Initial Chemical and Biological Characterization of Hydrotreated Solvent Refined Coal (SRC-II) Liquids: A Status Report

July 1980

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INITIAL CHEMICAL AND BIOLOGICAL
CHARACTERIZATION OF
HYDROTREATED SOLVENT REFINED
COAL (SRC-II) LIQUIDS:
A STATUS REPORT

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FOREWORD

This report presents the results of initial chemical and biological characterization studies on a solvent refined coal (SRC-II) distillate and two products resulting from the hydrotreatment of this feedstock, together with an engineering assessment of these materials as they relate to potential commercial-scale products. The work summarized here is dependent upon extensive chemical and biological characterization studies on a wide variety of SRC-II liquids. Results from these earlier studies at Pacific Northwest Laboratory are summarized in the status report "Biomedical Studies on Solvent Refined Coal (SRC-II) Liquefaction Materials" (PNL-3189, October 1979).

The data summarized in this report represent the efforts of four organizations. The Pittsburg and Midway Coal Mining Co. (P&M) provided the distillate blend sample and relevant process information from the Department of Energy's Solvent Refined Coal pilot plant at Fort Lewis, WA. The pilot-scale hydrotreating was performed by the Corporate Research Center of Universal Oil Products, Inc. (UOP), which also provided process information. The engineering assessment of the sample materials was made by Environmental Research and Technology, Inc. (ERT), and the chemical and biological characterization work was performed by the staff of Battelle at Pacific Northwest Laboratory (PNL). Section 2.0 of this report represents primarily the efforts of ERT using process information provided by Pittsburg and Midway Coal Mining Co. and Universal Oil Products. Sections 1.0, 3.0, and 4.0 represent the efforts of the staff of PNL, and 5.0 represents the combined efforts of PNL and ERT.

EXECUTIVE SUMMARY

This technical report presents the results of both chemical and biomedical research performed at Pacific Northwest Laboratory on a solvent refined coal (SRC-II) research material (distillate blend) which was produced by the pilot plant facility at Fort Lewis, Washington. Samples of this distillate blend were subjected to research-scale hydrotreatment by Universal Oil Products, Inc., prior to chemical and biological analysis at PNL. The process conditions under which this blended material was produced and the conditions of hydrotreatment are discussed, as well as the relationship between this material from the pilot plant and that projected for production by a demonstration-scale facility.

Samples of the distillate blend (2.9 parts middle distillate to 1.0 part heavy distillate) were obtained from the Fort Lewis pilot plant during operation in the SRC-II mode. The samples were obtained from the raw product storage section of the plant and represent material accumulated over an extended series of similar runs made under operating conditions close to currently projected demonstration plant design. However, the samples contain components produced not only during stable operation, but also during plant start-up and during upset conditions. The hydrotreating conditions employed are commercially feasible, but do not necessarily represent conditions that would actually be used on a commercial scale. The samples are therefore considered to be, in general, generically representative of raw or hydrotreated materials which might be produced by demonstration or commercial-scale facilities.

The above described feedstock and hydrotreated materials were analyzed for chemical composition both prior to and after chemical fractionation. The fractionation procedure used was an acid-base-neutral solvent extraction. The fractions produced, as well as the unfractionated materials, were subjected to microbial mutagenesis testing (Ames assay) and to further chemical analysis.

The principal components of the unmodified distillate blend are two and three ringed aromatic and heteroatomic species together with high concentrations of phenolic and polynuclear aromatic components relative to typical

levels found in petroleum crudes. The hydrotreating process yields predominately hydroaromatic species of lower overall molecular weight along with reduced concentrations of heteroatomic species. Most nitrogen-containing compounds underwent transformation during hydrotreatment which eliminated or greatly reduced their concentration in the resulting products. Hydrodesulfurization was effected by the upgrading, leaving only residual concentrations of sulfur-containing compounds in the form of thiophenes. Oxygen content was reduced resulting in lowered phenolic concentrations and the virtual elimination of the furans.

The Ames assay mutagenic response for the unfractionated material, as well as the fractions produced by the solvent separation, was reduced considerably in the hydrotreated materials compared to that of the feedstock. Total mutagenic response for the hydrotreated products was approximately 1% of that assayed in the untreated feedstock. The concentrations of two important genetically active compound classes, the polynuclear aromatic hydrocarbons and the primary aromatic amines, were considerably reduced in both of the hydrotreated products compared to the feedstock. Benzo[a]pyrene concentrations, for example, were reduced by at least 75% by hydrotreatment. Primary aromatic amines, which were detected and measured in the feedstock, were not detected in the hydrotreated materials when the same GC-MS methods were applied.

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INITIAL CHEMICAL AND BIOLOGICAL CHARACTERIZATION
OF HYDROTREATED SOLVENT REFINED COAL (SRC-II)
LIQUIDS: A STATUS REPORT

1.0 INTRODUCTION

OVERVIEW: DOE'S SRC ENVIRONMENTAL PROGRAM

In parallel with the process development for the commercialization of economically viable coal conversion technologies, the Department of Energy (DOE) has established a program of investigation to assess SRC coal liquids for their biomedical and environmental properties to help insure the ultimate environmental acceptability of these processes. DOE's environmental program has been outlined generically for liquefaction processes in the Environmental Development Plan (DOE/EDP-0012, March 1978) and has been addressed programmatically for SRC-I and SRC-II in a Project Environmental Plan (PEP). The environmental program presented in the PEP is implemented jointly by Fossil Energy (FE) and the Office of Environment (EV).

PNL'S ROLE IN THE ENVIRONMENTAL EVALUATION OF SRC-II

A number of organizations have been selected by DOE to evaluate the biomedical, environmental, and safety aspects of SRC-II. The Pittsburgh and Midway Coal Mining Co. (P&M) has been assigned responsibility for industrial toxicology. Oak Ridge Operations has been assigned responsibility for the writing of necessary Environmental Impact Statements and the filing for EPA construction permits. Environmental Research and Technology, Inc., (ERT) has been given responsibility for providing various environmental engineering support and evaluation services relating to coal liquefaction.

In this context, PNL has been charged with the responsibility for:

1. generation of a biomedical, chemical, and ecological data base for materials from the SRC processes, and

2. the development and application of appropriate protocols for the interpretation and use of these data for assessment of health and environmental impacts for the SRC processes.

STATUS OF THE PNL PROGRAM

PNL initiated chemical studies with SRC materials in FY 1976. Biomedical and environmental studies were initiated in FY 1978 as part of an expanded fossil fuel research effort. As an outgrowth of this research, PNL was requested to develop a comprehensive Program Plan for the evaluation of the health and ecological aspects of the SRC processes. A preliminary Program Plan was prepared in the first quarter of 1979 for review by FE, EV, and P&M staff. A revised comprehensive Program Plan has been submitted for DOE review and approval.

The present status report constitutes a technical presentation of the initial chemical and biological results of PNL research efforts with SRC-II materials which had undergone post-production upgrading treatment. This is the second in a series of status reports by PNL on SRC-II program activities, findings, and conclusions. The initial status report (PNL-3189, October 1979) dealt with the results of the PNL health effects research effort. A report on PNL ecological research with SRC-II materials is planned for the near future.

OUTLINE OF PRESENT STATUS REPORT

PNL recognizes the critical role of representative sampling for health and ecological characterization. To the extent possible, samples should be chosen in a manner allowing extrapolation of the data obtained from pilot plant, PDU, and bench-level materials to demonstration and commercial SRC materials. Accordingly, our status report discusses sample relevance to both pilot plant operations and to potential demonstration/commercial conditions. This discussion is followed by a comprehensive presentation of PNL's technical research efforts and findings to date regarding the chemical and biological characteristics of the hydrotreated SRC-II materials. The implications of these findings are then summarized.

2.0 ENGINEERING ASSESSMENT OF SAMPLE MATERIALS

A principal objective in the chemical and biological characterization of samples from pilot plant facilities is to relate these research results to the assessment of health and environmental impacts of anticipated demonstration and commercial scale SRC-II coal liquefaction plants and materials. Utilized effectively during this phase of the program, life science data can contribute significantly to the development of optimal plant designs.

