9	3620 ± 1110	1320 ± 130	
Biphenyl	248 ± 27	8260 ± 840	3060 ± 150	134 ± 20
2-Ethyl-naphthalene	951 ± 35	4960 ± 2460	3620 ^a ± 160	
2,6- or 2,7-Dimethylnaphthalene	796 ± 67	16300 ± 4790	2840 ± 190	
1,7-Dimethylnaphthalene	759 ± 36	1280 ± 533	1980 ± 130	
1,6- or 1,3-Dimethylnaphthalene	673 ± 19	1020		
2,3- or 1,4-Dimethylnaphthalene	882 ± 2	1530	2500 ± 90	
1,2-Dimethylnaphthalene	124		447 ± 47	
Acenaphthene	571 ± 45	545		
Dibenzofuran	440 ± 250	137	3110 ± 120	
2,3,6-Trimethylnaphthalene	292 ± 120		1280 ± 40	
Fluorene	404 ± 78	472	2590 ± 150	258 ± 15
Dihydrofluorene (m/z 168)	3430 ± 110	518	9150 ± 370	758 ± 78
Dihydrofluorene (m/z 168)	2640 ± 700		4780 ± 230	
2-Methylfluorene	319 ± 170	35	1290 ± 100	462 ± 48
Methyldihydrofluorene ^a (m/z 182)	3020 ± 390	132	10200 ± 300	1650 ± 280
Phenanthrene	2430 ± 200	120	5360 ± 640	1260 ± 220
3-Methylphenanthrene	1020 ± 110	143	1660 ± 110	324 ± 6
2-Methylphenanthrene	1630 ± 220	80	3250 ± 140	532 ± 24
9- or 4-Methylphenanthrene	1460 ± 180		2010 ± 610	558 ± 51
1-Methylphenanthrene	1200 ± 180	25	1870 ± 400	312 ± 97

^aCo-elutes with m/z 160

TABLE B4. (Continued)

Compound	HTR Products (Concentration, µg/g)			
	Feed (5226-061)	Light Fuel Oil (5226-062)	Distillation Column Bottoms (5226-059)	Recycle Pasting Solvent (5226-058)
Dihydrofluoranthene (m/z 204)	866 ± 51		2580 ^b ± 160	940 ± 32
Fluoranthene	872 ± 46		1020 ± 80	
Pyrene	4210 ± 120		5320 ± 210	2080 ± 230
Dihdropyrene ^d (m/z 204)	694 ± 170		1130 ± 110	
Benzo[b]fluorene, 2- or 4-methylpyrene	4210 ± 640		4150 ± 80	1600 ± 280
m/z 218 ^e	2930 ± 640		3050 ± 40	1380 ± 290
1-Methylpyrene	878 ± 186		961 ± 78	445 ± 111
6- or 4-Methylchrysene	3100 ± 270		1490 ± 150	1730 ± 110
Benzo[j or b]fluoranthene			118 ± 11	
Benzo[e]pyrene	791 ± 133		182	
Benzo[a]pyrene	1620 ± 240		279 ± 166	73

^bCo-elutes with m/z 208, hexahydrofluoranthene

^cCo-elutes with 1-methylfluorene

^dOr phenylnaphthalene

^ePossibly methylphenylnaphthalene

TABLE B5. Concentrations of Selected Compounds Determined by HRGC in N-PAC Fractions Isolated from SRC Reactor Products in the NTSL Mode Run #241

Compound	SRC Products (Concentration, $\mu\text{g/g}$)			
	Light Fuel Oil (5226-018)	1st-Stage Product Distillate (5226-019)	Deashed SRC (5226-020)	Ash Concentrate (5226-025)
C ₁ -Phenol (m/z 108)	4200 $\pm$ 300			
C ₂ -Phenols ^a (m/z 122)	90900 $\pm$ 21500			
Tetrahydroquinoline		4270 $\pm$ 610		
Quinoline	2700 $\pm$ 500	13200 $\pm$ 1710		
Isoquinoline		2270 $\pm$ 250		
C ₃ -Phenols ^a (m/z 136)	9500 $\pm$ 2000			
C ₁ -Tetrahydroquinoline		7000 $\pm$ 810		
Indole		22500 $\pm$ 3800		
2-Methylquinoline	2300 $\pm$ 500	25400 $\pm$ 1900		
8-Methylquinoline	620	3570 $\pm$ 1350		
C ₄ -Phenols ^b (m/z 150)	3900 $\pm$ 700			
7-Methylquinoline	340	18300 $\pm$ 1900		
3-Methylquinoline		13800 $\pm$ 900		
3-Methylindole		26600 $\pm$ 2800		
2,6- or 2,7-Dimethylquinoline	3000 $\pm$ 300	28100 $\pm$ 4500		
2,5-Dimethylindole		13100 $\pm$ 2000		
2,3-Dimethylindole		11700 $\pm$ 2300		
Benzo[h]quinoline		850 $\pm$ 185		
Acridine		631		
Benzo[f]quinoline, phenanthridine		962 $\pm$ 47		
Carbazole	480	7940 $\pm$ 170	18 $\pm$ 3	18 $\pm$ 1
1-Methylcarbazole		1480 $\pm$ 70	6 $\pm$ 1	6
3-Methylcarbazole		1490 $\pm$ 80	18 $\pm$ 1	16 $\pm$ 1
2-Methylcarbazole		869	9	4

