Biological Testing and Chemical Analysis of Materials from an Integrated Two Stage Coal Liquefaction Process: A Status Report

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September 1983

**Prepared for the U.S. Department of Energy
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**Pacific Northwest Laboratory
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BIOLOGICAL TESTING AND CHEMICAL ANALYSIS OF
PROCESS MATERIALS FROM AN INTEGRATED TWO
STAGE COAL LIQUEFACTION: A STATUS REPORT

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FOREWORD

This document reports results from laboratory tests for mutagenicity and carcinogenicity as well as from chemical analysis on process streams from an Integrated Two Stage Liquefaction (ITSL) Process Development Unit (PDU). This particular process is currently being developed by C. E. Lummus with major funding from the Assistant Secretary for Fossil Energy, U.S. Department of Energy. Where possible, results obtained from ITSL materials are compared to those from other direct liquefaction processes such as Solvent Refined Coal (SRC)-I and SRC-II. Work reported here was carried out by investigators in the Department of Biology and Chemistry, Pacific Northwest Laboratory, Richland, Washington.

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EXECUTIVE SUMMARY

Separation of the initial solvation or liquefaction from the hydrogenation or upgrading steps in direct coal liquefaction affords the opportunity to better optimize each as a unit operation. The Integrated Two Stage Liquefaction (ITSL) process currently being developed by C. E. Lummus, with support from the U.S. Department of Energy, integrates these separate functions to allow more efficient use of available hydrogen and thermal energy. ITSL relies on a low-severity short contact time (SCT) initial liquefaction step, followed by anti-solvent deashing and catalytic hydrogenation by a proprietary process called LC fining. Resids and underflow from the hydrogenation and deashing operations, respectively, make up the recycle solvent used to slurry fresh coal in the process.

Results from Process Development Unit (PDU) operations to date indicate that the SCT product can be effectively deashed by an antisolvent system; the SCT product can be upgraded by LC fining under fairly mild conditions without undue deactivation of the catalyst. The SCT approach results in minimal gas with most of the product oil produced in the 650° to 850°F boiling range.

Briefly, sets of samples were collected under normal operating conditions from runs 3LCF7 and 3LF9 during processing of Indiana No. 5 and Illinois No. 6 coal, respectively. Set 2 was taken during alternate operation, wherein feed to the LC finer catalytic hydrotreating unit was recycled back to the short contact time reactor, for an average of one cycle, prior to entering the LC finer for hydrotreatment to produce LC finer total liquid product. This mode of operation effectively increased the liquefaction reactor residence time for the process stream eventually entering the LC finer. This configuration does not constitute a regular operational mode for the ITSL process and was set up as a one time study only. Sample set 3 was collected subsequent to a significant exothermic excursion in the first two of three series-coupled LC fining reactors, during which their catalyst beds were exposed to temperatures as high as 900°F and 1000°F, respectively. It should be noted, however, that similar conditions may arise from catalyst deactivation resulting from extended run periods, etc.

Chemical analysis of these materials showed that SCT products were composed of fewer compounds than analogous materials from Solvent Refined Coal (SRC) processes. Major components in the SCT materials were three-, four-, five- and six-ring neutral polycyclic aromatic hydrocarbons (PAH). Methyl(C_1) and C_2 homologs of these compounds were present in relatively low concentrations, compared to their nonalkylated homologs. Organic nitrogen was primarily in the form of tertiary polycyclic aromatic nitrogen heterocycles (which will be designated here as 3°-PANH), and carbazoles (2°-PANH). Little or no amino PAH (APAH) or cyano PAH were detected in samples taken during normal PDU operations; however, mutagenic APAH were produced during off-normal operation as described below.

Compared to SRC materials, there were fewer different gas chromatographable organic compounds present in ITSL process streams; a fact which is due in part to higher initial boiling point of the ITSL liquids tested (650°F which is nominally 100°F higher than that of SRC-II). Comparison of LC finer product to SCT product material showed that substantial partial hydrogenation had occurred in the fining operation, with concurrent reduction in the heteroatom content and aromaticity of the LC finer product.

Catalyst condition in the LC finer reactors appeared to have substantial effect on chemical functional groups in the process streams as well as on their mutagenic activity: catalyst in good condition appeared to produce materials which were more highly hydrogenated and had substantially less mutagenicity than materials produced after the LC fining catalyst had undergone a slightly damaging exothermic temperature excursion. Total liquid product (TLP) from the LC finer produced during single recycle of the LC finer feed through the SCT reactor also showed increased mutagenic activity compared to products resulting from normal-mode operation. Mutagenic activity of both SCT and LC fining product materials, produced under normal operating conditions with good catalyst, was substantially lower than for SRC-II heavy distillate for example.

The ITSL process can generate a TLP which is low in mutagenic activity compared to the total liquids produced in the reactor of SRC-I and SRC-II processes. However, boiling ranges and composition of these materials are not directly comparable and none are analogous to products that would be produced

by a commercial facility. Thus, caution should be exercised when comparing mutagenicity of products produced by different processes.

Organic nitrogen was found in higher boiling distillate cuts in the ITSL process than in SRC processes. The difference is probably due to reduced C-N bond (thermolytic) scission in the ITSL SCT reactor. Microbial mutagenicity was attributed mainly to the presence of APAH. Formation of APAH was evident after an accidental exothermic temperature excursion of the catalyst bed, with much lower concentrations found in samples from normal LC finer operations. The slightly deactivated catalyst fails to promote deamination of nitrogen containing hydroaromatics. APAH were the most important microbial mutagens as shown by reduction of mutagenicity after nitrosation. However, measurements of APAH concentrations in the mutagenically-active fractions of the total liquid product (TLP) from the LC finer showed that the gas chromatographable APAH content alone was insufficient to account for all activity, suggesting possible synergism among TLP components.

Carcinogenic activity of ITSL materials, as assessed by tumors per animal in the initiation/promotion mouse skin painting assay, was slightly reduced for materials produced with good catalyst under normal operation compared to those collected during recycle of the LC finer feed. Initiation activity of the latter samples, however, were not significantly different from that of SRC-II coal-derived heavy distillate which has a lower initial boiling point. The observed initiation activity was not unexpected, considering analytical data which showed the presence of four-, five- and six-ring PAH in ITSL materials. However, if compared to SRC-II derived materials on an equivalent boiling range basis, the ITSL 650° to 850°F materials would probably be lower in initiating activity, since about 40 weight percent of the SRC-II heavy distillate boils between 550° and 650°F. For comparison, this would be equivalent to diluting the ITSL materials with 40 weight percent 650°F SRC-II distillate which has very low initiating activity.

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GLOSSARY

APAH	Amino Polycyclic Aromatic Compounds
APLC	Atmospheric Pressure Liquid Chromatography
B(a)P	Benzo(a)pyrene
CHO	Chinese Hamster Ovary (a mammalian cell assay for forward mutation)
DMBA	Dimethyl benzanthracene
ECD	Electron Capture Detector (for gas chromatograph)
GC	Gas Chromatography
GCMS	Gas Chromatography/Mass Spectrometry
HPAH	Hydroxylated Polycyclic Aromatic Hydrocarbons
HRGC	High Resolution Gas Chromatography
IOM	Insoluble Organic Matter
ITSL	Integrated Two Stage Liquefaction
LCF TLP	LC Finer Total Liquid Product
LCFF	LC Finer Feed
N-PAC	Nitrogen (containing) Polycyclic Aromatic Compounds
PAC	Polycyclic Aromatic Compounds
PAH	Polycyclic Aromatic Hydrocarbons
PANH	Polycyclic Aromatic Nitrogen Heterocycles
2°PANH	Secondary PANH (pyrrolic nitrogen compounds such as carbazole)
3°PANH	Tertiary PANH (aza compounds)
PASH	Polyaromatic Sulfur (containing) Heterocycles
PMA	Phorbol Myristate Acetate
SCT	Short Contact Time
TA98	Designation for strain of Salmonella used in Ames assay

TLP	Total Liquid Product
bp	boiling point
rev	revertants (reverted colonies in the Ames Salmonella Assay)

1.0 INTRODUCTION

1.1 PROGRAM OVERVIEW

The Department of Energy (DOE) is responsible for evaluating high-risk, potentially high-payoff energy technologies to provide a broad range of future energy options that are acceptable from a health and environmental standpoint. Energy technologies, as with most heavy industries, are likely to produce a variety of pollutants. Therefore control technologies to limit exposures to potentially harmful materials or upgrading/modification of harmful substances will be needed to ensure environmental acceptability.

Recognizing that a data base on health and environmental effects would be useful during early stages of technology development, DOE has supported research to evaluate changes in materials resulting from new technology developments, as well as feasible process modifications and/or refining and other upgrading options. Information developed by this research provides guidance for choosing among several seemingly equal technology options; for measuring the cost effectiveness of changing an instream process to minimize the need for end-of-stream emission or product controls; and for changing process configurations to modify product composition.

DOE has supported health and environmental studies on a number of energy technologies. For the coal conversion industry, one of the most important technologies is coal liquefaction. Coal liquefaction is a means by which abundant U.S. supplies of coal can be utilized to produce various liquid hydrocarbon products. These synthetic fuels can be used as petroleum substitutes or as more highly refined materials, blended with petroleum as additives or extenders. In the process, coal is dissolved under high temperature and pressure, hydrogen is added and the coal polymeric bonds are broken. Mineral ash is removed together with freed sulfur and nitrogen. The organic products are primarily aromatic hydrocarbons and heteroatom PAH species. These coal derived products generally have less sulfur than petroleum but may have 3 to 8 times the amount of oxygen and 4 to 10 times the amount of nitrogen.

Concerns have been raised about the potential adverse health and environmental effects which might be associated with coal liquefaction materials. For example, polyaromatic hydrocarbons present in coal liquids are known to produce tumors in laboratory animals. Early tests of full-boiling-range materials confirmed predictions that coal liquids were potentially more mutagenic and carcinogenic than petroleum or shale oil.

However, over the past few years significant advances have been made, not only in identifying causative bioactive agents but also in identifying potential engineering strategies to reduce or eliminate the concentrations of these compounds from coal liquefaction products. Research supported by DOE has identified major classes of compounds responsible for significant adverse health effects associated with coal liquids. APAH, for example, have been found to be the most active mutagens.⁽¹⁾ Multi-ring polycyclic aromatic hydrocarbons or similar compounds appear to be responsible for much of the potential carcinogenicity associated with coal liquid materials.⁽²⁾ The observation that these substances were concentrated in products boiling above 700°F⁽³⁾ was important in suggesting a number of mitigative methods and process configurations to minimize net production of these heavy-end materials. Product upgrading by post-production catalytic hydrotreatment of coal liquids was also investigated.⁽⁴⁾ Preliminary results indicate reduction in the bioactivity of full-boiling-range hydrotreated coal liquids.

In addition to process modifications and upgrading options, advanced second and third generation technology configurations show promise for reducing or eliminating bioactive materials from coal liquefaction products. One such process, two-stage liquefaction (TSL), appears to minimize production of aromatic amines. The <650°F product contains few of the potentially carcinogenic 4 and 5 ring PAHs. This status report presents a review of the TSL process and results of chemical and health related studies on materials produced during various process runs.

1.2 OBJECTIVES

A major goal for advanced development of 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 increase 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 effective process solvents are available.

Several process developers have chosen to separate, to the greatest extent possible, the initial coal solvation or liquefaction steps from subsequent hydrogenation or upgrading operations. This strategy allows hydrogen to be more effectively utilized, since it may be reacted directly with distillate materials which have been deashed and had most of their asphaltenic components removed. This approach also allows more effective use of catalysts to achieve denitrogenation and desulfurization and/or for hydrocracking of aromatic ring systems.

With regard to environmental and health concerns, our present understanding of the effects of certain process parameters on the biological activity of various coal liquids suggests that these same approaches may also reduce biological activity of process streams and potential products. For example, catalytic hydrogenation substantially reduced the mutagenic of an SRC-II derived fuel oil⁽⁵⁾ and both the mutagenic and carcinogenic potential of H-Coal derived oils.⁽⁶⁾

Coal liquefaction processes designed or modified (based on such considerations as reduced liquefaction severity, use of hydrogen-rich donor solvents, catalytic hydrogenation, and distillation with recycle of bottoms) include the liquid solvent extraction (LSE) process developed by the British National Coal Board, the SRC-I TSL process developed jointly by International Coal Refining Company and others with funding from DOE, the Exxon Donor Solvent (EDS) process, and the Integrated Two-Stage Liquefaction (ITSL) process being developed by C. E. Lummus with DOE funding.

This report presents results of detailed chemical analysis and biological testing of several ITSL processes streams where it was possible to obtain samples under both normal and off-normal operational conditions. The latter conditions represented situations which could occur as a result of upset operation of a scaled-up facility. Those effects attributed to catalyst degradation may

also result from extended periods of operation without some kind of catalyst recharge or reactivation. Samples represented both crude and fractionally distilled oils from several different process streams. Chemical and biological data are compared with process parameters to show how certain process conditions may effect the chemical make up and biological activity of process streams and potential product materials.

1.3 PROCESS DESCRIPTION

1.3.1 Background on the TSL Concept

The basic TSL concept is not new. It 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.⁽⁷⁾ A 125 ton/day coal plant was built and operated successfully using a coal-tar-pitch hydrogenation plant to provide the source of make-up solvent to slurry the coal. However, the coal-derived extract was never used as a hydrogenation feedstock. Instead it was utilized to make electrode coke.