While the specific details of the design and operation of a commercial coal-derived liquids refinery can only be hypothesized at present, hydrotreatment is an upgrading operation that may well become an integral part of the production process. Hydrotreating by catalytic hydrogenation is a standard petroleum refinery process which may be applied to a variety of feeds to produce both marketable products and feedstocks for downstream processing units. Hydrotreatment removes or modifies much of the heteroatomic material (sulfur, nitrogen, and oxygen-containing compounds) in the feedstock and results in some aromatic ring saturation and cracking, with product properties and yields for a given feedstock depending primarily on the extent of hydrogenation.

No detailed designs or design bases have been made for upgrading heavy SRC-II distillates^(a). The pilot plant process conditions corresponding to the hydrotreated samples discussed in this report can be evaluated to some extent in light of current demo plant design basis conditions. The hydrotreatment processing conditions, however, can be evaluated only in general terms.

The chemical characteristics of the bioactive materials in coal-derived liquids and the types of reactions which occur during hydrotreating are such that significant changes in biological activity may result from hydrotreatment. Exploratory chemical and biological characterization work described in this report was designed to provide initial data on such changes. This section

(a) The demonstration plant is scheduled to include a naphtha hydrodesulfurization unit which is also capable of processing light fuel oil, but no distillate hydrotreating is currently specified (21).

presents an engineering assessment of the relevance of the sample materials thus characterized to projected demonstration and possible commercial-scale materials. This is accomplished by first reviewing the pilot plant production and hydrotreatment processing histories of the samples and then relating this information to known or projected demonstration and commercial scale processing conditions.

PILOT PLANT CONDITIONS

The Pittsburgh and Midway Coal Mining Co. collected a sample of blended SRC-II middle and heavy distillates from its Fort Lewis, Washington, pilot plant on March 23, 1979 for hydrotreating experiments by Universal Oil Products, Inc. (UOP). (A description of the SRC-II process as well as pilot plant operation is contained in reference 1.) The sample was obtained from tankage which had been accumulating material generated over a series of pilot plant runs extending from October 1978. All of the runs had the same set of target operating conditions with the goal of accumulating large volume samples for in-field power generation and combustion testing. A middle-distillate to heavy-distillate blend ratio of 2.9 to 1.0 was determined from the average yield ratios of the runs during the accumulation period. The fact that the sample represented material accumulated over a long series of similar pilot plant runs reduces the uncertainties associated with representative sampling of a single pilot plant run. For example, the source of seal flush oil and start-up recycle slurry oil for any given run during this period consisted primarily of materials from similar runs. However, a long-term accumulation sample may present other difficulties in assessing sample representativeness and processing history due to:

1. material from all modes (ranging from steady state to upset conditions) of operation during the period being accumulated, and
2. some unavoidable product variability being introduced since operating conditions cannot be precisely duplicated from run to run.

Table 2.1 shows the target operating conditions for the pilot plant runs made during the sampling period in comparison to the average results achieved.

TABLE 2.1. Target and Achieved Operating Conditions for SRC-II Material Balance Runs 78SR-22 Through 78SR-29(13,14)

Operating Parameter	Target Condition	Average Condition Achieved ^(a)
Dehumidified Coal Feed Rate, lb/hr	2070	2095 $\pm$ 21
Feed Slurry Coal Concentration, wt%	30	29.7 $\pm$ 1.5
Feed Slurry Flowrate, lb/hr	6900	7065 $\pm$ 347
Feed Gas Hydrogen Purity, vol. %	85	85.6 $\pm$ 0.4
Feed Gas Flowrate, lb/hr	1030	1080 $\pm$ 146
Dissolver Pressure, psig	2000	2005 $\pm$ 2
Dissolver Outlet Temperature, °F	860 ^(b)	856 $\pm$ 3
H ₂ /Slurry Ratio: lb H ₂ /100 lb slurry	-- (c)	5.5 $\pm$ 1.0
Nominal Dissolver Residence Time, hrs	-- (c)	0.93 $\pm$ 0.04

(a) Mean $\pm$ std. dev. for eight material balance runs.

(b) Target reduced to 855°F for run 78SR-29.

(c) No target set.

The average results are for the eight material balance runs made during the accumulation period. Material balance run 78SR-22 began in early October, 1978 and run 78SR-29 ended in late December, 1978. The table shows that the target conditions were closely approached on the average, with generally minor variation in conditions between runs. The greatest variations from target conditions between runs were in the feed slurry and feed gas flowrates, as reflected in the relatively wide variation in hydrogen-to-slurry ratio.

The range of conditions shown by the results in Table 2.1 has some effect on reactor yield structures and product properties. Distillate yields, for example, increase with lower feed slurry coal concentration, longer dissolver residence times, and higher hydrogen partial pressures. Table 2.2 gives some indication of the variations in yield structures resulting from similar pilot plant runs by showing the average yields and corresponding standard deviations for liquid and SRC yields and hydrogen consumption. While the table shows significant variations, especially for heavy distillate yields, difficulties in accurately determining yields from pilot plant data are a major source of

TABLE 2.2. Average Balanced Elementaly Balanced Yields for SRC-II
Material Balance Runs 78SR-22 Through 78SR-29(13,14)

Component	Average Wt% MAF Coal Feed Yield, (a)
Hydrogen	-4.7 $\pm$ 0.5
Naphtha (C ₅ - 350°F)	9.2 $\pm$ 2.4
Middle Distillate (350-550°F)	24.4 $\pm$ 4.1
Heavy Distillate (550-850°F) (b)	8.5 $\pm$ 6.4
SRC (b,c)	28.1 $\pm$ 1.8

} Ratio of 2.9 to 1.0

(a) Mean $\pm$ std. dev. for eight material balance runs.

(b) SRC = vacuum bottoms - pyridine insolubles - ash.

(c) Yields not adjusted for differences in vacuum bottoms fusion point.

variation in addition to any actual yield differences. Table 2.2 also shows how the 2.9 to 1.0 middle-to-heavy distillate blending ratio was obtained. It is noteworthy that these ranged from a ratio of 1.1 to 1 to a ratio of 36 to 1 for individual material balance runs.

The eight material balance runs summarized in Tables 2.1 and 2.2 ranged from 25 to 95 hours in duration and comprised a total run time of 454 hours. This amounts to 21% of the onstream operating hours between October 1, 1978, and March 23, 1979, when the samples were collected. The material balance runs were all made during October through December, 1978, with additional production runs with Powhatan No. 5 coal being made during the first quarter of 1979. Material balance runs accounted for 31% of the on-stream operating time during the fourth quarter of 1978. The additional run time was spent either in approaching lined-out material balance run conditions or in upset conditions between lined-out operation. While the precise split between these two modes of operation is difficult to determine, it is the judgment of the pilot plant operators that severe upset conditions comprised only a small portion of the non-material-balance run operations. The pilot runs during the first quarter of 1979 were made for the purpose of generating additional sample material for combustion testing and were made under operating conditions similar to those during the earlier material balance runs. These runs processed

about 40% more coal than was processed during the material balance runs. For the purposes of this engineering assessment, it is assumed that material balance runs and yields are representative of most of the plant operating time during the sample accumulation period.

HYDROTREATING CONDITIONS

Two drums of the 2.9 to 1.0 middle-to-heavy SRC-II distillate blend were supplied to UOP for research-scale refinery upgrading experiments at its Corporate Research Center in Des Plaines, IL, under U.S. DOE contract No. EF-77-C-01-2566. These experiments included hydrotreating process variable studies, hydrotreating preparative runs [to generate fluid catalytic cracking (FCC) feedstocks], and varying feedstock FCC studies. Figure 2.1 outlines the work done by UOP, with materials sampled for PNL characterization indicated by bold outlining. These materials were the raw distillate blend (drum No. 1 - UOP No. 3777-6) and the 400⁰F+ products from mild (UOP No. 3777-34) and severe (UOP No. 3777-41) preparation run hydrotreatment.

The UOP hydrotreating experiments were carried out in standard research-scale reactors using a commercial UOP catalyst (UOP DCB catalyst consisting of Group VI and VIII metals on a high surface area refractory support). Figure 2.2 shows a schematic diagram of the research-scale hydrotreating plant. According to Dr. Armond deRossett at UOP, the reactor consists of 50 to 800 cc of catalyst in a fixed bed, depending on whether process variable studies or preparative runs are made, with concurrent downflow of oil, hydrogen, and recycle gas. The reactor product is scrubbed with water to remove H₂S and NH₃ and is then separated into a recycle gas (mainly hydrogen), sour water, and product oil.