^aComposite of 3 peaks

^bComposite of 2 peaks

TABLE B5. (Continued)

Compound	SRC Products (Concentration, $\mu\text{g/g}$)			
	Light Fuel Oil (5226-018)	1st-Stage Product Distillate (5226-019)	Deashed SRC (5226-020)	Ash Concentrate (5226-025)
4-Methylcarbazole			13	13
4-Azapyrene, azafluoranthene			13	5 ± 1
Benzo[a]carbazole			29 ± 8	26 ± 2
Benzo[b]carbazole			31	9 ± 6
Benzo[c]carbazole			68 ± 56	32 ± 3
Dibenzo[a,i]carbazole			1	
Dibenzo[a,g or c,g]carbazole			3	

TABLE B6. Concentrations of Selected Compounds Determined by HRGC in N-PAC Fractions Isolated from HTR Products in the NTSL Mode Run #241

Compound	HTR Products (Concentration, $\mu\text{g/g}$)			
	Feed (5226-021)	Light Fuel Oil (5226-023)	Distillation Column Bottoms (5226-022)	Vacuum Flash Bottoms (5226-024)
C ₁ -Phenol (m/z 108)		57900 $\pm$ 200		
C ₂ -Phenols ^a (m/z 122)		83200 $\pm$ 3200		
Quinoline		16700 $\pm$ 3100		
C ₃ -Phenols ^a (m/z 136)		43900 $\pm$ 2400		
2-Methylquinoline		9170 $\pm$ 2540		
8-Methylquinoline		1370 $\pm$ 110		
C ₄ -Phenols ^a (m/z 150)		28910 $\pm$ 6620		
7-Methylquinoline		5070 $\pm$ 150		
2,6- or 2,7-Dimethylquinoline		3150 $\pm$ 1130		
Octahydrobenzoquinoline (m/z 187)			732 $\pm$ 98	
Benzo[h]quinoline	208 $\pm$ 40			
C ₁ -Octahydrobenzoquinoline (m/z 201)			1080 $\pm$ 360	
Tetrahydrocarbazole (m/z 171)			620 $\pm$ 63	
Benzo[f]quinoline, phenanthridine	113 $\pm$ 18			
Octahydrobenzoquinoline (m/z 187)			770 $\pm$ 98	
Carbazole	254 $\pm$ 63	137	1950 $\pm$ 270	
2- or 3-Methylbenzo[f]quinoline	108 $\pm$ 11		322 $\pm$ 141	
1-Methylcarbazole	164 $\pm$ 14		1380 $\pm$ 140	
3-Methylcarbazole	258 $\pm$ 3		1570 $\pm$ 320	
2-Methylcarbazole	205 $\pm$ 2		1430 $\pm$ 300	
4-Methylcarbazole	199 $\pm$ 8		877 $\pm$ 161	
Hexahydroazafluoranthene (m/z 209)			1020 $\pm$ 160	
C ₁ -Hexahydroazafluoranthene (m/z 223)			749 $\pm$ 330	
4-Azapyrene, azafluoranthene	250 $\pm$ 23		1030 $\pm$ 540	

^aComposite of 3 peaks

TABLE B6. (Continued)

Compound	HTR Products (Concentration, µg/g)			
	Feed (5226-021)	Light Fuel Oil (5226-023)	Distillation Column Bottoms (5226-022)	Vacuum Flash Bottoms (5226-024)
C ₁ -Hexahydroazafluoranthene (m/z 223)			1000 ± 410	
C ₁ -Azapyrene, azabenzofluorene			684 ± 273	
C ₁ -Azapyrene, azabenzofluorene			1810 ± 430	
Tetrahydrobenzocarbazoles ^a (m/z 221)			4740 ± 1193	
Benzo[a]carbazole	181 ± 89		669 ± 97	4
1-Azachrysene			1170 ± 170	
Benzo[b]carbazole	54 ± 27		256	
Benzo[c]carbazole ^b	358		1820 ± 210	8
Azabenzopyrenes			883 ± 177	
Dibenzo[a,i]carbazole	20		157 ± 61	
Dibenzo[a,g or c,g]carbazole	94		286 ± 86	