The Consol Synthetic Fuel (CSF) process, developed by Consolidation Coal Company starting in the 1950s, was a two-stage process in which integrated operation was successfully established in a prepilot-scale program.⁽⁷⁾ The CSF process was the first application of an expanded bed hydrocracker to attempt the upgrading of a "clean" coal extract. Extraction yield was limited to about 75 percent for bituminous coal, because the extraction step was carried out at rather low temperature without added hydrogen from the gas phase. Hydrogen was donated to the coal via relatively low molecular weight condensed hydroaromatics. Attempts to scale the process to a pilot plant processing 20 ton per day of coal at Cresap, West Virginia, were not successful primarily because of various mechanical problems.⁽⁸⁾

A more recent two-stage concept is being developed at the NCB Coal Research Establishment near Cheltenham in the U.K.⁽⁹⁾ Both supercritical gas extraction and LSE have been evaluated as the initial stage for this technology. TSL process simulations have been described by Garg et al.,⁽¹⁰⁾ at Auburn University and Mitchell et al.,⁽¹¹⁾ at Mobil R&D Company.

DOE has supported three advanced coal liquefaction processes at the pilot plant stage which produced distillate liquid fuels: SRC-II, Exxon Donor Solvent and H-Coal. All three are considered one-stage processes, since the conversion from coal to distillate takes place in a single reactor by contacting coal, a process-derived solvent and hydrogen.

However, the conversion of coal to distillate involves a series of reactions of a somewhat different nature and it is not obvious that all steps can be optimized in a single reactor. TSL was of interest because separation of the primary extraction step from hydrocracking the extract to distillate showed promise with regard to improving the efficiency of each step and in terms of the overall integrated liquefaction process. DOE initiated a two-stage liquefaction program in early 1975, involving hydroextraction of coal, deashing of the extract, followed by hydrocracking of the "clean" extract, with the objective of producing high quality distillate fuels. Coal extract operations in bench-scale catalytic fix-bed hydrocracking prototype units at UOP, Inc., and Chevron R&D Co., were unsuccessful. At that time, Cities Service and C. E. Lummus opted to market a proprietary commercial petroleum resid upgrading process, based on expanded bed hydroprocessing called LC fining. DOE proposed testing the LC fining process on filtered SRC-I material, as a model feedstock and subsequently on SCT coal extract. Upgrading operations of the two coal extracts in a prototype LC fining catalytic cracking unit have been conducted under DOE contract at the C. E. Lummus Engineering Development facility, New Brunswick, New Jersey, since June 1976.

Successful upgrading of SCT extract led to the present integrated processing scheme in which SCT hydroextraction of coal is optimized by recycling the high boiling portion of the LC finer product. This hydrogen-rich fraction shows high coal dissolving power and excellent hydrogen donor effectiveness. The relatively low-severity reaction of this recycle solvent with coal produces an apparently stable solvent/coal with sufficiently low viscosity to be pumpable. Solids separation from the liquid portion of the extract is via Lummus antisolvent deashing (ASDA)[®] to produce a clean extract feed for the LC fining operation. Hydrocracking in the LC finer is conducted at relatively low

temperature to maximize hydrogenation of the clean extract and to produce a high-quality low-boiling distillate and a highly hydrogenated high-boiling recycle process solvent.

Operation in the integrated mode has been carried out since May 1980 and is scheduled to continue into 1984. Two bituminous coals have been processed-- Indiana No. 5 and Illinois No. 6. Samples of various process streams (from both coals) have been submitted to Conoco for characterization and process performance evaluation and to PNL for biological screening, including carcinogenicity and mutagenicity testing, and integrated chemical analyses to determine active components.

1.3.2 ITSL Process Flow Sheet

A schematic flow sheet of the TSL unit is shown in Figure 1.1. The Lummus (PDU) is capable of converting 135 to 320 kilograms of dry coal per day. It consists of three sections: coal extraction, solvent deashing of coal extract, and catalytic hydrocracking. Process streams identified by circled numbers in Figure 1.1 were selected for continuous sampling to closely monitor process changes from startup to steady state operation.

1.3.2.1 SCT Reactor

A slurry of coal and recycle process solvent is made up to contain 36 weight percent dry coal (stream #1). The slurry is transferred to a preheater/reactor where it is heated to a maximum outlet temperature of 450°C (840°F) with a residence time of 2 to 3 minutes. Other low-severity reaction combinations are being studied including lower temperatures/longer contact time, etc. Stream #2 represents this operation, where about 92 percent of the organic portion of the coal is dissolved, yielding an extract representing almost 70 percent of the coal. The extract is stripped of light materials (atmospheric flash operation not shown in Figure 1.1) and the +343°C (650°F) extract is fed to the Lummus ASDA unit, which produces a clean overhead extract (stream 3) representing 80 to 85 percent of the extract produced in the first stage or 56 to 60 percent of the original dry coal.

FIGURE 1.1. Schematic Flow Diagram of the Integrated Two-Stage Liquefaction Unit

1.3.2.2 ASDA

The antisolvent is a petroleum derived mixture of aliphatic and aromatic compounds which induces at first agglomeration of asphaltenes/preasphaltenes with the mineral matter and the insoluble organic matter (IOM), and subsequently a rapid sedimentation of the agglomerates. This sequence occurs because of the relatively low solubility of IOM in the antisolvent. The antisolvent has a boiling range sufficiently different from the heavy oil that it can be recovered with good yield by distillation. Not shown in Figure 1.1 are the recovery systems for antisolvent, the distillate portion of the underflow, or the underflow bottoms which contain virtually all the mineral ash and IOM. The latter stream will eventually go to a gasifier to generate hydrogen for the process, although at present these bottoms are being drummed.

1.3.2.3 LC Fining

Stream 3 is feed for the LC finer where about 50 percent of the +343°C extract is hydrocracked to -343°C. Stream 4 leaving the LC finer is heavily hydrogenated and is separated into two fractions by atmospheric or vacuum flash distillation: the -343°C fraction which constitutes the clean product; and the +343°C fraction which includes unconverted residue returned to the coal extraction stage as process solvent (stream 5). The total liquid yield (C₅-343°C) ranges from 49 to 53 weight percent, and the total hydrogen consumption for the two stages ranges from 4.2 to 4.7 weight percent, based on dry coal feed.

The net yield and elemental analysis of ITSL products and recycle solvent are shown in Table 1.1. The quality of the naphtha and fuel oil products are excellent in terms of nitrogen and sulfur concentration, both below 0.1 weight percent. The naphtha/fuel oil cut point of 177°C (350°F) was selected because the 177 to 204°C (350 to 400°F) fraction normally contains a high concentration, above 50 volume percent, of bicyclic and tricyclic naphthenes. At levels above 10 to 15 volume percent these polycyclic naphthenes cause rapid deactivation of the reforming catalyst. However, they are excellent components of the jet fuel or diesel fraction (-343°C) requiring no further hydrogenation to meet smoke point or cetane number specifications, respectively.

TABLE 1.1

ITSL - PRODUCTS AND RECYCLE SOLVENT
NET YIELD AND ELEMENTAL ANALYSIS

	MF Wt.%	MF Ton	Percent by Elemental Analysis				
			C	H	O	N	S
<u>NAPHTHA</u>							
C ₅ - 177°C	6	0.4	86	13	0.4	0.08	Traces
C - 350°F							
<u>FUEL OIL</u>	37	2.6	88	11	0.3	0.08	0.01
177 - 343°C							
350 - 650°F							
<u>RECYCLE SOLVENT</u>	-	-	86	8	3.0	0.50	0.50
+343°C (+650°F)							

Although the process solvent fraction (+343°C) contains a relatively high concentration of heteroatom compounds, data from high vacuum fractionation cuts reveal that most oxygen, nitrogen and sulfur compounds are confined to the +600°C residue. Data shown in Table 1.1 were obtained using a commercial Ni-Mo catalyst (Shell 324) in the LC finer.

Table 2.1 provides a more detailed account of conditions for run 3LCF8 from periods 8 through 54.

2.0 METHODS

2.1 SAMPLE ORIGIN

Samples were collected from the ITSL pilot plant in New Brunswick, New Jersey during both normal and off-normal operating conditions. Sample sets are numbered in chronological order according to their date of receipt at PNL. Run numbers and a brief summary of the process conditions associated with the samples are given in Table 2.1. Process conditions as reported by C. E. Lummus are shown in Table 2.2 for run 3LCF8 and in Table 2.3 for 3LCF7.

Sample sets 1 and 4 were collected under normal operating conditions from runs 3LCF7 and 3LCF9 during processing of Indiana 5 and Illinois 6 coal, respectively. Set 2 was taken during alternate mode operation wherein the LCFF was recycled back to the SCT reactor (for one cycle) prior to entering the LC finer. Set 3 was collected subsequent to a significant exothermic excursion in the first two of three series coupled LC fining reactors during which their catalyst beds were exposed to temperatures as high as 900°F and 1000°F, respectively.

To obtain data on biological activity as a function of boiling point, some ITSL materials were distilled to the nominal cut temperatures used in the process; thus a 850°F cut from both LCFF and LCF TLP were available for 3 of the runs along with 650° to 850°F, 500° to 650°F, 390° to 500°F and initiated boiling point (IBP) to 390°F cuts from run 3LCF7-52 only.

To compare results from these ITSL materials directly with those from single stage processes, an SRC-I process solvent collected from the Wilsonville, Alabama pilot plant and an SRC-II heavy distillate from the Fort Lewis, Washington pilot plant were subjected to the same analytical procedures, as were the ITSL materials. Both SRC samples were collected during normal operation of their respective pilot plants. In the case of SRC-I, it should be noted that the pilot plant has since been modified to allow both coupled and noncoupled two-stage operation. None of the coal liquid materials used here should be considered representative of eventual products which may be produced from commercial operation.

TABLE 2.1

SUMMARY OF OPERATING CONDITIONS WHEN ITSLS MATERIALS WERE SAMPLED
FOR THIS STUDY

<u>Sample Set No.</u>	<u>C. E. Lummus Run Number</u>	<u>Coal Type</u>	<u>SCT Reactor Outlet Temperature</u>	<u>Catalyst Age</u>	<u>Comments</u>
1	3LCF7-37	Indiana # 5	865°F	<u>500 lb 850°+</u> lb catalyst	Normal operating
2	3LCF7-90	Indiana # 5	865°F	<u>1025 lb 850°+</u> lb catalyst	LCFF recycled once before entering LC finer
3	3LCF8-52	Illinois # 6	830°F	<u>576 lb 850°+</u> lb catalyst	LC fining catalyst underwent tempera- ture increase in previous period
4	3LCF9-0524	Illinois # 6	840°F	<u>287 lb 850°+</u> lb catalyst	Normal operating conditions

TABLE 2.2

ENGINEERING SUMMARY OF 3LCF8 OPERATING CONDITIONS AND PERFORMANCE

Period	Catalyst Age (lbs 850°F+/ lb Cat.)	System Pressure (psig)	Maximum (Control) Temperature (°F)			Effective Temperature (°F)	Space Velocity (Vol. 850°F+/ Vol. Cat. Hr.)	Conversion (Vol. %)	Conversion Activity (Vol. 850°F+/ Vol. Cat. Hr)	Demitrogenation Activity (Vol. Feed/ Vol. Cat. Hr)
			DC31	DC32	DC33					
8-3	26	2700	750	750	750	719	0.37	38.49	0.19	1.18
8-8	67	2700	750	750	750	722	0.40	31.72	0.16	1.03
8-10	106	2700	770	770	770	744	0.49	46.92	0.34	1.22
8-12	139	2700	770	770	770	743	0.46	40.94	0.26	1.02
8-14	172	2700	770	770	770	743	0.46	40.17	0.26	1.04
8-16	208	2700	770	770	770	747	0.47	26.62	0.15	0.83
8-23	241	2700	770	770	770	751	0.56	34.36	0.25	0.98
8-25	270	2700	770	770	770	746	0.48	32.44	0.20	0.98
8-27	299	2700	770	770	770		0.51	29.55	0.19	0.86
8-32	346	2700	770	770	770	732	0.35	33.21	0.15	0.59
8-37(a)	389	2700	770	770	770	739	0.46	35.77	0.22	0.58
8-38	395	2700	770	770	770	736	0.50	29.58	0.19	0.91
8-40	420	2700	770	770	770	740	0.48	43.05	0.30	0.57
8-42	446	2700	770	770	770	744	0.34	37.28	0.17	0.48
8-44	471	2700	770	770	770	740	0.38	40.64	0.22	
8-46	502	2700	770	780	780	750	0.42	36.88	0.21	0.54
8-48(b)	526	2700	770	780	780	751	0.44	38.67	0.24	0.47
8-50(b)	547	2700	770	780	780	752	0.43	30.75	0.17	
8-52(b)	576	2700	770	780	780	748	0.40	23.25	0.11	
8-54(b)	596	2700	750	750	780	732	0.46	24.03	0.13	

(a) The hydrogen make-up rate was reduced to about half of the original setting.

(b) An exotherm occurred on DC31 and DC32 to 1000°F and 900°F, respectively, at the catalyst age of 375 lbs 850°F+ / lbs catalyst.