UOP began its SRC-II hydrotreating studies by parametrically studying the effects of pressure, temperature, and residence time on yields and product properties. Eighteen different runs covering three temperatures, three residence times, and two pressure levels were made. On the basis of the results obtained, two preparative scale runs were made to produce feeds for research scale FCC studies. The materials characterized by PNL are the 400⁰F+ products from these preparative scale runs (Figure 2.1).

FIGURE 2.1. Outline of UOP Upgrading Studies on SRC-II Distillate Blend(2a)

- (a) All yields are in wt.% relative to the two initial SRC-II gas oil drums.
 (b) UOP sample code No. 3777-XX indicates that UOP sample inspections were made.
 (c) Bold-outlined materials were sampled for characterization by PNL.

FIGURE 2.2. Schematic Diagram of UOP Research-Scale Hydrotreating Reactor System⁽¹⁵⁾

Table 2.3 summarizes the yields and processing conditions for the two preparative-scale hydrotreating runs, while Table 2.4 summarizes the inspections made by UOP of the feed and product materials. The run conditions shown (Table 2.3) are relative to base conditions which might be employed commercially for hydrotreating a typical Arabian vacuum gas oil⁽¹⁵⁾, and are within the range of commercially achievable operating conditions. Note that the volumes of product oil obtained are greater than the feed volume. This is due to reduced specific gravities as a result of hydrotreating (see Table 2.4). The feed and product inspections (Table 2.4) show that the two feeds were very similar, while the product inspections indicate the degree of heteroatom (S,O,N) removal and aromatic ring saturation and cracking which resulted from the hydrotreatment. The hydrogen content of the feed increased from 8.7% to 10.4% after mild hydrotreatment and to 11.2% after severe hydrotreatment. This is reflected in the significant increase in the paraffin and naphthene (hydroaromatic) content of the products. Sulfur levels were significantly reduced almost equally by moderate and severe hydrotreatment (96.1% and 97.4% removal, respectively), while nitrogen and oxygen removal was less efficient

TABLE 2.3. Yields and Run Conditions for Preparative-Scale Hydrotreating of SRC-II Distillate Blend by UOP(2a)

Run Conditions ^(a)	Moderate Hydrotreating	Severe Hydrotreating
Pressure, $P - P_{\text{base}}$, psi	0	500
Temperature, $T - T_{\text{base}}$, °F	-100	-65
Space Velocity, ^(b) LHSV/LHSV _{base}	0.8	0.4
<u>Yields, wt% (LV%) of feed</u>		
C ₁	0.01	0.04
C ₂	0.03	0.07
C ₃	0.02	0.06
C ₄	0.03	0.04
C ₅ and C ₆ (in plant gas)	0.33	0.26
Stripper Bottoms	99.47 (104.6)	99.40 (108.7)
400°F end point naphtha	21.4 (24.6)	30.0 (35.7)
400°F+ gas oil	78.1 (80.0)	69.4 (73.0)
H ₂ O	1.42	1.70
H ₂ S	0.32	0.39
NH ₃	<u>0.32</u>	<u>0.89</u>
TOTAL	101.95	102.85
H ₂ Consumption, wt% of feed	1.95	2.85
H ₂ Consumption, SCF/bbl feed	1290.0	1870.0

(a) Run conditions relative to base conditions which "represent conditions employed commercially for hydrotreating a typical Arabian vacuum gas oil"(15).

(b) Liquid hourly space velocity is defined as volume of oil/hr/volume of catalyst.

and more dependent on hydrotreating severity (32% and 79% nitrogen removal and 46% and 61% oxygen removal for moderate and severe hydrotreatment, respectively). These results indicate the relative ease of removing the various heteroatomic species. The distillations in Table 2.4 also show that hydrotreatment reduced the heavy end content of the feed and increased the naphtha (400°F endpoint) yield. Complete data from material inspections of the feed-stock and hydrotreated materials are available in UOP monthly reports^(2a, 2b).

TABLE 2.4. UOP Inspections of Raw and Hydrotreated SCR-II Distillate Blend^(2b)

Parameter	Feed		Mildly ^(a) Hydrotreated		Severely ^(b) Hydrotreated	
	Drum 1	Drum 2	WLP ^(c)	400°F+	WLP ^(c)	400°F+
UOP Sample No. ^(f)	3777-6	3777-7	3777-21	3777-34	3777-28	3777-41
API @ 60°F	9.7	10.1	17.0	13.6	23.4	17.7
Specific Gravity @ 60°F	1.0021	0.9993	0.9529	0.9752	0.9135	0.9484
Weight %						
Hydrogen	8.68	8.72	10.38	9.98	11.18	10.59
Carbon	85.83	86.13	86.91	86.84	87.17	84.86
Oxygen	2.02	1.73	1.08	0.98	0.67	0.83
Weight ppm						
Sulfur	3300	3815	129	106	98	109
Nitrogen	8100	9040	5510	6000	1900	1730
FIA ^(d) , Vol.%						
Color Band ^(e)	----	36.1	19.7	19.4	6.3	----
A	90.1	54.5	59.1	69.9	50.8	73.9
P&N	9.9	9.4	21.2	10.7	42.9	26.1
ASTM D 1160 Distillation, LV%, °F						
IBP/5	386/407	335/395	280/350	418/428	234/302	408/440
10/30	417/445	410/444	374/422	436/462	331/400	448/463
50	486	472	460	487	446	490
70/90	535/645	512/656	505/611	539/641	490/575	536/625
95/EP	711/799	705/810	687/779	691/790	628/724	668/748
% Over	99.0	99.0	99.0	99.0	99.0	99.0
TBP Distillation, LV%, °F ^(g)						
IBP	347	292	241	388	195	368
10	404	397	359	424	315	438
30	438	438	415	456	392	457

(a) Feed was Drum No. 1.

(b) Feed was Drum No. 2.

(c) Whole liquid product.

(d) Fluorescent indicator analysis for aromatics (A), paraffins (P), and naphthenes (N).

(e) Indicates highly polar compounds.

(f) Underlined samples were characterized by PNL.

(g) True boiling points based on standard correction of ASTM-D1160 distillation data. This correction method assumes that the D-1160 yields are the same as the TBP yields from the 50% point to the end point.⁽¹⁶⁾

RELEVANCE OF SAMPLES TO DEMONSTRATION/COMMERCIAL SCALE MATERIALS

There are two aspects in assessing the demonstration or commercial scale relevance of the sample materials characterized. The first is concerned with the pilot plant production of the raw SRC-II distillates, and the second involves the hydrotreating of the distillate blend sample. In both cases, the relevance of the samples to potential demonstration or commercial scale materials can be unequivocally assessed only by comparison with detailed process designs for larger scale facilities. Final detailed designs for the SRC-II demonstration plant are not presently available; however, some design basis conditions have been tentatively specified and may be used for comparison. No detailed design bases or conditions are presently available for hydrotreating SRC-II distillates so that pilot-plant hydrotreating conditions can only be evaluated in general terms.

Pilot Plant Conditions

One means for assessing the relevance of pilot plant samples to projected demonstration plant materials is to compare the physical/chemical properties which are expected to influence bioactivity and upgrading results. However, the properties of projected demonstration plant products have not yet been specified in detail so that such a direct comparison cannot be made. Therefore, the relevance of the pilot samples must be assessed indirectly by comparing the processing conditions which determine the properties of the product materials.