^aComposite of 3 peaks^bComposite of 2 peaks

TABLE B7. Concentrations of Selected Compounds Determined by HRGC in N-PAC Fractions Isolated from SRC Reactor Products in the ITSL Mode Run #242-720°B

Compound	SRC Products (Concentration, µg/g)				
	Light Fuel Oil (5226-055)	Distillate Process Solvent (5226-056)	1st-Stage Product Distillate (5226-057)	Deashed SRC (5226-063)	Ash Concentrate (5226-060)
C ₁ -Phenol (m/z 108)	1120 ± 210				
C ₂ -Phenols ^a (m/z 122)	64200 ± 2300				
Quinoline	8320 ± 1320		1350 ± 80		
Isoquinoline	304		750 ± 590		
C ₃ -Phenols ^a (m/z 136)	33100 ± 6900				
Indole		398 ± 62			
2-Methylquinoline	8040 ± 490	609 ± 27	3250 ± 170		
8-Methylquinoline	4580 ± 230	179 ± 127	2970 ± 520		
C ₄ -Phenols ^c (m/z 150)	10600 ± 2000		5070 ± 560		
7-Methylquinoline	7350 ± 290	835 ± 254	4760 ± 1440		
3-Methylquinoline	8540 ^d ± 830	139 ± 32	2650 ± 1560		
4-Methylquinoline		692 ± 208	3530 ± 410		
2,6- or 2,7-Dimethylquinoline	8480 ± 540	1960 ± 250	3320 ± 1020		
1,2-Dimethylquinoline		1090 ± 140	2850 ± 1040		
Benzo[h]quinoline	1120 ± 380	467 ± 134	252 ± 21		
Benzo[f]quinoline, phenanthridine	3600 ± 240	535 ± 107	470 ± 22		
Carbazole	12300 ± 300	1050 ± 250	967 ± 75		
2- or 3-Methylbenzo[f]quinoline	1690 ± 40	1000 ± 90	537 ± 71		
1-Methylcarbazole	3690 ± 60	901 ± 309	785 ± 148		
3-Methylcarbazole	7540 ± 920	2350 ± 270	1320 ± 120		
2-Methylcarbazole	4060 ± 230	1020 ± 90	660 ± 27		

^aComposite of 3 peaks

^bAll components present at less than 5 ppm

^cComposite of 2 peaks

^dCo-elutes with m/z 150

TABLE B7. (Continued)

Compound	SRC Products (Concentration, µg/g)				
	Light Fuel Oil (5226-055)	Distillate Process Solvent (5226-056)	1st-Stage Product Distillate (5226-057)	Deashed SRC (5226-063)	Ash Concentrate (5226-060)
4-Methylcarbazole	2440 ± 300	1110 ± 480	537		
4-Azapyrene, azafluoranthene	1240 ± 250	1390 ± 380			33
Benzo[a]carbazole	383	572 ± 40			
Benzo[b]carbazole		511			
Benzo[c]carbazole		735 ± 164			

^b All components present at less than 5 ppm

TABLE B8. Concentrations of Selected Compounds Determined by HRGC in N-PAC Fractions Isolated from HTR Products in the ITSL Mode Run #242-720°B

Compound	HTR Products (Concentration, µg/g)			
	Feed (5226-021)	Light Fuel Oil (5226-023)	Distillation Column Bottoms (5226-022)	Vacuum Flash Bottoms (5226-024)
C ₁ -Phenol (m/z 108)		94 ± 10		
C ₂ -Phenols ^a (m/z 122)		727 ± 268		
Quinoline		1610 ± 170		
C ₃ -Phenols (m/z 136)		1710 ± 410		
Indole	17 ± 2			
2-Methylquinoline	12	786 ^b ± 102	376 ± 127	
8-Methylquinoline	12 ± 1	1180 ± 100		
C ₄ -Phenols		243 ± 67	773 ± 168	
7-Methylquinoline		430 ± 42		
2,6- or 2,7-Dimethylquinoline	39 ± 39	340 ± 168	2240 ± 1090	
Benzo[h]quinoline	37 ± 16		987 ± 258	
Benzo[f]quinoline, Phenanthridine	44		1130 ± 380	
Carbazole	49 ± 9		2250 ± 330	<20
2- or 3-Methybenzo[f]quinoline	51 ± 10		673 ± 100	
1-Methylcarbazole	26 ± 6		1720 ± 300	<20
3-Methylcarbazole	90 ± 25		1540 ± 100	<20
2-Methylcarbazole	55 ± 2		1350 ± 280	<20
4-Methylcarbazole	68 ± 14		1220 ± 160	<20
4-Azapyrene, Azafluoranthene	69 ± 14		838 ± 120	
Benzo[a]carbazole	33 ± 17			
Benzo[b]carbazole	5			
Benzo[c]carbazole	53			