TABLE 2.3
OPERATING CONDITIONS AND CATALYST PERFORMANCE OF THE 3LCF7 UNIT

Run No.	7-69	7-71	7-73	7-78	7-80	7-82	7-85	7-86	7-88	7-90
Pressure (psig)	2700	2700	2700	2700	2700	2700	2700	2700	2700	2700
Reactor Temperature (°F)										
Maximum	780	780	780	780	780	a	a	a	a	b
Average	751	749	749	751	751	762	759	759	760	766
Space Velocity (Vol. 850°F+/Vol. Settled Cat. Hr)	0.47	0.52	0.43	0.56	0.55	0.59	0.47	0.47	0.45	0.47
Catalyst Lift (Lb. 850°F+/Lb Catalyst)	695	730	760	799	838	879	930	947	980	1025
850°F+ Conversion (Vol.%)	30.23	32.26	41.29	32.82	27.36	25.67	33.34	30.03	27.16	37.09
Kinetic Constant (k) (Vol. 850°F+/Vol. Settled Cat. Hr)	0.18	0.21	0.27	0.24	0.19	0.18	0.21	0.18	0.17	0.24
Arrhenius Constant (k x 10 ⁶) (Vol. 850°F+/Vol. Settled Cat. Hr)	7.66	9.51	11.73	11.03	6.89	6.64	7.98	7.09	6.25	8.28

a Maximum temperatures were 700°F, 780°F, and 790°F, respectively, for the three reactors.

b Maximum temperatures were 780°F, 800°F, and 800°F, respectively, for the three reactors.

2.2 BIOLOGICAL ASSAYS

2.2.1 Mutagenicity Assays

Mutagenic potentials for crude materials and their chemical class fractions were estimated using both the standard plate incorporation and preincubation version of the Ames assay. Additionally, nitrosation was carried out on several of the nitrogen-rich fractions to assess the importance of APAH in the mutagenic response to these materials.

2.2.1.1 Standard Ames Test

Standard agar plate mutagenicity assays were performed as described by Ames et al.⁽¹¹⁾ using Salmonella typhimurium TA98. Dimethylsulfoxide (DMSO) was used as a solvent. In addition to the mutagens used to check the phenotypes of Ames/Salmonella strains, fixed concentrations of 2-aminoanthracene, benzo[a]pyrene and a complex basic fraction from SRC-II heavy distillate were tested against Aroclor-induced rat liver (S9) homogenates used for metabolic activation. Optimum levels for S9 were established and monitored daily during the course of the experiments. Negative controls included the Ames/Salmonella typhimurium test strains plus and minus microsomal enzymes (S9), and appropriate solvent controls. Revertant (rev) colonies per petri plate were counted electronically using a Biotran II automated colony counter.

Specific mutagenic activity of crude products or their chemical fractions was expressed as revertant colonies of S. typhimurium TA98/ μg of test material, estimated by linear regression analysis of dose-response data. A positive test was one having a maximum mutagenic response in revertant colonies twofold or greater above background. Mutagenic potency was estimated by linear regression analysis of dose-response data. Dose-response data are presented in Appendix C 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 4-point dose-range, approximate doubling of response for doubling of dose concentration, a correlation coefficient of 0.8 or greater, and an intercept on the response (ordinate) axis within 20 percent of the negative control for the day. To estimate recovery of genetic activity, Ames experiments were replicated several times to obtain an

average value for the slope of the regression line, or mutagenic potency in rev/ μ g. The average slope value was then multiplied by the weight percent of a given fraction to yield a weighted mutagenic activity relative to the crude material or fraction.

2.2.1.2 Preincubation Ames Test

The preincubation procedure used was similar to that described by Yokagi et al.⁽¹²⁾ and Ames et al.⁽¹³⁾ An aliquot of an overnight culture containing $\sim 2.5 \times 10^8$ target cells of TA98 were exposed to the coal liquids or their chemical fractions in a 5-ml aqueous system for 60 minutes at 37°C.

2.2.1.3 Nitrous Acid Experiments

Nitrosation experiments were conducted using a modification of the procedure described by Yoshida and Matsumoto.⁽¹⁴⁾ Sodium nitrite solution was prepared by dissolving 600 mg of the salt in 30 ml 0.3 HCl (v/v). A 0.3 percent hydrochloric acid solution was used as a control on the acidic nitrite solution. Both acidic solutions were filter-sterilized prior to use. To begin nitrosation experiments, 100 to 1500 μ g of a given pure chemical or 100 to 5000 μ g of a given complex chemical mixture were added to 2 ml of acidic nitrite solution or the acid solution without nitrite. The complex fractions or pure chemicals were also added to 2 ml DMSO, the solvent usually used for introducing mutagens in the Ames/Salmonella assay. Both the acidic and DMSO mixtures were mixed vigorously and allowed to stand 90 minutes at room temperature (about 25°C). From 5 to 50 μ l of acid or DMSO mixture were removed and added directly to the 45°C liquid top-agar already containing the other components of the Ames test minus the activating enzymes. Activating enzymes contained in the Aroclor-induced crude microsomal (S9) homogenates were added last. Contents of the top-agar varied in pH from 6.6 to 7.2, depending on the volume of acidic solution added. This range of pH values did not affect sensitivity of the assay.

2.2.1.4 CHO Test

A well characterized assay system for measuring mutation frequency in mammalian cells was described by Hsie et al.⁽¹⁵⁾ This assay uses Chinese Hamster

Ovary (CHO) cells as indicators, and measures forward mutation at the hypoxanthine guanine phosphoribosyl transferase (HGPT) locus. The functional protein coded for at the locus is one of the enzymes involved in salvaging preformed purines, and converting them into nucleotides which can be used for a variety of functions (e.g., energy transfer, nucleic acid synthesis, etc.).

Modifications of this assay procedure were necessary to conduct the experiments described in this report. Among changes was the use of activating enzymes prepared from rat liver homogenates. This modification was necessary to screen for compounds that required metabolic activation before their mutagenic potential could be detected.

Monolayered cultures of CHO cells containing $\sim 1 \times 10^6$ exponentially growing cells were rinsed with saline and graded doses of test materials diluted in DMSO were added (in the presence of activating enzymes). A typical experiment consists of controls (positive, negative, and solvent) as well as five doses of test compounds. Duplicate samples were assayed for each dose. Cells were exposed to the test compounds for 5 hours at 37°C in a controlled atmosphere incubator.

Exposure mixtures consisted of 1.5 ml of medium, 0.5 ml of activating enzymes and cofactors, and 15 μ l of DMSO containing appropriate concentrations of test material. To expose cells, fresh culture medium was first added to each culture, then a 0.5 ml mixture of liver enzymes and cofactors was added. The cofactors included: 3.3 mM glucose-6-phosphate, 1.5 mM $MgCl_2$, 10 mM $CaCl_2$ and 50 mM $NaPO_4$ buffer at pH 8.0. The concentration of protein (rat liver activating enzymes) was 0.6 mg/ml. After gentle mixing, the test compound (in solvent) was added to each culture and the culture fluids mixed a second time.

Following exposure, the cultures were rinsed, the cells were removed with trypsin, washed to remove trypsin, counted and 150 cells/well (6 well Linbro chamber) were plated to determine cell survival. Remaining cells ($\sim 1 \times 10^6$) were placed in growth medium and incubated at 37°C. These cultures were then transferred and diluted back to 1×10^6 cells at 2-day intervals. After an 8-day expression period, the cells were again trypsinized, washed and counted. The cloning efficiency and mutant cell frequencies were then determined.

To obtain cloning efficiency for each treatment flask, cells were harvested and one 6-well plate was seeded with 150 cells. Another plate was seeded with 300 cells per well, each in 4 ml of hypoxanthine-free growth medium. For selection of mutants, each well (of the 6-well plate) was seeded with 50,000 cells in 4 ml of selective medium (containing 6 μ g/ml of 6-thioguanine). A total of 1.2×10^6 cells (24 wells) were screened for each data point. The dishes are all incubated at 37°C in a 100 percent humidified incubator with a 5 percent CO₂, 95 percent air atmosphere. Dishes are fixed and stained (using dilute crystal violet) after 7 days. Colonies were counted and the mutation frequency was calculated by dividing the total number of mutant colonies by the number of cells plated, corrected for cloning efficiency.

2.2.2 Initiation/Promotion Assay For Mouse Skin Carcinogenicity

The initiation/promotion (I/P) skin tumor assay is based on the concept developed by Barenblum⁽¹⁶⁾ and others which holds that skin tumorigenesis consists of at least two events, initiation and promotion. Initiation occurs rapidly, is essentially nonreversible, and probably involves interaction of the initiator with DNA. Promotion is reversible and requires repeated application of the promoting agent. The concept of I/P may be readily demonstrated experimentally by applying a single small dose of an agent such as dimethyl benzan-thracene (DMBA) or benz(a)pyrene (BaP) to mouse skin. If the initial application is followed by repeated application of phorbol myristate acetate (PMA), tumors develop. If no promoter is used or if an initiator does not precede application of the promoter, no tumors develop. Complete carcinogens, such as BaP and DMBA, are capable if high enough doses are used of both initiation and promotion. However, initiation occurs at doses much smaller than those required for promotion. PMA is a more effective promoter than equivalent amounts of BaP or DMBA.

Recent work by Calkins et al.⁽¹⁷⁾ suggested that the I/P system may be useful for screening synthetic fuel mixtures for skin carcinogenic activity. We have screened numerous coal-derived liquids for their ability to initiate skin tumorigenesis. Some of these have also been assayed in chronic skin painting studies as well as in in vitro mutagenicity tests.

Samples were selected for I/P testing based on Ames test results and chemical analysis. LC finer feed and TLP (sample set no. 1) from a run under normal operating conditions (3LCF7-37) were compared to similar materials from a run (3LCF7-90), during which the deashed SCT extract was recycled as a coal slurry solvent once before entering the SCT reactor (sample set no. 2). The former materials showed little or no mutagenic activity in the Ames assay, while the TLP from set no. 2 was quite mutagenic. See Section 3.4 for chemical data on these samples. Data relative to process conditions are shown in Table 2.1.

The I/P assay for mouse skin carcinogenicity was described by Calkins et al. Female CD-1 mice (Charles River, Portage, Maine) at 6 weeks of age were housed five per cage on standard bedding material (Sani-Cel, Paxton Processing Co., Paxton, Illinois) with food (Wayne & Lab-Blox, Allied Mills, Libertyville, Illinois) and tap water available ad libitum. Prior to administration of the test materials, the animals were ear-tagged for identification, weighed, shaved, and assigned to a test group (28 to 30 mice per group). Each test material was diluted 1:1 with acetone and 50 μ l of the diluted material was applied to the shaved backs of the mice. Two groups of animals were initiated with 50 μ g of DMBA (Eastman Chemical Company) or BaP (Sigma Chemical Company) to serve as positive controls. In addition, 50 μ g of several amino polycyclic aromatic compounds (9-aminophenanthrene, 3-aminopyrene, 6-aminochrysene, 2-aminoanthracene) were applied as initiators for reference purposes. Two weeks postinitiation, 50 μ l of PMA acetate (Sigma Chemical Company, 0.1 mg/ml of acetone) were applied to the initiated area twice weekly for a period of six months. The mice were shaved as necessary throughout the study, usually once per week. Animals were observed regularly for tumor growth. Sketches of approximate tumor location and size were recorded each week to record progression of papilloma development.

2.3 ANALYTICAL CHEMISTRY

2.3.1 Chemical Class Preseparation

ITSL samples were fractionated into chemical classes by atmospheric pressure liquid chromatography (APLC) on alumina and silica adsorbents according to

the method described by Later et al.⁽¹⁸⁾ The method was developed specifically for the pre separation of coal-derived materials and is schematically shown in Figure 2.1. The various classes of polycyclic aromatic compounds (PAC) determined in this study are listed in Table 2.4 along with typical structures and the acronyms used in this report.

The alumina step produces well-defined chemical class fractions for aliphatic hydrocarbons, neutral PAC such as the PAH, nitrogen-containing PAC N-PAC, and hydroxylated PAH (HPAH). Alumina was strictly standardized with respect to water content for this particular class separation method.

To facilitate detailed analysis, the N-PAC in fraction A-3 (see Figure 2.1) as further separated on silicic acid to yield 2°-polycyclic aromatic nitrogen heterocycles (2°-PANH; e.g., carbazoles), 3°-polycyclic aromatic nitrogen heterocycles (3°-PANH; e.g., phenanthridine and benzoquinolines), and the amino PAH (APAH; e.g., aminonaphthalene). Again, properly activated adsorbent was employed for this APLC step. To enable the selective detection of the mutagenic APAH by capillary column gas chromatography (GC) with electron capture detection, fluorinated acid anhydrides were used to quantitatively derivatize this class of compounds to their respective fluoroamides. The exact details of this procedure have been described elsewhere.⁽¹⁹⁾ Each fraction was dried of solvent and weighed to obtain an approximation of chemical composition from weight distribution data.

2.3.2 Gas Chromatography (GC)

High resolution capillary column (HRGC) was performed using a Hewlett-Packard (HP) 5880 gas chromatograph equipped with a 25 m x 0.25 mm fused silica capillary column coated with DB-5 (0.25 μ m film thickness). The capillary vaporization injection system was operated in the splitless mode at 260°C as samples were introduced. The oven temperature was held for 2 min at 50°C, then temperature-programmed at a rate of either 3° or 4°C/min to 280°C. A flame ionization detector (FID) was used to analyze for neutral PAC and nitrogen-containing PAC fractions, and a ⁶³Ni electron capture detector (ECD) was used for the analysis of aromatic amine fractions. Both detectors were operated at 300°C.