Feed Coal

The Powhatan No. 5 feed coal and processing conditions for material balance runs 78SR-22 through 78SR-29 are fairly representative of the current demonstration plant design basis. The Powhatan No. 5 coal is from the Ohio West Virginia "Panhandle Area" and the coal selected for Phase I demonstration plant design was based on representative coals from this area. Table 2.5 shows the range of design basis Panhandle feed coal compositions compared to the analysis of a composite sample of a Powhatan No. 5 coal shipment received by the Fort Lewis pilot plant. Table 2.5 illustrates both the variability in coal composition that the demonstration plant will be designed to handle and the fact that Powhatan No. 5 coal is within this range except for nitrogen and

TABLE 2.5. Comparison of Powhatan No. 5 and Demonstration Plant Design Basis Coal Analyses, Weight Percent MF Basis

Component	Demo Plant Design Basis Panhandle Feed Coal Composition ⁽¹²⁾			Composite of Fort Lewis Pilot Plant Powhatan No.5 Coal Shipment
	Low	Design	High	
	Reactivity	Reactivity	Reactivity	
Carbon	73.93	70.49	67.50	72.25
Hydrogen	5.11	4.88	4.69	4.94
Nitrogen	1.22	1.12	1.32	0.83
Oxygen	7.54	7.87	8.27	6.68
Sulfur				
Pyrites	1.8	2.0	2.2	1.91
Organic	1.3	1.54	1.9	1.70
Sulfate	<u>0.07</u>	<u>0.05</u>	<u>0.05</u>	<u>0.05</u>
TOTAL	3.17	3.59	4.15	3.66
Chlorine	0.03	0.05	0.07	0.07
Ash	9.0	12.0	14.0	11.57
(Iron Content)	<u>(1.58)</u>	<u>(1.75)</u>	<u>(1.93)</u>	<u>(1.92)</u>
TOTAL	100.00	100.00	100.00	100.00

oxygen content. The lower nitrogen and oxygen levels for the pilot plant Powhatan No. 5 coal mean that the demonstration plant distillates may have higher nitrogen and oxygen contents than the UOP samples characterized by PNL. Both of these factors could affect the hydrotreatment and the bio-activity of these materials.

Reactor Conditions

The five independent reactor operating variables which primarily affect the yields from the SRC-II process are⁽¹²⁾:

- Dissolver Temperature
- Dissolver Slurry Space Velocity
- Dissolver Outlet Hydrogen Partial Pressure
- Feed Slurry Coal Concentration
- Feed Slurry Ash Concentration

Table 2.6 compares the average pilot plant operating conditions related to these key variables for the material balance runs against the current demo

TABLE 2.6. Comparison of Demonstration Plant Design Basis and Average Pilot Plant Operating Conditions During Hydrotreatment Sample Collection

	Demo Plant Design Basis(a)	Average Conditions During Pilot Plant Material Balance Runs 78SR-22 thru 29(b)
Dissolver Temperature, °F	860	856 $\pm$ 3
Dissolver Pressure, psia	2000	2020 $\pm$ 2
Dissolver Slurry Space Velocity, hr ⁻¹	(c)	1.08 $\pm$ 0.04 ^(d)
Feed Slurry Coal Concentration, wt %	30	29.7 $\pm$ 1.5
Feed Slurry Ash Concentration, wt %	(c)	10.1 $\pm$ 0.9 ^(e)
H ₂ /Slurry Ratio, lb H ₂ /100 lb slurry	(f)	5.5 $\pm$ 1.0

(a) Ref. No. 12.

(b) Mean $\pm$ std. dev. for eight runs (Table 2.1)(13,14)

(c) Not specified yet and/or proprietary.

(d) Inverse of dissolver residence time, Table 2.1.

(e) Ash due to recycle slurry; does not include ash in coal.

(f) This and/or other measures of hydrogen reactant are considered to be proprietary.

plant design conditions. Dissolver temperature and pressure and feed slurry coal concentration conditions are very similar, while dissolver slurry space velocity, outlet hydrogen partial pressure and feed slurry ash concentration cannot be compared due to the limited demo design data currently available publicly. In general, the pilot plant conditions for these variables should not differ markedly from expected demo plant design conditions. This indicates that pilot plant and demo distillate product properties should be roughly comparable.

Product Yields

Table 2.7 compares the yields of the demo plant design basis with the average pilot plant yields for the hydrotreating sample accumulation material balance runs. These comparisons indicate similarities in processing results and, hence, product properties between the pilot plant and the projected demo plant. The table shows that the average pilot plant yields are within the

TABLE 2.7. Comparison of Demonstration Plant Design Basis Yields and Average Pilot Plant Yields During Hydrotreatment Sample Collection, Wt. Pct. MAF Coal Basis

Component	Demo Plant Design Basis Yields ^(a)			Average Yields During Pilot Plant Material Balance Runs 78SR-22 thru 29 ^(b)
	Low Reactivity	Design Reactivity	High Reactivity	
Hydrogen	-4.4	-5.0	-5.5	-4.7 $\pm$ 0.5
C ₁ - C ₄	16.6	18.8	20.6	17.8 $\pm$ 2.5
C ₅ - 350°F	8.0	9.0	9.5	9.2 $\pm$ 2.4
350 - 550°F	17.7	19.4	19.9	24.4 $\pm$ 4.1
550 - 900°F ^(c)	13.0	12.5	12.2	8.5 $\pm$ 6.4
SRC ^(h)	31.9	27.3	24.0	28.1 $\pm$ 1.8
IOM ^(d)	5.6	5.2	5.4	6.0 $\pm$ 0.8
Misc. Gases ^(e)	10.5	11.6	12.5	10.7 $\pm$ 1.1
Residual S & C1 ^(f)	1.1	1.2	1.4	-----
Total	100.0	100.0	100.0	100.0

(a) Ref. No. 12.

(b) Mean $\pm$ std. dev. for 8 runs(13,14).

(c) Pilot plant endpoint was nominally 850°F, with 850 - 900°F material reporting to vacuum bottoms

(d) Insoluble organic matter.

(e) H₂S, H₂O, NH₃, CO, and CO₂.

(f) Not reported in pilot plant material balances.

(g) Standard deviation obtained by square root of the sum of squares of the individual standard deviations.

(h) SRC = vacuum bottoms - pyridine insolubles - ash.

range of the demo design for a similar hydrogen consumption level except for the distillate yields and IOM (insoluble organic matter). The difference in the overall distillate yields is greater than indicated in Table 2.7 (it is less for the heavy distillate) since the demo plant design heavy distillate endpoint is 900⁰F compared to the 800 to 850⁰F endpoint achievable with the pilot plant vacuum flash tower. It is not clear that the differences are truly significant, however, given the uncertainty associated with the pilot plant yield data. This is shown by the fact that the magnitude of the standard deviations are comparable to the magnitude of the yield differences.

Product Properties

Although detailed demonstration design basis product properties have not yet been specified, pilot and demo products should be similar for given boiling range cuts produced under comparable processing conditions since the various compounds produced, although perhaps different in proportions, will be similar. Figure 2.3 compares the true boiling point (TBP) distillation curves for the UOP/PNL distillate blend sample and the projected demo plant liquid product, with the UOP distillation renormalized to correspond to the demo plant curve at 400⁰F. Note that the demo distillation curves are on a weight percent basis while the UOP distillation is on a volume basis, since no definitive data are available for converting the two curves to a common basis. The pilot and demo curves plotted on a common basis would be somewhat closer together (by roughly two percent) since naphtha yields are greater on a volume basis than on a weight basis, while heavy distillate yields are lower on a volume basis than on a weight basis.

The differences shown in relative boiling range distribution and endpoint between the UOP/PNL sample and the projected demonstration plant product mean that the pilot plant sample contained relatively less heavy end material and essentially no 800⁰F+ material. This is clearly shown by Table 2.8, which compares the approximate distribution of 400⁰F+ material between sequential 100⁰F boiling range cuts for the pilot and projected demo materials. While the chemical properties of any one of these cuts are expected to be roughly comparable for the pilot and projected demo products based on similar

FIGURE 2.3. Comparison of Distillation Curves for Projected Demo Plant Product and UOP Hydrotreating Pilot Plant Sample

- (a) Wt.% yields based on nominal C_5 IBP of 90°F (12).
 (b) Vol.% yields normalized to 400°F at demo plant 33% point
 (see Table 2.4)

processing conditions as described above, the differences in relative proportions of these cuts may affect both the bioactivity and the upgrading requirements of the overall distillate blend. The fact that the pilot plant sample contains less heavy ends is especially significant because heavier material is

TABLE 2.8. Comparison of Approximate 100°F Boiling Cut Yields for Projected Demonstration Plant Product and UOP Hydrotreatment Pilot Plant Sample

Cut TBP Boiling Range	Design Demo Plant Product, wt%(a)			UOP Sample		
	Low Reactivity	Design Reactivity	High Reactivity	LV%(a)	Assumed sp. gr.(b)	Wt%(c)
400 to 500°F	34	36	38	56	0.99	54.5
500 to 600°F	30	30	30	27	1.04	27.6
600 to 700°F	16	18	18	11	1.06	11.5
700 to 800°F	12	11	10	6	1.09	6.4
800 to 900°F	<u>6</u>	<u>5</u>	<u>4</u>	<u>0</u>	<u>---</u>	<u>----</u>
	100	100	100	100		100.0

(a) Obtained from renormalization of Figure 2.3 distillation curves.