^aComposite of 3 peaks

^bCo-elutes with m/z 150

APPENDIX C

LOW VOLTAGE, PROBE INLET MASS SPECTRA ARE CONTAINED IN THIS APPENDIX OF CHEMICAL CLASS FRACTIONS A_1 , A_2 , A_3 , and A_4 OF THE FOLLOWING NTSL/ITSL PROCESS MATERIALS: ITSL SRC DISTILLATE PROCESS SOLVENT (T-102, TRAY 8; PNL #5226-056), NTSL HTR FEED (PNL #5226-021), ITSL HTR FEED (PNL #5226-0610, NTSL HTR DISTILLATION COLUMN BOTTOMS (PNL #5226-022), AND ITSL HTR DISTILLATION COLUMN BOTTOMS (PNL #5226-059). THREE TABLES FOR INTERPRETATION OF POSSIBLE MASS IDENTIFICATIONS FOR ALKYLATED NEUTRAL PAH, HYDROXY-PAH, AND N-PAC HAVE ALSO BEEN INCLUDED AS KEYS TO THE FIGURES.

TABLE C1. 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
Phenyl-naphthalene	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
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/ 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.

TABLE C2. Key to 12-eV Mass Spectra: Nominal Masses for Alkylated Homologous Series of Representative N-PAC

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/Iso-quinoline	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/Aza-fluoranthene	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 N-PAC have been considered. Hydro-substituted N-PAC 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.

TABLE C3. 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.

FIGURE C1. 12-eV Mass Spectrum of Fraction A₁ of the ITSL SRC Distillate (056) Process Solvent.

FIGURE C2. 12-eV Mass Spectrum of Fraction A₂ of the ITSL SRC Distillate (056) Process Solvent.

FIGURE C3. 12-eV Mass Spectrum of Fraction A₃ of the ITSL SRC Distillate (056) Process Solvent.

FIGURE C4. 12-eV Mass Spectrum of Fraction A₄ of the ITSL SRC Distillate (056) Process Solvent.

FIGURE C5. 12-eV Mass Spectrum of Fraction A₁ of the NTSL HTR Feed (021).

FIGURE C6. 12-eV Mass Spectrum of Fraction A₂ of the NTSL HTR Feed (021).

FIGURE C7. 12-eV Mass Spectrum of Fraction A₃ of the NTSL HTR Feed (021).

FIGURE C8. 12-eV Mass Spectrum of Fraction A₄ of the NTSL HTR Feed (021).

FIGURE C9. 12-eV Mass Spectrum of Fraction A₁ of the ITSL HTR Feed (061).

FIGURE C10. 12-eV Mass Spectrum of Fraction A₂ of the ITSL HTR Feed (061).

FIGURE C11. 12-eV Mass Spectrum of Fraction A₃ of the ITSL HTR Feed (061).

FIGURE C12. 12-eV Mass Spectrum of Fraction A₄ of the ITSL HTR Feed (061).

FIGURE C13. 12-eV Mass Spectrum of Fraction A₁ of the NTSL HTR Distillation Column Bottoms (022).

FIGURE C14. 12-eV Mass Spectrum of Fraction A₂ of the NTSL HTR Distillation Column Bottoms (022).

FIGURE C15. 12-eV Mass Spectrum of Fraction A₃ of the NTSL HTR Distillation Column Bottoms (022).

FIGURE C16. 12-eV Mass Spectrum of Fraction A₄ of the NTSL HTR Distillation Column Bottoms (022).

FIGURE C17. 12-eV Mass Spectrum of Fraction A₁ of the ITSL HTR Distillation Column Bottoms (059).

FIGURE C18. 12-eV Mass Spectrum of Fraction A₂ of the ITSL HTR Distillation Column Bottoms (059).

FIGURE C19. 12-eV Mass Spectrum of Fraction A₃ of the ITSL HTR Distillation Column Bottoms (059).

FIGURE C20. 12-eV Mass Spectrum of Fraction A₄ of the ITSL HTR Distillation Column Bottoms (059).

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