FIGURE 2.1. Atomspheric Pressure Liquid Chromatography Separation Scheme For Chemical Class Fractionation

TABLE 2.4

POLYCYCLIC AROMATIC COMPOUND (PAC) CLASSES IN COAL-DERIVED MATERIALS

<u>Structure</u>	<u>Name</u>	<u>Class</u>	<u>Acronym</u>
Phenanthrene	Polycyclic Aromatic Hydrocarbons	PAH
Dibenzothiophene	Polycyclic Aromatic Sulfur Heterocycles	PASH
Dibenzofuran	Polycyclic Aromatic Oxygen Heterocycles	PAOH ^(a)
2-Hydroxyanthracene	Hydroxyl Polycyclic Aromatic Hydrocarbons	HPAH ^(a)
Acridine	3°-Polycyclic Aromatic Nitrogen Heterocycles	3°-PANH ^(b)
Carbazole	2°-Polycyclic Aromatic Nitrogen Heterocycles	2°-PANH ^(b)
2-Aminoanthracene	Amino Polycyclic Aromatic Hydrocarbons	APAH ^(b)

(a) The oxygen-containing polycyclic aromatic compounds are referred to collectively as O-PAC.

(b) The nitrogen-containing polycyclic aromatic compounds are referred to collectively as N-PAC.

A retention index system specially designed for the determination of PAC using temperature-programmed capillary GC⁽²⁰⁾ was one means used to qualitatively and quantitatively analyze compounds in ITSL samples. The 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. Identification of PAC in samples involved comparing retention indices of actual sample components with library values.

The other GC method used for qualitative and quantitative analysis of fractions involved calibration in the internal standard mode using the HP 5880 computer-assisted integrator. An internal standard, 2-chloroanthracene, was added to all fractions. Minimum and absolute retention times were calculated for all available standard compounds that would be present in the fractions to be analyzed. Response factors were extrapolated for compounds identified by retention indices and quantified in the absence of standards. For example, a response factor was calculated for benzo(b)fluorene because a standard was available; however, a benzo(a)fluorene standard was not available so the same response factor was used. All factors were analyzed at two different dilutions: 2.5 mg/ml, and 5.0 mg/ml. All results are in ppm with a minimum detectable limit of 20 ppm. The mean and standard deviations from the mean for three determinations are given as the amount for each component quantitated in the fractions.

2.3.3 Gas Chromatography/Mass Spectrometry (GC/MS)

GC/MS analyses were performed either on a HP5982A quadrupole mass spectrometer interfaced to a HP5710 gas chromatograph equipped with a 25 m x 0.30 mm, SE-52, DB-1 or DB-5 fused silica capillary column or a VG micromass ZAB 1F double focusing mass spectrometer interfaced to an HP5840A GC-fitted with the same column. The GC transfer lines of both spectrometers were modified so that the fused silica could be inserted to within 3 to 4 mm of the ion source. This modification enhanced the resolution and interpretability of the GC/MS chromatograms. GC conditions were similar to those previously described. The quadrupole was operated in the electron impact mode at 70 eV, and scan rates were typically 100 amu/sec. Spectra of the capillary gas

chromatographic peaks were acquired and processed with a HP5934A data system. The ZAB system was operated in the GC/MS mode at a nominal resolution of 1000, with a scan rate of 1.5 seconds per decade. Spectra and chromatograms were processed on a VG2035 data system.

2.3.4 Probe Inlet MS

To determine compounds present in higher-molecular-weight materials which may not be amenable to GC (owing to their low volatility), and to compare the relative average molecular weights of the samples, each of the crude materials were analyzed by probe inlet MS on the ZAB 1F double focusing mass spectrometer. Using the data system, several spectra were averaged together and used to estimate the mean molecular weight of each sample. The data were then compared to GC data to confirm the rank order of average molecular weights assigned to various samples.

Some samples were also analyzed by high resolution probe inlet mass spectrometry (HRMS) to determine elemental composition of suspected di-nitrogen compounds. For these measurements, the mass spectrometer was adjusted to a dynamic resolution of about 12,000, and mass spectra were acquired at a rate of 30 seconds per decade. Perfluoroalkane was leaked into the ion source as a calibration standard. Possible elemental compositions for ions of interest were generated by the VG2035 data system.

3.0. RESULTS

3.1 AMES ASSAY RESULTS

Tables 3.1 and 3.2 show the selected microbial mutagenicity data for ITSL samples. ITSL process streams obtained under normal operating conditions were generally less active than analogous SRC materials, or those from ITSL collected under off normal run conditions. In off normal run conditions the main factor resulting in increased mutagenicity of ITSL materials appeared to be the reduced deamination rate of the LC fining reactor after initial C-N bond scission (see Figure 3.1). The difference relative to the normal operation runs appears due primarily to degraded catalyst activity, although differences in feed properties may also be involved. (It should be noted that, according to serial kinetics, low concentration APAH would be expected even if the deamination rate greatly exceeded that of primary amine formation.)

The view that APAH formed are the LC finer is primarily responsible for increased activity under off normal run conditions is strongly supported by quantitative measurements by instrumental analysis of APAH content in LCF TLP, as well as by the elimination of activity after nitrosation of the APAH subfractions of these materials. (Nitrosation with HNO_2 converts the primary amino functionality to a phenol, rendering the parent ring structure mutagenically inactive.)

3.1.1 Mutagenicity Related To Boiling Point

Table 3.3 shows microbial mutagenicity data for LCF TLP from run 3LCF7-90 (LCFF recycle mode), and relates mutagenicity to nominal boiling point ranges, some of which are used in the process to designate various streams. For example, the 850°F+ material is recycled as a component of the pasting or process recycle solvent; the 650 to 850°F cut is a prototype product fuel oil component as is the 500 to 650°F cut. Data for the N-PAC fractions of these materials are also given. The general pattern of activity versus boiling point for these materials appears similar to that found for SRC-I and SRC-II materials; that is, materials containing components boiling between 700°F and 750°F show some activity, and such activity is concentrated in the N-PAC

TABLE 3.1

MICROBIAL MUTAGENICITY OF ITSL MATERIALS^(a)

PNL #	RUN #	SAMPLE	CRUDE	Fraction						
				A1	A2	A3	A4	S1	S2	S3
3LCF7-37 ^(b)										
092		LCFF	0+	0	0	N.S.	0	0	0	0
094		LCFF 850°F+	10.2	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
095		LCF TLP	0	0	0	N.S.	0	0	2	0
100		LCF 850°F+	0	0	0	0	0	0	0	0
3LCF790 ^(c)										
116		LCFF	(8.5)	+(NDR)	+(NDR)	24.4	0.7	2.6	12.9	7.5
117		LCF TLP	18	0	0	124.3	2.5	22.1	176.3	71.4
118		TLP IBP-390°F	0	0	0	0	0	0	N.S.	N.S.
119		TLP 390° - 500°F	0	0	0	N.S.	0	N.S.	N.S.	N.S.
120		TLP 500° - 650°F	0	0	0	73.6	0.8	N.S.	N.S.	N.S.
121		TLP 650° - 850°F	43.5,54.1	0	0	793.3	1.1	N.S.	N.S.	N.S.
122		TLP 850°F+	25.9,73.5	0	0	75.7	4.8	7.9	70.2	81.1

(a) Units are in revertants/μg (TA98).

(b) Run periods considered here as "normal" operation.

(c) Run periods considered here as "off normal" operation.

* At 100 μl 59.

+ Activity in preincubation.

o Single point.

NDR No data received.

N.S. Not significant.

TABLE 3.2

MICROBIAL MUTAGENICITY OF ITSL MATERIALS^(a)

PNL #	RUN #	SAMPLE	Fraction							
			CRUDE	A1	A2	A3	A4	S1	S2	S3
	3LCF8-52(c)									
131		LCFF	0	0	0	13.2	5.0	0	29.9	14.8
						37.9				
132		LCF TLP	6.9	0	0+(NDR)				71.7	55.8
						81.7				
136		Recycle Solvent	(17.7)	0	0.7*	42.9	2.8			
137		SCT Heavy Oil	0.6(o)	0	2.6*	62.9	1.9			
139		8 in. BDU BTMS	2.9	-	-	-	-	-	-	-
140		Gasifier Feed	12.5	-	-	-	-	-	-	-
135		LCF 650 Dist.	0	-	-	-	-	-	-	-
133		LCF (Heavy Prod.)	4.7	-	-	-	-	-	-	-
	3LCF9-0524(b)									
007		LCF TLP	(0,0.1)	0	0.3	0	5.3	0	0	5.5
		SRC-II HD	51	-	-	574	-	-	-	-
		SRC-I PS	15	-	-	-	-	-	-	-

(a) Units are in revertants/ μ g (TA98).

(b) Run periods considered here as "normal" operation.

(c) Run periods considered here as "off normal" operation.

* At 100 μ l 59.

+ Activity in preincubation.

o Single point.

NDR No data received.

TABLE 3.3

MUTAGENIC ACTIVITY AS A FUNCTION OF
BOILING POINT FOR LCF TLP

<u>BP Range</u>	<u>Revertants per μg (TA98)</u>	
	<u>Crude</u>	<u>N-PAC</u>
1BP-350°F	0	0
390-500°F	0	0
500-650°F	0	13
650-850°F	40	120
850°F+	25	15

fractions. More precise boiling point cuts of ITSL process streams will be required to clearly delineate the temperature for onset of activity (e.g., SRC materials were distilled to 50°F cuts). These data indicate that for off normal operation, <650°F materials should have no mutagenic activity. Direct measurement of the 650° to 850°F cut (i.e., LCF TLP) from normal operation with Illinois 6 coal also shows no mutagenic activity (see Figure 3.4 for example).

3.1.2 Microbial Mutagenicity Related to Process Conditions

Weighted mutagenic activities for crude samples from normal and off normal operation are shown in Figures 3.1 and 3.2. Relationships among samples within the process is indicated by a simplified block diagram of the ITSL PDU. The most complete sample set obtained included recycle solvent, batch distillation bottoms, SCT heavy oil, and gasifier feed, along with LCFF and LCTLP, and was from run 3LCF8-52 (subsequent to the exothermic excursion in the LC finer). Thus, this sample set was not representative of normal run conditions as specified by the process developer. However, owing to the coupled nature of the process unit operations, particularly in the case of the heavy-end materials that are recycled, it may be assumed that the rank order of mutagenic activity of process streams would not vary greatly. Therefore, either the LCFF or the LCF product, as crude materials, are likely to represent the highest

FIGURE 3.1. Schematic for Reaction Sequences Occurring in Hydrogenation of PAH and N-PAC Compounds (bracketed intermediates for APAH are generally thought to be short-lived, particularly under catalytic conditions)

FIGURE 3.2. Weighted Mutagenic Activities in rev/μg TA98 for ITSL Process Streams Sampled Under Normal (dotted) and Off-Normal (hatched) Operating Conditions

mutagenic activities among process streams. LC fining appears to be the most important unit operation in determining mutagenicity of various ITSL process streams.

Results in Figure 3.2 indicate that at least two factors must be considered as determining the activity of crude ITSL process materials: namely mutagen content and overall complexity. For example, SCT heavy oil, as a crude, does not exhibit good slope correlation in the Ames test. However, after clean up by chemical separation, the N-PAC fraction of SCT heavy oil shows appreciable activity. Anti-solvent deashing apparently has somewhat the same effect, since the sum total activity of streams leaving the deasher shows more activity as a crude material than did the SCT heavy oil feed.

Figure 3.3 shows results from preincubation Ames tests on the LCFF and LCF TLP materials from runs 3LCF7-37 (normal operation), 3LCF7-90 (off normal operation), and 3LCF8-52 (off normal operation) and the LCF TLP from 3LCF9-0524 (normal operation). These data agree with standard Ames data as to relative activity of the various ITSL materials. Thus, under normal operating conditions (Figure 3.2) the ITSL process can generate LCF TLP distillate which is low in mutagenic activity compared to single stage processes such as SRC-I and SRC-II.

3.2 CHO MUTATION ASSAY

Several ITSL samples were tested for mutagenic potential in mammalian cell systems. Cultured mammalian cells were exposed to a series of doses of test material and the mutagenic responses (based on slope) were compared. Good dose-related response relationships were observed. Data indicate that the 850°F+ component of LCF TLP from run 3LCF7-37 exhibits low but detectable mutagenic activity. The observed activity was substantially lower than that observed for SRC-II 850°F⁺ crude.

Preliminary data for ITSL samples in the CHO mutation assay are summarized in Table 3.4. Although all ITSL samples tested caused detectable increases in mutation frequency, these materials were poor mutagens compared to SRC-II 850°F+ or to pure positive control compounds. Fractionation of LCF TLP from 3LCF7-37 into its PAH and APAH constituents allowed the detection of

FIGURE 3.3. Results from Preincubation Ames Testing of LCFF and LCF TLP Materials from ITSL Runs 3LCF7-37 (normal), 3LCF7-90 (off normal), 3LCF8-52 (off normal), and LCF TLP only from 3LCF9-0524 (normal)

TABLE 3.4.

MUTAGENIC ACTIVITY OF ITSL CRUDE MATERIALS AND FRACTIONS IN THE
CHINESE HAMSTER OVARY ASSAY

<u>Sample</u>	<u>Mutants/μg</u>	<u>Correlation Coefficient</u>
<u>ITSL Crude Materials</u>		
LCFF	0.48	0.79
LCFF 850°F+	0.26	0.8
LCF TLP	0.18	0.93
TLP 850°F+	0.21	0.84
SRC-II 850°F+	1.24	0.81
<u>Chemical Fractions</u>		
LCF TLP APAH	2.4	0.9
PAH Fraction	0.9	0.58
<u>Controls</u>		
Benzo(a)pyrene	10	0.95
6 Aminochrysene	2.1	0.87
Dimethyl Benzacridine	10.9	0.83

considerably more mutagenic activity than was evident prior to fractionation. The preliminary nature of these data do not allow conclusions concerning possible antagonistic or agonistic effects of PAH and N-PAC materials on CHO cell mutation. Figure 3.4 compares Ames and CHO mutation assay data for the 850°F+ component of ITSL LCF TLP and SRC-II HD. Although these two assays are comparable to crude materials the CHO system appears to be more sensitive to PAH mutagens than is the Ames assay.