(b) Approximate example specific gravities assumed based on UOP data from topping drum No. 2 sample (UOP No. 3777-7, sp. gr. 0.9993) of 0.9291 sp. gr. 400°F EP naphtha (UOP No. 3777-35) and 1.0173 sp. gr. 400°F+ gas oil (UOP No. 3777-35)(2b).

(c) Obtained from $(LV\%) \times (sp. gr.) = 101.73$.

harder to process in upgrading operations and because there are indications (see Section 4.0) that the heavy end contains most of the genotoxic activity.

Differences between distillation yields from the pilot plant and those projected for the demo plant are due to a combination of factors. These include pilot plant limitations in achieving high distillate endpoints and possible differences in yield structures due to variations in processing conditions and/or reactor geometries. The first item is inherent in the pilot plant design and operation, while the second is somewhat subject to control. Future work will need to address these issues because of the probable importance of representative heavy end samples in upgrading and bioactivity studies.

The pilot plant sample was found to contain nine weight percent diphenyl ether. This compound is a major component of Dowtherm A, which is a heat transfer fluid that is used extensively at the Fort Lewis pilot plant. While contamination of pilot plant products by Dowtherm leakage has been common, a level of nine weight percent is unusually high. This may have resulted from stratification in the storage tanks or a one-time slug of heavy Dowtherm

contamination. In any event, it is clearly not representative of projected demo plant product, although the precise effect of the contamination on hydrotreating and bioactivity results aside from that of simple dilution is not known at present.

Hydrotreating Conditions

A significant amount of research-scale work has been performed on the feasibility of upgrading SRC-II and other coal liquids using standard petroleum refinery processes such as hydrotreating, hydrocracking, reforming, and fluid catalytic cracking. These studies indicate that upgrading coal-derived liquids into acceptable transportation and heating fuels is feasible and may be economically viable^(17,18). In this context, the hydrotreating conditions employed by UOP represent a feasible upgrading step, but not necessarily the actual or final upgrading step that would be employed commercially. More or less severe hydrotreatment could be used commercially, depending on specific feedstock properties, the desired product slate, and the overall refining scheme employed. Chevron Research Company, for example, has successfully hydrotreated a full boiling range SRC-II pilot plant sample to yield a product with less than 1 ppm nitrogen, requiring about 3000 SCF/bbl hydrogen, which provided an excellent naphtha reformer feed and a premium jet fuel⁽¹⁸⁾. However, the feed contained significantly lower concentrations of the heavy end components compared to the projected demo plant product. While this hydrotreatment does not necessarily represent the mode in which SRC-II liquids would be commercially upgraded, it does indicate the range of hydrotreating conditions which could be employed.

SUMMARY

The pilot plant processing conditions during sample accumulation were fairly close to demonstration plant design conditions during material balance run periods, which accounted for approximately one-fifth of the pilot plant operations time during the accumulation period. The balance of the plant operations time involved generally similar operating conditions, although a portion of the accumulated material sampled was produced during poorly characterized and nonrepresentative upset conditions. The UOP hydrotreating

conditions employed are commercially feasible, although they do not necessarily represent the conditions that would actually be employed in a commercial upgrading operation. Thus, the effects of hydrotreatment on the pilot plant coal liquids are likely similar in a generic sense to those expected from the hydrotreatment of demonstration or commercial scale materials. The quantitative results for various chemical constituents may vary somewhat from the results presented here, depending on the individual species abundance in demonstration or commercial materials.

Some special problems as they relate to the pilot plant samples in this study that should be noted include:

1. the lower nitrogen and oxygen content of the pilot plant Powhatan No. 5 coal compared to the demonstration plant design basis coal could affect the concentrations of respective heteroatomic compounds in the distillates;
2. the lower heavy distillate content and endpoint of the pilot plant distillate blend compared to the demonstration plant design product may affect the hydrotreating and bioactivity behavior of the distillates;
3. the effect of the high diphenylether (Dowtherm A) content of the pilot plant sample on the hydrotreating and bioactivity results is unknown.

3.0 SUMMARY OF CHEMICAL CHARACTERIZATION RESULTS

INTRODUCTION

The SRC II distillate blend feedstock and the hydrotreated product materials were subjected to chemical analysis by several methods to determine changes in concentrations of the principal compound classes as a function of hydrogenation severity. Normally, such information is useful in evaluating the catalysts employed in hydrogenation as well as in predicting the effects of the upgraded product on catalytic systems encountered during further refining. A primary objective of these analyses, however, was to study the fate of nitrogen compounds during upgrading. Such compounds are of interest because of their adverse effects on refining catalysts, as well as their contribution to NO_x emissions upon combustion.

Nitrogen compounds are of primary concern, however, with regard to the biological activity exhibited by coal liquids^(3,4). Mutagenicity of these liquids, as measured in the Ames test, resides almost exclusively in nitrogen-rich fractions. Previous work in this laboratory has yielded strong evidence⁽⁵⁾ that multi-ring primary aromatic amines (PAA) are major contributors to the mutagenicity of the active materials; hence, particular attention was paid to determination of PAA concentrations in the materials studied.

EXPERIMENTAL

Solvent Fractionation

The SRC-II distillate blend and its hydrogenated products were fractionated by an acid-base-neutral solvent extraction sequence. These materials were dissolved in isooctane and then partitioned sequentially with 1N HCl, 1N NaOH and dimethylsulfoxide. The resulting fractions are designated isooctane-insoluble tar, basic, acid-induced tar, acidic, base-induced tar, neutral and polynuclear aromatic hydrocarbon (PAH). This separation scheme is depicted in Figure 3.1.

GC-MS Analysis

Both electron impact and chemical ionization mode GC-MS analyses were performed on a Hewlett Packard 5985-A GC-MS system using either a 60 m x 0.25 mm

FIGURE 3.1. Solvent Fractionation of SRC Materials

ID WCOT glass column coated with SP-2250 liquid phase or a specially prepared 25 m x 0.25 mm ID WCOT glass column with SE-52 phase. Splitless mode injection was employed for the capillary columns. The eluate stream was split to allow simultaneous flame ionization (FID) and mass spectrometric detection. The FID trace was automatically integrated for GC peak quantitation and the MS data were used for peak identification. Concentrations of those PAH compounds having four or more rings were determined by GC alone using a 4 mm ID x 2 m glass column packed with an SP-301 (liquid crystal) stationary phase at 270^o isothermal.

PAH concentrations were determined both directly and in the PAH fractions using benzo[a]pyrene, benzo[e]pyrene and perylene as external standards. Primary aromatic amine and nitrogen heterocycle concentrations were estimated from the basic and tar fractions on both the SP-2250 and SE-52 columns using methylenedianiline and d₁₀ anthracene as internal standards. Phenol, aromatic and hydroaromatic concentrations were determined in the intact materials using the SE-52 column. Undetermined amounts of the more volatile anilines (or pyridines), alkyl benzenes, and cyclohexanes were lost during the fractionation procedure; hence, no quantitative data are presented for these lower molecular weight components.

RESULTS

Solvent Fractionation/GC-MS

As expected, the gross composition of the SRC-II feedstock was substantially altered by the catalytic hydrotreating as illustrated by comparing the chromatograms in Figures 3.2a and 3.2b and data in Table 3.1. These data are graphically summarized for gross chemical class composition in Figure 3.3. Overall, compounds having lower boiling points were produced, suggesting that the higher molecular weight aromatic compounds in the SRC-II feedstock had undergone extensive hydrogenolysis. This resulted in the almost exclusive formation of a series of hydroaromatic compounds and their alkylated homologs. Comparative data from the solvent fractionation of the three materials is listed in Table 3.2. The substantial decrease in the weight percentages of

FIGURE 3.2a. Reconstructed Total Ion Chromatogram of SRC-II Distillate Blend

FIGURE 3.2b. Reconstructed Total Ion Chromatogram of Severely Hydrotreated SRC-II Distillate Blend

LEGEND TO FIGURES 3.2a & 3.2b

Reconstructed total ion chromatograms comparing unfractionated SRC-II feedstock, Figure 3.2a, with the severely hydrotreated material, Figure 3.2b. Principal peaks are identified in both chromatograms: (a) 1: phenol, 2: C₁ phenol, 3: tetralin, 4: naphthalene, 5: indole, 6: C₃ phenol, 7: C₁ naphthalene, 8: biphenyl, 9: C₂ naphthalene, 10: phenylether, 11: dibenzofuran, 12: acenaphthene, 13: fluorene, 14: C₁ fluorene, 15: dibenzothiophene, 16: phenanthrene. (b) 1: methyldecalin, 2: methylindan, 3: methyltetralin, 4: tetralin, 5: dimethylindan, 6: dimethylindan, 7: methyltetralin, 8: dimethylindan, 9: methyltetralin, 10: ethyltetralin + dimethylbenzofuran, 11: ethyltetralin, 12: ethyletralin, 13: biphenyl + hexahydroacenaphthylene, 14: phenylether, 15: C₄-indene, 16: C₄-tetralin, 17: C₃-dihydronaphthalene, 18: tetradecahydroanthracene, 19: tetradecahydrophenanthrene, 20: C₃-dihydronaphthalene, 21: C₄-tetralin, 22: C₅-indan or C₄-tetralin, 23: C₅-indan or C₄-tetralin, 24: C₄-dihydronaphthalene, 25: hexadecahydropyrene, 26: octahydroanthracene.

FIGURE 3.3. Gross Chemical Composition Related to Severity of Hydrotreatment

TABLE 3.1. Alteration in Chemical Composition of SRC-II Distillate Due to Hydrotreatment for Five Compound Classes^(d,e)

Material	Phenols ^(a)	N-heterocycles ^(b)	Primary Aromatic Amines ^(b)	Aromatics and Hydroaromatics ^(a)	Polynuclear Aromatics ^(c)
Feedstock	Σ phenols 130	Σ N-heterocycles 28	Σ primary aromatic amines 1.9	Σ aromatics + hydroaromatics 450	Σ polynuclear aromatics 110
	C ₁ phenols 41	quinoline 3.6	aminonaphthalenes 0.09	naphthalene 97	C ₁₄ H ₁₀ 38
	C ₂ phenols 35	C ₁ quinoline 1.4	aminoanthracene/ aminophenanthrene 0.07	C ₁ naphthalenes 82	C ₁₆ H ₁₀ 9.2
	phenol 27	carbazole 1.3	aminobiphenyls 0.03	C ₂ naphthalenes 65	C ₁₈ H ₁₂ 3.5
	C ₃ phenols 16	C ₂ quinoline 0.8	aminopyrene/ aminofluoranthene 0.03	tetralin 57	benzo(a)pyrene 0.041
	o-cresol 9	acridine 0.1	aminochrysene 0.02	C ₁ tetralin 26	benzo(e)pyrene 0.077
			aminocarbazoles trace	biphenyl 24	
Moderately Hydrotreated	Σ phenols 30	Σ N-heterocycles 1.2	Σ primary aromatic amines ≤ 0.005	Σ aromatics + hydroaromatics 660	Σ polynuclear aromatics 18
	C ₁ phenols 5.5	tetrahydroquinoline 0.08		tetralin 71	C ₁₄ H ₁₀ 2.5
	C ₂ phenols 2.6	tetrahydrocarbazole 0.06	none detected ≤ 0.005	C ₂ tetralins 51	C ₁₆ H ₁₀ 0.8
	phenol 1.6	carbazole 0.04		C ₁ tetralins 48	C ₁₈ H ₁₂ 0.4
	C ₃ phenols 1.2	C ₁ quinoline 0.03		C ₁ naphthalenes 41	benzo(a)pyrene ≤ 0.010
		tetrahydroazapyrene 0.02			benzo(e)pyrene ≤ 0.010
Severely Hydrotreated	Σ phenols 17	Σ N-heterocycles 1.0	Σ primary aromatic amines ≤ 0.005	Σ aromatics + hydroaromatics 780	Σ polynuclear aromatics 7.5
	C ₁ phenols 4.3	tetrahydrocarbazole 0.07	1	C ₁ tetralins 120	C ₁₄ H ₁₀ 1.9
	C ₂ phenols 2.1	tetrahydroquinoline 0.05	none detected ≤ 0.005	C ₂ tetralins 41	C ₁₆ H ₁₀ 0.5
	phenol 1.2	carbazole trace		tetralin 34	benzo(a)pyrene ≤ 0.010
	C ₃ phenol 0.8	C ₁ quinoline trace		C ₃ tetralins 27	benzo(e)pyrene ≤ 0.005

(a) Estimated directly in the unfractionated material by GC and GCMS.

(b) Estimated in the basic fraction by GCMS. Concentrations given have been calculated for the unfractionated material.

(c) Estimated in the unfractionated material and in the PAH fraction by GC and GCMS. Concentrations given have been calculated for the unfractionated material.

(d) The contributions listed do not total 100% due to the presence of compound classes not listed (e.g., aliphatics) and losses during extraction. Specific compounds listed under each heading are those found in the highest concentrations within that class.

(e) Concentrations are given in parts per thousand.

TABLE 3.2. Distribution of Chemical Classes by Solvent Fractionation of SRC-II Distillate Blend Material

<u>Fraction</u>	<u>Feedstock</u>	<u>Moderately Hydrotreated</u>	<u>Severely Hydrotreated</u>
Acidic	8.5	4.6	3.3
Basic	2.4	1.8	0.8
Neutral	44.0	50.0	78.0
PAH	42.0	6.0	5.0
Base-Induced Tar	2.4	1.1	0.7
Acid-Induced Tar	3.8	1.7	0.3
Isooctane Insoluble Tar	1.5	None Recovered	None Recovered
Weight Percent Recovery	98.0	65.0	88.0

the polar and PAH fractions, with the concomitant increase in the neutral fraction weight percent, provides a qualitative indication of the overall effect of hydrotreatment on the coal liquid tested.

Inspection of the single ion chromatograms and mass spectra also indicate a substantial decrease in the concentration of larger heteroatomic species in the hydrotreated samples. However, sulfur- and oxygen-containing compounds were still detected in these materials, the sulfur being in thiophenic species and the oxygen in the form of benzofurans, phenols and phenylether. Tetrahydroquinolines were the only nitrogen-containing species detectable in the intact hydrotreated materials. Examination of the solvent-produced fractions provided additional data regarding the effects of the hydrogenation, hydrodenitrogenation, and hydrodesulfurization which occurred during the upgrading.

Acid Fraction

The total ion chromatogram of the acid fraction from both of the hydrotreated products was dominated by alkyl phenols having molecular weights of 122 (4 isomers), 136 (3 isomers), 164 and 178, according to the mass spectra. Comparison of the reconstructed single ion and total ion chromatograms from the hydrogenated products with those from the feedstock indicated that the concentrations of phenolic compounds were lowered (Table 3.1), and that some other acidic compounds (probably sulfur-containing) were not detectable after

hydrotreatment. Overall phenolic content of the hydrotreated products was between 13% and 23% of that in the feedstock, depending on the severity of the reaction conditions.

Basic Fraction

Table 3.1 lists the approximate concentrations of several nitrogen compounds detected in the three materials. As can be seen, the feedstock contained relatively large amounts of several nitrogen heterocycles along with lower concentrations of several primary aromatic amines. More than 100 peaks were resolved in the FID chromatograms; however, most represented insufficient material to allow mass spectral identification.

After severe hydrotreatment, the basic fractions constituted only about 0.8% of the total recovered sample weight compared to 2.4% for the untreated starting material. Nitrogen compounds which were detected were present in low concentrations and consisted essentially of tetrahydroquinolines, tetrahydrocarbazoles, carbazoles and alkyl quinolines. Hydroaromatic and small amounts of phenolic compounds which partitioned into the basic and tar fractions of the hydrotreated materials contributed to their weight percentages making these higher than would be indicated by the concentrations of nitrogen bases present. No primary aromatic amines were detected in any of the hydrotreated fractions.