FIGURE 3.4. Comparison of Ames and CHO Data for the 850°F+ TLP Materials from Run 3LCF7-37 (normal operation). (These results are in turn compared to those from the 850°F+ cut from SRC-II heavy distillate).

3.3 INITIATION PROMOTION ASSAY

Data for tumor yield (total number of tumors in a population of 30 mice) with four ITSL materials from run 3LCF7-37 (normal operation) are shown in Figure 3.5. Tumor incidence data (the percentage of animals in the test population having one or more tumors) for these materials are shown in Figure 3.6. For comparison, results from positive control compounds [B(a)P and DMBA] and those for Wilmington Crude petroleum and SRC-II HD are shown in Figures 3.7 and 3.8. In comparing ITSL results with those from SRC, it should be remembered that SRC-II HD is a 550°F+ material while the ITSL materials are 650°F+. We previously showed that for raw SRC coal liquids, carcinogenic activity in the I/P assay exhibits a strong positive correlation to boiling point, particularly above 600°F. Materials resulting from normal operation appear to be somewhat less carcinogenic than those produced during LCFF recycle operation. Both tumor incidence and tumor yield data show this trend; however, these differences were not statistically significant in these studies.

Tables 3.7 and 3.8 show that the relative concentrations of known carcinogenic compounds, such as B(a)P, DMBA and methylchrysene in ITSL materials, are reduced in LCF TLP from normal operation (3LCF7-37) compared to LCF TLP from the LCF recycle mode (3LCF7-90). Thus, reduced mutagenic activity of normal-operation products would be expected. However, what was unexpected, based on results of chemical analysis, was the similarity in activities of LCFF and LCF TLP in samples from both runs. Analytical data show that LC fining significantly reduces the heavier aromatic content in LCF TLP compared to LCFF, and we initially expected to see these differences reflected in lower I/P activity for the TLP material.

There are several possibilities to explain this contradiction. Lack of good dose response in the I/P system is one possible explanation. However, dose response data on both SRC-II HD and standard materials indicate that the I/P system does exhibit positive dose response characteristics in the dose ranges used, and therefore should differentiate among materials containing 1770 and 3750 ppm B(a)P, if B(a)P were the PAH responsible for tumor initiation. The obvious conclusion is that B(a)P or DMBA concentrations alone are poor indicators of carcinogenic activity in complex matrices.

FIGURE 3.5. Tumor Yield Data for LCFF and LCF TLP from ITSL Runs 3LCF7-90 (off normal operation) and 3LCF7-37 (normal operation)

FIGURE 3.6. Tumor Incidence Data for LCFF and LCF TLP from ITSL Runs 3LCF7-90 and 3LCFL7-37

FIGURE 3.7. Tumor Yield Data for Benz(a)pyrene and Dimethylbenzanthracene, Used as Positive Controls

FIGURE 3.8. Tumor Incidence Data for Two Dose Levels of SRC-II Heavy Distillate (data are also shown for Wilmington Crude and Petroleum Derived No. 2 Diesel Fuel)

A second explanation is that both agonistic and antagonistic agents to the carcinogenic response in the I/P system occur in ITSL mixtures and that antagonists are susceptible to hydrogenation to an extent comparable to that of agonistic agents. Thus, the relative concentrations of agonist and antagonist become more important than the absolute concentration of agonist. If both agonists and antagonists are present and are deactivated or destroyed at comparable rates by hydrogenation, then one would expect to see little or no difference in the I/P activities of LCFF and LCF TLP.

3.4 CHEMICAL ANALYSIS

Substantial effort has been invested in chemically characterizing ITSL materials to better understand the chemical basis for the reduction in observed biological activity relative to single stage processes. It has also been possible to relate the chemistry of ITSL process streams to different operating conditions under which samples were collected. These studies have also allowed some insight into the chemical basis for the improved solvent quality of ITSL-generated process solvents.

3.4.1 Atmospheric Pressure Liquid Chromatographic Separation

Weight distributions of LCFF and TLP among chemical class fractions for samples from runs 3LCF7, 3LCF8 and 3LCF9 are shown in Table 3.5. The weight of the hydroxy PAH fraction generally decreases after LC fining due to removal of oxygen heteroatoms. This effect is particularly noticeable in samples from 3LCF7 with Indiana 5 coal.

Comparisons of materials by this method, before and after LC fining, generally show an increase in the weight of the A1 fraction which is composed of aliphatic compounds and some small (one or two-ring) neutral aromatics and their alkyl homologs. The increase reflects the lower molecular weight of LC finer product material relative to the feed, and is due to formation of smaller alkylated aromatic compounds by carbon-carbon bond scission and ring opening of larger PAH during hydrotreating.

TABLE 3.5

PERCENTAGE OF ITSL MATERIALS WHICH PARTITIONED INTO THE VARIOUS
CHEMICAL CLASS FRACTIONS DURING APLC SEPARATION^(a)

Material	Fraction				Recovery Total (%)
	A-1	A-2	A-3	A-4	
LC Finer Feed (3LCF7-37, PNL-092)	10	35	12	25	82
LC Finer Total Liquid Product (3LCF7-37, PNL-095)	46	27	6.5	2	82
LC Finer Feed (3LCF7-90, PNL-116)	2.7	35	17	23	78
LC Finer Total Liquid Product (3LCF7-90, PNL-117)	16	37	19	18	90
LC Finer Feed (3LCF8-52, PNL-131)	7	43	14	31	95
LC Finer TLP (3LCF8-52, PNL-132)	21	41	15	20.5	97
LCF TLP (3LCF9-0524, PNL-007)	23	38	14	19	94

(a) Numbers are in percent of total crude by weight.

Table 3.6 shows APLC separation results for the 850°F+ component of LCFF and LCF TLP materials from ITSL during normal and off normal ITSL operating conditions. Results for the 850°F+ component of SRC-II are included for comparison. The data show that LC fining is effective in hydrogenating the 850°F+ component of the feed as well as the lower boiling components. The data also indicate that hydrogenation of heavy ends (850°F+ materials) suffers more from reduction in catalyst activity than does hydrogenation of 850°F minus materials (compare LCF TLP from 3LCF-90 to LCFF from 3LCF-37). Quantitative differences with respect to specific compounds are given in Tables 3.7 and 3.8.

TABLE 3.6

PERCENTAGE OF ITSL MATERIALS WHICH PARTITIONED INTO VARIOUS
CHEMICAL CLASS FRACTIONS DURING APLC SEPARATION

<u>RUN #</u>	<u>Material</u>	<u>A-1 Aliphatic</u>	<u>A-2 PAH</u>	<u>A-3 N-PAC</u>	<u>A-4 HPAH</u>	<u>Recovery</u>
3LCF7-37						
	LCFF 850°F+	1	15	18	45	79
	LCF TLP 850°F+	1	37	32	24	98
3LCF7-90						
	LCF TLP 850°F+	1	20	36	45	101
SRC-II HD	850°F+	1	46	36	25	107

3.4.2 Quantitative Determination of PAH

Tables 3.7 and 3.8 show concentrations (ppm) of some forty PAH compounds which were monitored by HRGC in PAH fractions of selected ITSL samples. Estimated concentrations for several hydroaromatic species, based both on HRGC and GC/MS analysis, are shown in Table 3.9. Relative concentrations for fully aromatic five ring compounds such as B(a)P and B(e)P were substantially lower in materials produced under normal as compared to off-normal operating conditions. B(a)P content was about 2200 ppm in LCF TLP from 3LCF7-57 (normal operation) compared to about 5360 ppm in LCF TLP 3LCF7-90 (off-normal operation). The differences were not so marked for four-ring aromatic compounds but the trend was similar (i.e., normal operation for a given coal type resulted in lower concentrations of aromatics than did off normal conditions).

No SRC material was available which was directly comparable in boiling point range to an ITSL sample. However, PAH values from SRC-II HD and SRC-I PS are shown in Table 3.7.

3.4.3 Quantitative Determination of 2°-PANH and 3°-PANH

Tables 3.10 and 3.11 list concentrations of some 32 nitrogen-containing compounds in the N-PAC fractions from several ITSL materials. APAH were not in sufficient concentration to be detected by this method and further separation and derivatization was required to detect them in ITSL materials. Organic nitrogen in ITSL materials was found in higher boiling cuts than in SRC coal

TABLE 3.7

CONCENTRATIONS OF SELECTED COMPOUNDS IN NEUTRAL POLYCYCLIC AROMATIC COMPOUND FRACTIONS OF ITSL MATERIALS

Compounds	RUN PNL Material	3LCF8-52 (137) SCT		3LCF8-52 (136) Recycle Solvent		220 () SRC-1 Process Solvent		() SRC-II Heavy Distillate	
		Heavy	Oil	Heavy	Solvent	Process	Solvent	Heavy	Distillate
Naphthalene		260 ±	20	380 ±	20	580 ±	0		
2-methylnaphthalene		1100 ±	80	980 ±	60	24760 ±	580	360 ±	20
1-methylnaphthalene		600 ±	60	540 ±	40	4880 ±	100		
Biphenyl		300 ±	20	240 ±	20	18020 ±	380	260 ±	20
1,6-dimethylnaphthalene(3)		620 ±	80	500 ±	60	5960 ±	120	180 ±	20
Acenaphthylene						120			
Acenaphthene		2120 ±	120	1900 ±	80	17180 ±	420	980 ±	120
Dibenzofuran		2320 ±	140	2720 ±	100	37060 ±	1300	2540 ±	120
Fluorene		6060 ±	320	7700 ±	220	41480 ±	1200	19680 ±	800
1-methylfluorene		1200 ±	340	1160 ±	240	8520 ±	880	8620 ±	620
Dibenzothiophene		4780 ±	300	3700 ±	100	15880 ±	360	16820 ±	540
Phenanthrene		30240 ±	1860	34180 ±	1180	153000 ±	360	117000 ±	4540
Anthracene		2720 ±	160	4760 ±	140	4720 ±	200	3360 ±	60
3-methylphenanthrene		5520 ±	240	5560 ±	120	21560 ±	120	33680 ±	1160
2-methylphenanthrene		6040 ±	240	6160 ±	100	23240 ±	480	40220 ±	1440
4-H-cyclopenta(def)phenanthrene		3560 ±	300	3700 ±	140	4220 ±	180	2060 ±	620
1-methylphenanthrene		2700 ±	420	2660 ±	120	7980 ±	160	8680 ±	280
Fluoranthene		26480 ±	820	26020 ±	740	21980 ±	460	13740 ±	720
Acephenanthrylene		1680 ±	120	960 ±	260	820 ±	460	1940 ±	100
Pyrene		68660 ±	3120	71000 ±	3760	24180 ±	1160	64000 ±	3320
Benzo(a)fluorene		6280 ±	800	5980 ±	580	5480 ±	1100	11060 ±	1200
Benzo(b)fluorene(1)		18440 ±	940	15980 ±	4860	3040 ±	80	40940 ±	4040
1-methylpyrene		5520 ±	240	5340 ±	260	2360 ±	120	4340 ±	500
Benzo(b)naphtho(2,1-d)thiophene		1060 ±	80	1460 ±	240	1460 ±	120	1960 ±	220
Benzo(ghi)fluoranthene		280		1660 ±	80	740 ±	200	2100 ±	160
Benzo(a)anthracene		11000 ±	1400	9814 ±	2198	2260 ±	100	4100 ±	160
Chrysene(2)		15820 ±	2120	14840 ±	3080	3040 ±	140	8160 ±	520
3-methylchrysene		5480 ±	160	80075 ±	1680	1240 ±	20	2640 ±	320
2-methylchrysene(4)		3660 ±	720	3620 ±	1300	660 ±	60	1580 ±	180
5-methylchrysene		660 ±	300	580 ±	200	520 ±	20	820 ±	100
6-or 4-methylchrysene		7940 ±	420	11280 ±	2320	1020 ±	60	2920 ±	220
1-methylchrysene		5180 ±	260	4420 ±	1940	500 ±	200	1420 ±	660
Benzo(j or b)fluoranthene		17340 ±	3300	15440 ±	4000	280 ±	20	2340 ±	220
Benzo(k)fluoranthene		10380 ±	2840	8800 ±	2340	60		1400 ±	220
Benzo(e)pyrene		14900 ±	3120	14320 ±	3620	120		2020 ±	80
Benzo(a)pyrene		13180 ±	2480	10180 ±	2540	380 ±	40	1220 ±	120
Perylene		7380 ±	1480	4540 ±	1080			620 ±	60
Indeno(1,2,3-cd)pyrene		4520 ±	1240	4740 ±	1480	100		600 ±	40
Dibenz(a,h)anthracene		1460 ±	340	1440 ±	640			220	
Benzo(ghi)pery		8280 ±	2400	10160 ±	3340	380 ±	160	1180 ±	340