Neutral and PAH Fractions

Changes brought about by hydrotreatment were apparent in the neutral and PAH fractions. While aromatic compounds such as naphthalenes, phenanthrenes, biphenyls and pyrenes were in high concentrations in the feedstock (Table 3.1), a series of hydroaromatics having molecular ions at m/e 132, 146, 160, 174 and 186 were the most prominent in the gas chromatograms of the hydrotreated products. Dihydro-, tetrahydro-, hexahydro-, octahydro- and decahydroaromatic species having up to four rings were detected in the hydrotreated products, along with traces of some aromatics such as naphthalenes, acenaphthenes, anthracenes and phenanthrenes. PAH compounds detected having four or more rings constituted a total concentration of approximately 14 parts per thousand in the feedstock. Their concentrations were reduced substantially by hydrotreatment; however, the amount of reduction was not uniform for the various

species present. Electronically integrated area percent ratios from the FID chromatograms indicated that between 90% and 95% of the neutral fraction weight in the severely treated product was comprised of hydrogenated or partially hydrogenated species.

Tar Fractions

The acid-induced and isooctane-insoluble tar fractions obtained from the distillate blend feedstock were relatively rich in carbazoles and contained other nitrogen bases including primary aromatic amines. As has been characteristic of these two types of tars in the coal liquids studied thus far, higher molecular weight nitrogen compounds, particularly azapyrenes and aminopyrenes, were present in higher concentrations than in any other fraction. The same tar fractions from the hydrotreated materials contained reduced concentrations of carbazoles, partially hydrogenated carbazoles, phenanthridine and tetrahydroazapyrenes and azapyrenes. The base-induced tar contained some phenolic compounds; however, for the hydrotreated materials, the tar fraction weight was due mainly to hydroaromatic species which had partitioned into the tar phase during fractionation.

DISCUSSION

The most probable series of reactions leading to eventual loss of heterocyclic nitrogen begins with the addition of hydrogen across carbon-carbon bonds followed by carbon-nitrogen bond cleavage and the addition of hydrogen to form primary amino functionalities which, in turn, are rapidly deaminated⁽⁷⁾. The presence of compounds such as alkyl tetrahydroquinolines and tetrahydrocarbazoles as major constituents of the residual basic components in the hydrotreated product lend support to this view. PAA's themselves are thought to deaminate very easily in the process since no primary amines were found in the hydrotreated product. Thus, the overall process can be seen as one of successive destruction of larger ring systems to form lighter weight alkylated and/or hydrogenated species with loss of sulfur, nitrogen and oxygen in the form of H_2S , NH_3 , and H_2O respectively (see reference 6). A second mechanism which may also be important for the removal of nitrogen during hydrotreatment is one in which relatively volatile nitrogen-containing constituents are produced and then

removed during "topping" operations (separation of naphtha and gas oil products). Nitrogen in the form of alkyl anilines and alkyl pyridines may have been removed in this manner.

The chemical characterization results presented above may be compared with data from high resolution mass spectral (HRMS) analysis of the distillate blend feedstock by deRossett and Riedl of UOP^(2a). HRMS is an accepted method for the rapid chemical characterization of petroleum products. The results obtained by UOP are in good agreement with PNL chemical composition data acquired during the same time period on identical samples. Excerpts of the UOP results are included in Table 3.3 for reference purposes. These data provide information on the overall class composition of the SRC-II distillate blend feedstock.

TABLE 3.3. High Resolution Mass Spectral Characterization of SRC-II Gas Oil Drum No. 1 3777-6

Hydrocarbon Types Analysis			
<u>z No.</u>	<u>Compound Types $C_nH_{2n-z}^{**}$</u>	<u>Wt-%</u>	<u>Avg. MW</u>
z=-2	Paraffins	3.6	226
z=0	1 Ring Naphthenes	1.3	224
z=2	2 Ring Naphthenes	1.8	208
z=4	3 Ring Naphthenes	1.3	206
z=6	4 Ring Naphthenes	0.4	190
		8.4	216
Aromatic Hydrocarbons			
<u>z No.</u>	<u>Compound Types $C_nH_{2n-z}^{**}$</u>		
z=6	Benzenes	0.9	158
z=8	Indans/Tetralins	10.3	165
z=10	Dinaphthene Benzenes	2.7	185
z=12	Naphthalenes	12.1	159
z=14	Acenaphthenes/Biphenyls	7.5	185
z=16	Fluorenes	4.4	205
z=18	Phenanthrenes	6.7	197
z=20	Aceanthrenes	2.6	227
z=22	Pyrenes	4.7	223
z=24	Chrysenes	0.9	246
z=26	Benzofluoranthenes	0.3	276
z=28	Benzopyrenes	0.6	280
z=30	Dibenzanthracenes	<0.1	292
z=32	Benzoperylenes	T	
z=34	Dibenzopyrenes	T	
z=36	Coronenes	T	
		53.8	186
Aromatic Oxygens			
<u>z No.</u>	<u>Compound Types, $C_nH_{2n-z}O^{**}$</u>		
z=6	Phenols	14.4	131
z=8	Naphthenophenols	5.7	154
z=10	Benzofurans	0.6	183
z=12	Naphthols	<0.1	180
z=14	Naphthenonaphthols	3.2	180
z=16	Dibenzofurans	2.6	202
z=18	Hydroxyanthracenes	0.3	230
z=20	Hydroxynaphthenoanthracenes	0.2	233
z=22	Hydroxypyrenes	0.5	232
z=24	Hydroxychrysenes	T	
		27.6	153
Aromatic Dioxygenates			
<u>z No.</u>	<u>Compound Types, $C_nH_{2n-z}O_2^{**}$</u>	<u>Wt-%**</u>	<u>Avg. MW</u>
z=6	Hydroxyphenols	0.3*	120
z=14	Hydroxynaphthenonaphthols	0.7*	218
z=16	Hydroxydibenzofurans	0.5*	215
z=18	Dihydroxyanthracenes	<0.1*	247
z=20	Dihydroxynaphthenoanthracenes	<0.1*	278
		1.7*	203

* Estimates due to lack of sensitivity data.

** Suggested compound types
Multiheteroaromatics normalized
out of the results
T ≤ 0.05%

TABLE 3.3. (contd)

Aromatic Trioxxygenates					
<u>z No.</u>	<u>Compound Types, C_nH_{2n}-zO₃**</u>	<u>Wt-%**</u>	<u>Avg. MW</u>		
z=6	Dihydroxyphenols	<0.1*	204		
z=12	Dihydroxynaphthol	0.2*	211		
z=14	Dihydroxynaphthenonaphthols	T *			
		0.3*	212		
Aromatic Nitrogens					
<u>z No.</u>	<u>Compound Types, C_nH_{2n}-zN**</u>				
z=5 ^N	Pyridines	1.5	130		
z=7 ^N	Naphthenopyridines	1.1	153		
z=9 ^N	Indoles	0.6	152		
z=11 ^N	Quinolines	1.3	156		
z=13 ^N	Naphthenoquinolines	0.6	198		
z=15 ^N	Carbazoles	0.6	191		
z=17 ^N	Acridines	0.6	202		
z=19 ^N	Naphthenobenzoquinolines	<0.1	222		
z=21 ^N	Benzocarbazoles	0.5	228		
z=23 ^N	Benzacridines	<0.1	254		
z=25 ^N	Naphthenobenzacridines	T			
z=27 ^N	Dibenzocarbazoles	T			
		7.0	167		
Aromatic Sulfurs					
<u>z No.</u>	<u>Compound Types, C_nH_{2n}-zS**</u>				
z=6 ^S	Benzenethiols	T			
z=8 ^S	Dihydrothionaphthenes	0.2	199		
z=10 ^S	Benzo thiophenes	<0.1	172		
z=12 ^S	Naphthenobenzothiophenes	T			
z=14 ^S	Indenothiophenes	T			
z=16 ^S	Dibenzothiophenes	0.6	205		
z=18 ^S	Acenaphthenothiophenes	<0.1	239		
z=20 ^S	Fluoreno thiophenes	T			
z=22 ^S	Tribenzothiophenes	<0.1	250		
z=24 ^S	Acephenanthrylenethiophenes	T			
z=26 ^S	Pyrenothiophenes	T			
		1.2	209		
Sample Analysis Summary					
<u>Compound Type</u>	<u>C_nH_{2n}-z</u>	<u>Wt-%</u>	<u>Avg. C No.</u>	<u>Avg. MW</u>	<u>Avg. z No.</u>
Saturated Hydrocarbons (P+N)		8.4	15.5	216	0.7
Aromatic Hydrocarbons		53.8	14.3	186	14.1
Aromatic Nitrogens		7.0	11.7	167	10.8
Aromatic Oxygens		27.6	10.4	153	8.9
Aromatic Sulfurs		1.2	13.7	209	14.6
Aromatic Dioxygenates		1.7	13.1	203	13.5
Aromatic Trioxxygenates		0.3	12.5	212	10.8
Elemental Analysis by MS					
Atomic Carbon		87.72			
Atomic Hydrogen		8.29			
Atomic Nitrogen		0.59			
Atomic Oxygen		3.22			
Atomic Sulfur		0.18			
		100.00			

* Estimates due to lack of sensitivity data.