(1) Co-elutes with 2- and 4-methylpyrene

(2) Co-elutes with triphenylene

(3) Co-elutes with 1,3-dimethylnaphthalene

(4) Co-elutes with 4- and 12-methylbenz(a)anthracene

TABLE 3.8

CONCENTRATIONS OF SELECTED COMPOUNDS IN NEUTRAL POLYCYCLIC AROMATIC
FRACTIONS OF ITS L MATERIALS

Compounds	RUN PNL Material	3LC7-37		3LC7-90		3LC9-0524	
		(092)	(095)	(116)	(117)	(007)	
		LCFF	LCF TLP	LCFF	LCF TLP	LCF TLP	
Naphthalene		3240 ± 240	900 ± 100	180 ± 40	1560 ± 140	280 ± 40	
2-methylnaphthalene		3680 ± 240	3860 ± 360	100	4760 ± 380	940 ± 140	
1-methylnaphthalene		1960 ± 140	1700 ± 160	1820 ± 160	220 ± 40		
Biphenyl		860 ± 60	1260 ± 120	760 ± 60	340 ± 40		
1,6-dimethylnaphthalene(3)		1520 ± 100	900 ± 120	100	1000 ± 120	280 ± 60	
Acenaphthylene		180 ± 100	160	140 ± 60			
Acenaphthene		4840 ± 260	640 ± 80	880 ± 200	1140 ± 180	380 ± 60	
Dibenzofuran		4120 ± 220	1660 ± 160	640 ± 180	400 ± 60	300 ± 140	
Fluorene		7580 ± 280	2380 ± 200	2000 ± 360	2700 ± 140	1480 ± 180	
1-methylfluorene		1400 ± 240	1480 ± 120	180 ± 20	1920 ± 100	860 ± 260	
Dibenzothiophene		8760 ± 300	2140 ± 200	2380 ± 240	3260 ± 240	1480 ± 300	
Phenanthrene		42600 ± 900	4260 ± 420	24180 ± 1800	10420 ± 540	2960 ± 640	
Anthracene		7180 ± 260	780 ± 140	5040 ± 320	360 ± 160	340	
3-methylphenanthrene		6500 ± 220	1380 ± 140	3460 ± 100	2300 ± 100	1420 ± 120	
2-methylphenanthrene		7420 ± 260	3620 ± 360	4320 ± 140	3100 ± 140	2580 ± 420	
4-H-cyclopenta(def)phenanthrene		5460 ± 300	880 ± 520	2560 ± 20	2360 ± 380	1640 ± 500	
1-methylphenanthrene		3660 ± 500	560 ± 280	2080 ± 20	1480 ± 440	460 ± 280	
Fluoranthene		46260 ± 2220	1320 ± 80	41280 ± 2780	8960 ± 1380	1540 ± 760	
Acphenanthrylene		1880 ± 180	2300 ± 660	1880 ± 200	1660 ± 20	520 ± 180	
Pyrene		82560 ± 6300	40520 ± 1340	58080 ± 4800	48180 ± 1780	37400 ± 480	
Benzo(a)fluorene		8580 ± 820	1680 ± 800	10620 ± 3120	3060 ± 700	740 ± 380	
Benzo(b)fluorene(1)		15260 ± 2760	11160 ± 540	11800 ± 2240	14720 ± 880	13580 ± 620	
1-methylpyrene		6840 ± 680	4040 ± 500	5540 ± 740	4300 ± 460	3520 ± 360	
Benzo(b)naphtho(2,1-d)thiophene		3860 ± 540		6560 ± 1100	260	1240	
Benzo(ghi)fluoranthene		2860 ± 500	2240 ± 160	4260 ± 800	580 ± 440	560 ± 20	
Benzo(a)anthracene		19060 ± 3320	760 ± 120	35180 ± 6940	3840 ± 640	1540 ± 420	
Chrysene(2)		21580 ± 3340	700 ± 220	38840 ± 8140	11480 ± 1520	1220 ± 630	
3-methylchrysene		5580 ± 1110	1500 ± 220	11920 ± 2800	4880 ± 940	4920 ± 680	
2-methylchrysene(4)		3560 ± 800	180 ± 100	6840 ± 1640	2100 ± 580	1140 ± 140	
5-methylchrysene		1760 ± 460	220 ± 180	3200 ± 740		2380 ± 160	
6-or 4-methylchrysene		5660 ± 1340	8180 ± 1140	2940 ± 700	8380 ± 1220	12120 ± 2160	
1-methylchrysene		5440 ± 1360	1100 ± 160	7120 ± 1740	2140 ± 580	1780 ± 300	
Benzo(j or b)fluoranthene		18180 ± 3020	2460 ± 660	46060 ± 13940	15480 ± 4040	5980 ± 1420	
Benzo(k)fluoranthene		8240 ± 2100	960 ± 280	16420 ± 5940	3700 ± 970	1500 ± 320	
Benzo(e)pyrene		13020 ± 2840	2440 ± 400	22840 ± 5080	12160 ± 2960	7540 ± 2260	
Benzo(a)pyrene		15220 ± 3300	2200 ± 640	30120 ± 9640	5360 ± 1460	3640 ± 880	
Perylene		5300 ± 1200	320 ± 200	8900 ± 2520	1920 ± 420	820 ± 440	
Indeno(1,2,3-cd)pyrene		5180 ± 620	2220 ± 920	10180 ± 3840	4820 ± 1640	4620 ± 1120	
Dibenz(a,h)anthracene		1600 ± 320	560 ± 240	3200 ± 1140	1260 ± 500	1100 ± 240	
Benzo(ghi)perylene		6280 ± 1680	5920 ± 1820	9880 ± 3660	8760 ± 2880	12300 ± 2960	

(1) Co-elutes with 2- and 4-methylpyrene

(2) Co-elutes with Triphenylene

(3) Co-elutes with 1,3-dimethylnaphthalene

(4) Co-elutes with 4- and 12-methylbenz(a)anthracene

TABLE 3.9

CONCENTRATION (ppm) FOR HYDROAROMATIC ANALOGS OF MAJOR
PAH STRUCTURES IN LCFF AND LCF TLP

Compound	Mol. Wt. %	(a)	(b)
		LCFF	LCF TLD
octahydro 178	186	60	3700 ± 220
hexahydro 178	184	680 ± 120	3660 ± 180
octa + dihydro 178	186, 180	200 ± 60	2520 ± 180
dihydro 178	180	260 ± 40	1940 ± 80
dihydro 178	180	180 ± 80	880 ± 40
octahydro 178	186	420 ± 120	3600 ± 160
tetrahydro 178	182	2420 ± 260	6700 ± 320
decahydro 202	212	540 ± 160	5640 ± 660
octahydro 202	210	340 ± 120	1100 ± 60
decahydro 202	212	460 ± 280	3340 ± 200
octahydro 202	210	540 ± 80	2640 ± 180
octahydro 202	210	560 ± 80	1640 ± 120
octahydro 202	210	540 ± 100	1200 ± 120
hexahydro 202	208	1200 ± 780	4260 ± 340
tetrahydro 202	206	160	6340 ± 280
hexahydro 202	208	380 ± 120	6880 ± 240
hexahydro 202	208	380 ± 260	7500 ± 380
dihydro 202	204	1580 ± 140	1520 ± 160
octahydro 228	236	5180 ± 1000	3400 ± 480
tetrahydro 228	232	7240 ± 1180	13700 ± 1500
dihydro 228	230	1760 ± 320	2400 ± 320
tetrahydro 228	232	5520 ± 1940	9260 ± 1040
dodecahydro 252 ^(a)	264	1900 ± 60	1260 ± 330
dodecahydro 252 ^(a)	264	4260 ± 780	2280 ± 340
decahydro 252 ^(a)	262	1180 ± 240	780 ± 140
hexahydro 252	258	15740 ± 3260	21080 ± 3240
tetrahydro 252	256	4740 ± 1340	6220 ± 1080
hexahydro 252	258	--	4620 ± 420
tetrahydro 252	256	3080 ± 1020	8040 ± 1980
tetrahydro 252	256	1720 ± 640	3060 ± 820

(a) These compounds have been identified as benzofluoranthene isomers by their relative retention times.

(b) Samples from new SLCF7-90.

liquids (Figure 3.9). Along with increased molecular weight of N-PAC in ITSL, relative to SRC, there appeared to be differences in nitrogen functionalities between the two types of materials.

TABLE 3.10

CONCENTRATIONS OF SELECTED NITROGEN CONTAINING COMPOUNDS IN NITROGEN POLYCYCLIC AROMATIC FRACTIONS OF ITS L MATERIALS

Compounds	RUN PNL Material	3LCF8-52 (137) SCT Heavy Oil	3LCF8-52 (136) Recycle Solvent	220 () SRC-I Process Solvent	() SRC-II Heavy Distillate
Quinoline		40		2440 ± 20	60
Isoquinoline		60		420 ± 40	
Indole				4160 ± 40	80
2-methylquinoline				6180 ± 320	260 ± 40
3-methylquinoline				4280 ± 100	200 ± 60
4-methylquinoline		80		1180 ± 820	100 ± 20
1,2-dimethylindole		100 ± 20	60 ± 0	6380 ± 1840	880 ± 280
2,5-dimethylindole		40 ± 0	20	4140 ± 1960	140 ± 0
2,3-dimethylindole		80 ± 20	40	1260 ± 60	180 ± 20
4-azafluorene		20 ± 0	80 ± 40	940 ± 200	740 ± 220
Phenazine		20 ± 0	80 ± 40	740 ± 320	1300 ± 280
Benzo[h]quinoline		660 ± 60	680 ± 100	5520 ± 680	9960 ± 1040
Acridine		940 ± 100	920 ± 60	3940 ± 520	5660
Phenanthridine		700 ± 40	760 ± 80	7840 ± 780	20780 ± 1140
Benzo[f]quinoline		160 ± 0	200 ± 80	1960 ± 220	2680
Carbazole		6380 ± 640	6480	32020 ± 2940	90320 ± 10560
2-or 3-methylbenzo[f]quinoline		300 ± 100	100 ± 80	2780 ± 900	6800 ± 700
2-methylacridine or lime carbazole		260 ± 120	360 ± 160	3840 ± 4140	13240 ± 260
2-methylcarbazole		680 ± 20	700 ± 20	9600 ± 440	31560 ± 3340
1 or 2-azafluoranthene or		400 ± 20	440 ± 120	1260 ± 60	1740 ± 780
7-azafluoranthene		260 ± 60	420 ± 80	760	2060 ± 320
1-azapyrene or 4-azapyrene		1980 ± 380	1340 ± 320	1760 ± 820	14000 ± 3880
Benzo[def]carbazole		630 ± 120	840 ± 220	1220 ± 380	780 ± 40
9-phenylcarbazole		80 ± 60	40 ± 0	60	1920 ± 980
Benzo[c]acridine		2440 ± 360	2500 ± 340	1320 ± 0	1660 ± 220
Benzo[a]acridine		1440 ± 400	1460 ± 140	1480 ± 280	860 ± 220
Benzo[a]carbazole		5500 ± 900	5380 ± 580	2360 ± 80	7600 ± 600
1-azachrysene		380 ± 80	340 ± 160	160 ± 0	520 ± 200
Benzo[b]carbazole		3360 ± 560	3180 ± 320	1620 ± 40	3900 ± 420
2-azachrysene or Benzo[c]carbazole		4602 ± 830	4480 ± 500	1820 ± 60	6740 ± 160
7,10-dibenz[c]acridine		660 ± 340	320 ± 120	100	320 ± 280
10-azabenz[a]pyrene		3900 ± 650	1460 ± 460	120 ± 20	620 ± 200
Dibenz[a,i]carbazole or					
Dibenz[a,j]acridine		60	300 ± 140		190 ± 40
Dibenz[a,g] or [c,g]carbazole		3520 ± 1034	3180 ± 420		560 ± 340

TABLE 3.11

CONCENTRATIONS OF SELECTED NITROGEN COMPOUNDS IN NITROGEN CONTAINING POLYCYCLIC AROMATIC COMPOUND FRACTIONS OF ITSLS MATERIALS

Compounds	RUN PNL Material	3LC7-37		3LC7-90		3LC9-0524	
		(092)	(095)	(116)	(117)	(007)	
		LCFF	LCF TLP	LCFF	LCF TLP	LCF TLP	
Quinoline		300 ± 120					
Isoquinoline		300 ± 320					
Indole		120 ± 0					
2-methylquinoline		180 ± 0					
3-methylquinoline		60					
4-methylquinoline		180 ± 20					
1,2-dimethylindole		180 ± 60			80		
2,5-dimethylindole		80 ± 0					
2,3-dimethylindole		120 ± 20					
4-azafluorene		80 ± 40		100	40		
Phenazine		100 ± 40		80 ± 40	120 ± 60	60	
Benzo[h]quinoline		1120 ± 120		800 ± 60		80	
Acridine		1780 ± 160		1140 ± 80	240 ± 20	100 ± 20	
Phenanthridine		1400 ± 80		1060 ± 40	160 ± 20	80 ± 0	
Benzo[f]quinoline		220 ± 60					
Carbazole		10220 ± 700	200 ± 60	6220 ± 360	1360 ± 40	300 ± 60	
2-or 3-methylbenzo[f]quinoline		580 ± 300		260 ± 40	200 ± 20	40 ± 40	
2-methylacridine or lime carbazole		420 ± 20	40	300 ± 20	260 ± 60	120 ± 20	
2-methylcarbazole		900 ± 180	20	720 ± 180	300 ± 80	80 ± 0	
1 or 2-azafluoranthene or		1080 ± 120	140 ± 20	900 ± 280	220 ± 140	80 ± 20	
7-azafluoranthene		660 ± 170	160 ± 40	940 ± 220	240 ± 0	160 ± 40	
1-azapyrene or 4-azapyrene		2720 ± 140	80	2640 ± 320	1160 ± 240	120 ± 60	
Benzo[def]carbazole		2020 ± 240	20	2140 ± 300	120 ± 20	80 ± 20	
9-phenylcarbazole		340 ± 80		420 ± 220	140 ± 120	40 ± 40	
Benzo[c]acridine		2280 ± 300	160 ± 60	2480 ± 380	2560 ± 620	1460 ± 360	
Benzo[a]acridine		3240 ± 820	60 ± 20	57760 ± 820	1060 ± 80	680 ± 120	
Benzo[a]carbazole		10340 ± 1540	120 ± 30	17300 ± 2720	2680 ± 880	500 ± 120	
1-azachrysene		520 ± 60	20	1140 ± 220	300 ± 120	20 ± 80	
Benzo[b]carbazole		5780 ± 960		8920 ± 1560	1480 ± 80	340 ± 40	
2-azachrysene or Benzo[c]carbazole		7180 ± 1160	140 ± 60	12420 ± 2060	3100 ± 620	940 ± 340	
7,10-dibenz[c]acridine		280 ± 40	280 ± 40	5840 ± 1220	360 ± 200	140	
10-azabenz[a]pyrene		12520 ± 760	300 ± 80	360 ± 500	780 ± 340	320 ± 100	
Dibenz[a,i]carbazole or Dibenz[a,j]acridine		560 ± 200		640 ± 240	160	40	
Dibenz[a,g] or [c,g] carbazole		3900 ± 1960	2040 ± 240	3480 ± 1960	1260 ± 380	200 ± 580

FIGURE 3.9. Nitrogen Compounds by Weight Percent as a Function of Boiling Point: Comparison of ITSL to SRC-II Full-Boiling-Range-Distillate Materials

Organic nitrogen in ITSL materials under normal run conditions was almost exclusively in the form of 2-PANH and 3-PANH with some diaza compounds and trace levels of APAH. Partially hydrogenated analogs of these compounds (including APAH) were also present, particularly in LCF TLP. By comparison, nitrogen has been found in SRC materials amino 3°-PANH, amino 2°-PANH,⁽¹⁹⁾ thiazoles, cyano PAH, phenoxazines, phenothiazines and phenazines at low concentrations. The 2°-PANH, 3°-PANH, diaza, and APAH compounds were present at relatively higher levels. The reason for these differences is not clear; they may simply reflect feed coal type. It is more likely, however, that the decreased reaction severity in the ITSL SCT reactor minimizes or precludes formation of certain of these compounds. In the case of phenoxazines, phenazines and phenothiazines [which are thought to be condensation products of a phenol and an aniline, two anilines, and an aryl thiol with aniline, respectively, reaction severity (particular residence time) in the SCT reactor] is probably insufficient to produce the precursors. Similarly, the SCT reactor probably does not provide an environment with oxidative conditions sufficient to produce cyano-PAH.

In any case, LC fining is effective in removing organic nitrogen from the LCFF (compare Figures 3.10 and 3.11 which are HRGC chromatograms of the N-PAC fraction from LCFF and a LCF TLP, respectively).

3.4.4 Quantitative Determination of APAH

Compared to SRC-I PS and SRC-II HD, APAH concentrations in ITSL materials were low. Figure 3.12 compares the ECD chromatograms of the APAH fractions from LCFF and LCF TLP (both from off normal operations) with that from SRC-II HD. On scale ECD gas chromatograms of the APAH (S-2) subtractions from SRC-I PS and SRC-II HD are shown in Figure 3.12A for comparison. LCFF appears to contain only a few APAH at trace concentrations, these having three or four aromatic rings. Although in low concentration compared to SRC-I, these compounds are still easily distinguished. However, after hydrotreatment there are increased numbers of APAH present, but at still lower concentrations and molecular weights. Individual compounds can no longer be easily distinguished by retention time. The GC MS methods used were not sensitive enough to provide reliable mass spectra of any of these compounds. However, the overall number

FIGURE 3.10. High Resolution Gas Chromatogram of the NPAC Fraction of LCFF Collected from Run 3LCF7-90

FIGURE 3.11. High Resolution Gas Chromatogram of the NPAC Fraction of LCF TLP
Collected from Run 3LCF7-90

FIGURE 3.12. Comparison of ECD Gas Chromatograms for the Derivatized APAH Fractions from: a) SRC-II HD, b) LCFF, and c) LCF TLP (the ITSL materials were from run 3LCF7-90)

FIGURE 12a. Comparison of ECD Chromatograms from the APAH Fractions of SRC-I Process Solvent and SRC-II HD

of peaks detected in the early part of the chromatogram indicates that some primary amino groups may be attached to partially hydrogenated and/or alkylated ring structures. To obtain the SRC-II and LCFF chromatograms, 2.5 mg each were injected: 5 mg were injected to obtain the LCF TLP trace. We estimate that total APAH content in ITSL samples was an order of magnitude less than that in the SRC-II sample. However, microbial mutagenicity was not reduced accordingly. Based on the response (revertants/ μ g) of SRC-I and SRC-II materials, APAH content alone does not account for the activity observed for N-PAC or APAH fractions of ITSL materials. Even though results from nitrosation experiments show that when APAH are selectively converted to the corresponding phenol, the indirect acting mutagenicity essentially disappears. If confirmed in further testing, this may indicate a synergistic effect, or that the unidentified APAH in the LCF TLP are more potent mutagens than those in the LCFF or SRC II-HD.

The relative pattern of APAH chromatograms from LCFF and LCF TLP is easily rationalized as resulting from carbon-carbon and carbon-nitrogen bond cleavage in the hydrotreater. However, the ECD response after derivatization of LCF TLP indicates that in run 3LCF7-90 deamination after C-N bond scission was not as effective as in 3LCF7-37 (see Table 3.12).

3.4.5 Chemical Composition Related to Process Stream

This section compares the general properties of various process streams sampled, with particular attention to their hydroaromatic and nitrogen content. ITSL recycle solvent is also compared to SRC-I PS produced during single stage operation.

Figure 3.13 compares gas chromatograms for a conventional SRC-I PS to the ITSL recycle solvent used for the same purpose. Both samples were obtained during steady state operation. Note that the ITSL recycle solvent (Figure 3.13b) is composed of fewer compounds than is SRC-I PS. These are primarily stable PAH and their C_1 alkyl homologs. ITSL is also of higher average molecular weight. Although both recycle solvents contain hydroaromatic species, the ITSL material has more than 80 percent of its partial saturation in species having four or more rings. SRC-I PS has most of its hydroaromatics as two or three ringed species.

TABLE 3.12

ESTIMATED CONCENTRATIONS^(a) OF APAH IN S-2 FRACTIONS AND CRUDE MATERIALS FROM SELECTED ITSL AND SRC SAMPLES

Compound	ppm Concentrations In APAH Fraction			ppm Concentrations In Crude Sample		
	(136)					
	(007) 3LCF7-37 LCFF	3LCF8-52 Recycle Solvent	SCR-II	(007) SLCF9-0524 LCF TLP	(136) Recycle Solvent	SRC-II HD
5-aminoindan	150	220	150	1.5	2.3	2
1-aminonaphthelene	160	270	3,900	1.7	2.9	70
2-aminobiphenyl	70	130	1,480	0.7	1.9	20
2-aminonaphthalene	60	230	17,100	0.6	2.4	290
4-aminobiphenyl	80	370	3,160	0.8	3.9	510
2-aminofluorene	160	430	58,000	1.6	4.5	980
1-aminoanthracene	130	700	17,350	1.3	7.4	290
9-aminophenanthrene	110			1.1		
2-aminopanthracene	120	150	19,750	1.2	151.0	330
3-aminofluoranthene	140	430	2,500	1.4	4.5	40
1-aminopyrene	90	950	4,720	0.9	10.0	80
6-aminochrysene	570	1770	0	6.0	32.0	

(a) Concentrations rounded to two significant figures.

ITSL recycle solvent (or pasting solvent) is blended from antisolvent deasher underflow and heavy end (850F+) materials from the LC fining stage. Mass spectra of the 8-in. batch distillation unit (BDU) bottoms from the deasher and the 850°F+ material from the LC fining operation are shown in Figures 3.14 and 3.15. An averaged mass spectrum of the recycle solvent is shown in Figure 3.16. Compared to the organic component of the gasifier feed from the deasher, streams making up the recycle solvent are of lower molecular weight with pyrene the constituent in highest concentration. Major constituents in the gasifier feed (Figure 3.17) have molecular weights distributed about five aromatic rings. Mass spectra comparing LCFF and LCF TLP are shown in Figures 3.18 and 3.19. Note the reduction in overall molecular

FIGURE 3.13 (a,b). High Resolution Gas Chromatogram of a) SRC-I Process Solvent and b) ITSL Recycle Solvent

139CP . 0 17-AUG-74 CAL: C812 STA: A. BG SCAN = 3
3399-139 CRUDE. LCF 8"BDU BTMS. W/INT STDS. AVE

0:23

FIGURE 3.14. Averaged Probe Inlet Mass Spectrum of the 8-in. Batch Distillation Unit Bottoms (the most abundant compound appears to be pyrene at M/Z 202)

100CP . G 17-AUG-74 CAL: C812 STR: A. BG SCAN = 0
 3399-100 CRUDE, LCF TLP 850+F, PROBE, AVE

0:23

FIGURE 3.15. Averaged Probe Inlet Mass Spectrum of the 850°F+ Cut from LCF TLP (run period 3LCF7-57)

136CP . 0 16-AUG-74 CAL: C812 STA: A. BG SCAN = 3
3399-136 CRUDE LCF RECYCLE PROC SOLV. PROBE. AVE

0:16

FIGURE 3.16. Averaged Probe Inlet Mass Spectrum of Crude Recycled Process Solvent from Run 3LCF8-52

140CP . 0 17-AUG-74 CAL: C812 STA: A. BG SCAN = 3
 3399-140 CRUDE, LCF GASIFIER FEED, W/INT STDS, AVE

0:23

FIGURE 3.17. Averaged Probe Inlet Mass Spectrum of Gasifier Feed from Run 3LCF8-52
 (note that the average molecular weight of this material is some 50 amu
 higher than that of the BDU bottoms)

116A2P. 0 19-AUG-74 CAL: C819 STA: A. BG SCAN = 7
3399-116 A-2, LC FINE FEED, PROBE AVE. W/INT STDS

0:28

FIGURE 3.18. Probe Inlet Mass Spectrum of LCFF (averaged of all S from about 50°C to 300°C probe temperature)

L007PS. G 28-JUL-82 CAL: C726 STA: A. B6 SCAN = 7

0:21

FIGURE 3.19. Probe Inlet Mass Spectrum of LCF TLP from Run 3LCF9-0524

weight due to LC fining and the persistence of the m/z 202 in representing pyrene. The resistance of pericondensed four-, five- and six-ring structures to ring opening (and hence destruction in the LC finer) suggests that as hydroaromatics these structures may be responsible for the greatly enhanced efficiency of ITSL solvents. This is in contrast to the lower molecular weight materials produced under higher severity liquefaction conditions that are used as recycle solvents in processes such as SRC-II and SRC-I.

The resistance to carbon-carbon bond scission of heavier pericondensed PAHs such as pyrenes, benzopyrenes, anthanthrenes and benzo(ghi)perylene under catalytic hydrogenation/hydrocracking conditions prompted us to make a detailed analysis of these compounds and their hydroaromatic analogs in the various streams and under several operating conditions.

3.4.6 Hydroaromatic Species in ITSL Materials

Table 3.13 shows concentration ratios of hydroaromatic to aromatic species before and after LC fining for materials from run SLCF7-90. Figures 3.20, 3.21, and 3.22 show selected ion chromatograms for several hydroaromatic analogs of compounds such as benzopyrenes, benzofluoranthenes and perylene which have a molecular weight of 252. Thus, m/z 254 represents the dihydro species, m/z 256 represents the tetrahydro species, etc. (m/z 256 is isomeric with the dibenzanthracenes, but these may be distinguished from the hydroaromatic compounds by their relatively later retention time). Figure 3.20 shows traces for the LCF TLP from run LCF0-0524. The chromatographic pattern of the m/z 252 trace is repeated most clearly for the tetrahydro (m/z 256) and octahydro (m/z 260) components. Having identified these components by GC/MS as hydroaromatic, it was possible to quantitatively estimate their concentration by HRGC. Table 3.9 shows estimated concentrations for several hydroaromatics based on the FID response factors for their fully aromatic precursors. Reliable identifications of various isomers of hydroaromatic structures is difficult due to lack of authentic standards. However, in many cases the isomeric structures can be inferred from elution patterns (such as the distinct pattern at m/z 256 which is essentially the same as m/z 252 only displaced to earlier retention time).

TABLE 3.13

CONCENTRATION RATIO (ppm) OF HYDROGENATED SPECIES VERSUS
FULLY AROMATIC PARENT COMPOUND^(a)

<u>Mol. wt.</u>	<u>LCFF</u>	<u>LCF TLP</u>
178 ^(b)	0.14	2.13
202 ^(c)	0.06	0.96
228 ^(d)	0.27	1.88
252 ^(e)	0.25	1.21

-
- (a) Based on the GC response factors of the parent compounds 25 percent error could be expected.
 (b) 7 hydrogenated species were used versus phenanthrene and anthracene.
 (c) 11 hydrogenated species were used versus fluoranthene, pyrene, and acephenanthrylene.
 (d) 4 hydrogenated species were used versus benz[a]anthracene, chrysene, and triphenylene.
 (e) 8 hydrogenated species were used versus benzo(j,b,k)fluoranthene, benzo(e,a)pyrene, and perylene.

Comparison of Figures 3.21 and 3.22 shows that benzofluoranthene structures were more hydrogenated in the LCFF material than were the more highly condensed benzopyrene structures. Accordingly, in the LC fining process both the fluoranthenes and benzofluoranthenes apparently undergo ring opening to a greater extent than do pyrenes and benzopyrenes; concentrations of the former compounds (particularly fluoranthene) decrease dramatically during LC fining (see Tables 3.7 and 3.8). The susceptibility of catacondensed compounds such as benzanthracenes to hydrogenation in complex mixtures and under ITSL conditions appears to be intermediate between that of the pericondensed pyrenes/benzopyrenes and that of the fluoranthenes/benzofluoranthenes.

Although speculative, the following is suggested: in the SCT reactor, hydroaromatic compounds (mainly pericondensed) donate hydrogen to satisfy requirements of free radicals formed mainly from single covalent bond

FIGURE 3.20. GC MS Data of LCF TLP from Run 3LCF9-0524 Showing Total Ion Current Chromatogram (bottom) and Selected Ion Chromatograms of the Dihydro, Tetrahydro, Hexahydro, Octahydro, Decahydro, and Dodecahydro Molecular Ions Arising from Hydrogenation of PAH Species Having Molecular Weight of 252

FIGURE 3.21. GC MS Data of LCFF from Run 3LCF7-90 Showing Total Ion Current Chromatogram (bottom) and Selected Ion Chromatograms of the Dihydro, Tetrahydro, Hexahydro, Octahydro, Decahydro, and Dodecahydro Molecular Ions Arising from Hydrogenation of PAH Species Having Molecular Weight of 252

FIGURE 3.22. GC MS Data of LCF TLP from Run 3LCF7-90 Showing Total Ion Current Chromatogram (bottom) and Selected Ion Chromatograms of the Dihydro, Tetrahydro, Hexahydro, Octahydro, Decahydro, and Dodecahydro Molecular Ions Arising from Hydrogenation of PAH Species Having Molecular Weight of 252

scissions, and to stabilize products formed from the disruption of hydrogen bonding. Heteroatomic or methylene bridging groups between more condensed aromatic moieties are assumed to be more important in formation of free radicals than are aromatic carbon-carbon or aromatic carbon-nitrogen bond scission. This assumption is based on the reduced alkylation and reduced nitrogen (APAH) and exocyclic oxygen (hydroxyl) content of ITSL materials compared to other process materials. The reduced concentrations of alkylated compounds in LCFF compared to SRC-II HD support the view that aromatic bond scission occurs to a lesser extent in the ITSL SCT reactor than in the SRC reactor. Hydrogen bonding is also probably more important in determining secondary and tertiary coal structure in three space than previously recognized. This view is based in part upon the ability of supercritical extractions to give high yields at temperatures too low to effect covalent bond cleavage.

The limited number of compounds seen in low severity SCT extracts also supports this view. Under these relatively mild conditions, the main carriers of hydroaromatic hydrogen from the SCT reactor appear to be higher molecular weight benzofluoranthenes. Mechanisms for the formation of fluoranthene and benzofluoranthene structures can be suggested after cleavage of one or more bridging structures between aromatic moieties. Thus, relatively high concentrations of benzofluoranthene structures, many of which are already partially hydrogenated, occur in the LCFF. There is little partial hydrogenation of pericondensed structures in LCFF.

However, during LC fining benzofluoranthene and fluoranthene compounds undergo ring opening to a greater extent than do pericondensed structures. Concentrations of the former structures are reduced during hydrotreatment with concurrent appearance of alkyl naphthalenes, alkyl benzenes and alkyl naphthenes in the LCF TLP (see Tables 3.7 and 3.8).

In contrast, the pericondensed structures show up in the LCF TLP primarily as dia and tetra hydroaromatics but may have up to as many as 12 additional hydrogens in their ring systems. We assume these structures are the major donors of hydrogen in the recycle solvent since they reappear after the SCT reaction as again fully aromatic.

Summary of Major Results by Sample Set

This section summarizes the major results from the various assays according to sample set and operating conditions of the ITSL PDU.

Sample set 1 was collected under normal operating conditions with a catalyst of age 500 lbs 850°F+ per Lb of catalyst on Indiana No. 5 feed coal. Data from chemical class separation of the TLP showed some enhancement of the amount of material in the A-1 fraction containing aliphatic and some small ring aromatic compounds. There was also concurrent decrease in the N-PAC fraction weights relative to materials taken at other times. This probably reflects higher activity of the LC fining catalyst relative to other runs sampled.

ECD gas chromatography of the nitrogen APAH subfraction showed only trace amounts of APAH (see Table 3.12). These results agree with Ames and CHO data showing greatly decreased mutagenic activity relative to materials sampled during off normal run conditions.

Figure 3.23 shows the retention time for 5-ring PAH in the gas chromatograms of the 850°F+ distillate cuts from the LCFF and LCF TLP. The effects of hydrogenation are obvious, even at these higher molecular weights. Using, for comparison, benzo(ghi)perylene (which is highly condensed and, therefore, not as amenable to hydrogenation as other species eluting in this region) one sees that the relative height of major constituents in this region such as the fully aromatic benzofluoranthenes and benzopyrenes have been substantially reduced by LC fining, and that several partially-hydrogenated species have appeared in this region.

Sample set 2 was collected during run 3LCF7-90 when the LCFF was recycled once to the SCT reactor prior to entering the LC finer. The PDU had been in this configuration since period 82 of run 3LCF7. One effect of this operational mode is that residence time in the SCT reactor for material entering the LC finer is doubled. Hence, the material entering the LC was a product of higher severity liquefaction than normal.

Analytical data from period 90 shows that the weight of the nitrogen fraction from LC finer TLP was substantially higher than that measured during

FIGURE 3.23. Sections of Gas Chromatograms Showing Detail Around the Retention Time for the 5-Ring PAH in the 850°F+ Cuts from LCFF and LCF TLP

period 37 (prior to operation in the LC finer feed recycle mode). Estimated concentrations of APAH also increased for these materials relative to those from period 37 (see Table 3.12). Microbial mutagenicity for the LCF TLD was also higher than for period 37 due to the presence of higher APAH concentrations. We assume that contributing factors to the failure of the LC fining operation (to more effectively deaminate the recycled LC finer feed) included the higher aromaticity of the feed, and the presence of higher concentrations of refractory nitrogen compounds owing to increased SCT reactor residence time.

The ITSL PDU was operated in the LCFF recycle mode to check for degradation of recycle solvent quality, which did in fact occur after period 82. Thus, composition of the LCFF affects overall operation of the two stage system, and particularly deamination of feed materials in the LC finer.

Figure 3.24 is a gas chromatogram of the LCFF from sample set 2. The LCFF consists mainly of neutral PAH and their C_1 homologs. There is little material at GC retention times prior to phenanthrene due to a previous distillation step. In contrast, LCF TLP fractions (see Figure 3.24) have relatively higher concentrations of partially hydrogenated compounds with considerable material eluting prior to phenanthrene. Compounds eluting prior to phenanthrene are products of carbon-carbon bond scission and multiple ring openings in the LC finer. Figures 3.10 and 3.11 show gas chromatograms of the N-PAC fractions from the LCFF and LCF TLP from sample set 2. Removal of gas chromatographable N-PAC from the feed by LC fining is apparent, particularly when one notes the relative height of the internal standard peak.

Sample set 3 was collected during normal operating conditions during run 3LCF8-52 with Illinois 6 coal. Prior to period 52, however, the first two of three coupled LC fining reactors suffered exothermic temperature excursions that exposed the catalyst beds to nominal temperatures of 900°F and 1000°F. Subsequent to the excursion, the measured denitrogenation rate constant decreased (Table 3.3), indicating some loss of catalyst activity.

As with sample set 2, microbial mutagenicity increased measurably in the LCF TLP. Slight increases in microbial mutagenicity of LCFF probably reflect carry over of APAH via the recycle solvent through the SCT reactor.

FIGURE 3.24. High Resolution Gas Chromatogram of the PAH Fractions from LCFF from ITSL
Run 3LCF7-90

Figures 3.25 and 3.26 are gas chromatograms of the LCFF and LCF TLP PAH fraction from sample set 3. Note that the dihydropyrene to pyrene ratio is lower for the TLP from this run compared to the TLD from sample sets 1 or 4.

Sample no. 4 was collected under normal operating conditions with Illinois 6 coal at a catalyst age of 287 lb 850°F+ per lb catalyst. No significant off-normal events such as temperature excursions had occurred during this run prior to sample collection. This sample consisted only of LCF TLP to confirm that nonmutagenic materials were being produced during normal run conditions on Illinois 6 coal. Both mutagenicity assay results and analytical chemistry data indicate that LC fining in run 9 was effective in removing or preventing the formation of mutagenic nitrogen-containing compounds. Figure 3.27 is a chromatogram of the LCF TLP from this sample. Comparison with the other TLP gas chromatograms indicates that the main features, such as relative hydroaromatic to aromatic ratio and average molecular weight, are more dependent on process parameters and catalyst than on the differences between Indiana No. 5 and Illinois No. 6 feed coals.

FIGURE 3.25. High Resolution Gas Chromatogram of the PAH Fraction of LCF TLP from ITSL Run 3LCF8-52. (NOTE: substantial reduction in the relative concentration of fluoranthene and benzofluoranthenes in the LCF TLP relative to the LCFF.)

FIGURE 3.26. High Resolution Gas Chromatogram of the PAH Fraction from LCFF from ITSL Run 3LCF8-52

FIGURE 3.27. High Resolution Gas Chromatogram of the PAH Fraction from LCF TLP Collected from ITSL Run 3LCF9-0524

4.0 DISCUSSION

4.1 BIOLOGICAL ACTIVITY

It should be emphasized that causative links between positive responses in these laboratory tests and epidemiologically validated human health effects are tenuous. Higher molecular weight PAH (such as the dimethyl benzantracenes, benzo(a)pyrene and 5-methyl chrysene found in the ITSL materials) are potent skin carcinogens in rodents, and may be presumed to be human carcinogens based upon epidemiological data including that from the coaking industry. Although not well understood at this time, it appears that there are matrix effects in the ITSL 650+ materials which inhibit expression of these carcinogens, based upon their measured concentrations with respect to the initiation/promotion activity of the ITSL liquids (conversely, there may be agonistic matrix effects in the SR-II HD).

Of the chemical classes mentioned as compounds of concern because they resulted in positive responses in laboratory assays, certain members of the APAH (such as 2 aminonaphthalene and 4 aminobiphenyl) are demonstrated industrial carcinogens.⁽²¹⁾ Thus, the reduction in APAH concentrations in these distillates relative to SRC materials is considered of importance.

During normal operation, the ITSL PDU produced materials of significantly lower mutagenic activity than that of SRC materials. Mutagenicity of ITSL materials was also lower than that reported⁽⁶⁾ for analogous materials from several other direct liquefaction processes, including H-Coal, EDS, and Synthoil. ITSL materials collected during off normal operation or after exothermal excursion of the catalyst showed that mutagenic activity of the TLP was increased relative to that of the LCFF. Thus, it appears that C-N bond scission occurred in the LC fining unit, but that deamination was incomplete and slower under off-normal conditions than under normal conditions. This results in the accumulation of trace amounts of APAH in the TLP, which reflects the observed mutagenic activity. Mutagenic activity was also observed in other process streams which contain components of TLP. Where catalytic activity (as measured by the denitrogenation constant) was reduced by exothermicity, the mechanism for the reduced deamination rate is evident.

Less clear is the reason for increased mutagenic activity during LCFF recycle operation. We believe that the effective increase in severity of the initial liquefaction step, represented by additional residence time in the SCT reactor during recycle, increased the amount of C-N and other covalent bond cleavages. Analytical data tend to confirm this view and we interpret this to be the cause of the increased mutagenicity of the LCFF for sample set 2. Additional research is required to determine the mechanism of the mutagenic response which appears to arise from ultra-trace levels of APAH in hydrotreated LCF TLP.

4.2 SOLVENT QUALITY

In addition to understanding the effects of process changes on biological activity of various process streams, these studies have provided some insight into the chemical basis for improved ITSL solvent quality. The relative hydrogen content of solvents does not always allow good prediction of their relative quality; both ITSL and SRC-I process solvents contain about 11 percent hydrogen, by weight. With carbon at just over 85 percent, this corresponds to a molar hydrogen to carbon ratio of about 1.2 to 1.

In SRC-I PS, more hydrogen is in alkyl side chains than it is in ITSL material. That which is hydroaromatic is contained, to a larger extent, in lower molecular weight structures such as tetralins and cyclohexanes. Nonaromatic hydrogen in ITSL TLP materials, in contrast, is in primarily hydroaromatic structures having four or more rings. These higher molecular weight compounds appear to be superior hydrogen donors in complex mixtures, particularly if lower molecular weight hydroaromatics are present, than are lower molecular weight compounds alone. Thus, the form and molecular weight of structures bearing the nonaromatic hydrogen appear to be of equal or greater importance than relative hydrogen content in determining solvent quality.

It is probably also important that heteroatomic nitrogen (and to some extent sulfur and oxygen) is concentrated in heavy-end ITSL materials that are recycled to make up the process solvent. These more polar compounds are assumed to improve the solvation of polar constituents within the undissolved coal matrix. For example, basic nitrogen-containing aromatic compounds may be

particularly effective in shuttling hydrogen to newly formed exocyclic oxygen functionalities, thus stabilizing them and preventing retrograde reactions. The unshared pair of electrons carried by heterocyclic nitrogen is also thought to perturb hydrogen bonding in the coal structure, facilitating the solution of noncovalently linked organic constituents. Thus, a mixture of higher molecular weight aromatic and hydroaromatic compounds with both acidic and basic heteroatomic functionalities appears to be an excellent liquid-phase analog to the coal matrix itself, and therefore able to act as an effective solvent.

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