** Suggested compound types

Multiheteroaromatics normalized
out of the results

T ≤ 0.05%

4.0 SUMMARY OF BIOLOGICAL CHARACTERIZATION RESULTS

INTRODUCTION

The SRC-II distillate blend and the upgraded products have been assayed for microbial mutagenic activity using the Salmonella typhimurium TA98 test strain⁽⁸⁾. In this first tier biological testing protocol as applied to the various fossil fuels, TA98 has proven to be the most sensitive of the Ames tester strains to mutagens contained in the SRC-II liquids. Moreover, the mutagenicity data obtained with TA98 have correlated well with rodent skin painting tests where tumorigenesis is the endpoint, insofar as the unfractionated SRC-II distillates are concerned⁽¹⁰⁾. Ames assay results from chemical fractions of the distillates are less closely matched to the animal skin painting results. However, in terms of potency, the mutagenicity (in vitro) and tumorigenicity results are correlated for SRC liquids and their chemical fractions. Hence, the Ames Salmonella test appears to be a useful tool in identifying potential carcinogens in SRC-II liquids.

Employing positive mutagenic response as a means of tracing biologically active compounds through a series of iterative chemical fractionation, chemical analysis, and Ames assay steps, we have obtained evidence suggesting that polycyclic primary aromatic amines (PAA's) are responsible for most of the mutagenicity of SRC-II liquids. The PAA's thus become logical candidates as principal tumorigenic agents in SRC liquids either as a direct consequence of their genotoxicity, or independently due to synergistic effects which they may exert in combination with other compounds. The perspective afforded by comparison of Ames and rodent skin painting results obtained from fractions and coupled with chemical analyses should eventually allow the formulation of models which relate responses in specific systems to specific compounds, compound classes or combinations of compounds in complex mixtures.

The specific objectives of the biological screening tests reported here include the following:

1. Assessment of any changes in the measured mutagenic activity of the SRC-II distillate blend as a result of catalytic hydrogenation.

2. Correlation of the mutagenic response data with the concentration of certain compound classes, especially primary aromatic amines, thought to be major contributors to the mutagenicity of the active coal liquid fractions.
3. Use of the mutagenic response to check for possible chemical transformations in the liquids due to hydrotreatment which may result in newly formed compounds having mutagenic activity.
4. Incorporation of the results thus obtained into the growing data base which will help to delineate the utility of microbial mutagenicity testing in predicting the genotoxic response of in vitro and in vivo mammalian test systems (tiers 2 and 3) when exposed to fossil fuel test materials.

EXPERIMENTAL

Mutagenesis Assays

Agar plate mutagenicity assays were carried out essentially as described by Ames et al⁽⁹⁾. Dimethylsulfoxide was used as solvent for all of the chemicals and complex chemical fractions. A liquid (45°C) top-agar layer was poured onto the 37°C plates and they were incubated in the upright position for several hours to allow hardening of the semisolid top agars. The assay plates were then inverted and incubated for 24 to 36 hr to allow expression of mutant colonies. These Ames assays were carried out with aliquots of the same culture of TA98 and samples from the same batch of liver (S9) homogenates induced with Aroclor 1254. Colonies were counted on an automated colony counter.

Fractional Distillation

The SRC-II distillate blend feedstock was subjected to fractional distillation under continuous nitrogen flow. Fractions were collected at approximate 10°C intervals. Collections were initiated and terminated as the temperature within the distillation vessel peaked and subsequently dropped. Twenty fractions were collected (fraction No. 20 being the pot residue at 265°C) and subjected to Ames assay.

RESULTS

Unfractionated Coal Liquids and Solvent-Derived Fractions

The solvent extraction procedure described in Section 3.0 was used to generate chemical fractions for Ames assay. As observed in previous studies on the high molecular weight, high-boiling distillates, the most mutagenically active materials were found in the nitrogen-enriched basic, acid-insoluble tar and isooctane-insoluble tar fractions of the distillate blend feedstock. Slight activity was also noted in the base-insoluble tar. No mutagenic activity was detected in the acid, PAH, or neutral fractions. The dose-response data for the feedstock is summarized in the left-hand panel of Figure 4.1. Note that concentration ranges of two orders of magnitude were used in these experiments. (The dose/response curves sometime peak and then yield a negative slope due to toxicity effects. Only data from the linear portions of the curves are used.) These dose-response curves were used to estimate mutagenic potency (slopes of response curves) and total recovery of mutagenic activity (potency x weight percent) for each chemical fraction (Table 4.1). Thus, based upon recovery data from the chemical fractions, the mutagenic potencies of the unfractionated feedstock and the hydrotreated derivatives ranged from 0.01-1.20 revertants/ μ g. The lower values were for the hydrotreated materials and the higher for the feedstock.

The basic fractions were, in each case, the most active of the chemical fractions, followed by the tars. It is noteworthy that the mutagenicity associated with the tars was completely eliminated by hydrotreatment, while that of the basic fraction was strongly reduced. For example, moderate hydrotreatment reduced the potency of the basic fraction from 16.2 to 2.2 revertants/ μ g (Figure 4.1, center panel; Table 4.1) and the weighted contribution to total mutagenicity from 0.86 to 0.03 revertants/ μ g feedstock. The tar fractions were reduced in potency to levels below limits of detection. Approximately 50% of the mutagenicity in the whole feedstock was recovered in the chemical fractions. The tabular presentation of all the Ames results is given in Table 4.1.

FIGURE 4.1. Microbial Mutagenicity Dose-Response for SRC-II Distillate Blend and Products of Hydrotreated Distillate Blend^(a)

(a) Fractions not shown were not active.

TABLE 4.1. The Effect of Catalytic Hydrogenation on the Mutagenicity of SRC-II Distillate Blend

Material	Chemical Fraction(b)	% of Total Wt.	Revertants (TA98) per μg Fraction(c)	Weighted Response(a)	Total Revertants Fractionated Material	Total Revertants Unfractionated Material
Feedstock	Basic	5.3	16.2	0.86	$\Sigma = 1.20$	2.54
	Acid-Induced Tar	5.9	2.7	0.16		
	Base-Induced Tar	1.4	5.6	0.08		
	Isooctane In- soluble Tar	1.2	8.9	0.10		
Moderately Hydrotreated	Basic	1.4	2.2	0.03	$\Sigma = 0.03$	None detected above background
	Acid-Induced Tar	0.06	0	0		
	Base-Induced Tar	0.03	0	0		
	Isooctane In- soluble Tar	0.44	0	0		
Severely Hydrotreated	Basic	0.99	0.79	0.01	$\Sigma = 0.01$	None detected above background
	Acid-Induced Tar	1.3	0	0		
	Base-Induced Tar	0.03	0	0		
	Isooctane In- soluble Tar	0.44	0	0		

(a) (Revertants per μg) $\times$ (percent total weight)/100.

(b) Fractions not shown were not active.

(c) Zero values are below the limit of detection of approximately 0.05 rev/ μg .

Based on direct measurements of unfractionated materials, only the feedstock was genetically active in the Ames assay system. The activity of the unfractionated hydrotreated samples was evidently masked. In any case, the microbial mutagenicity associated with the distillate blend feedstock was sharply reduced by both moderate and severe hydrotreatment.

Fractional Distillation

The associations of mutagenicity with nitrogen-rich fractions is presumably due to multi-ring primary amines or other high molecular weight polar compounds which reside in these fractions. Some direct evidence to support this point of view is supplied by the data in Figure 4.2 from the analyses of the samples prepared by fractional distillation. As can be seen, when mutagenicity of the distillate blend feedstock was plotted against distillation temperature, the most active mutagens were concentrated in compounds of three rings or greater. The highest activity was found in the residue fraction, which did not distill at temperatures up to 265°C. These data, along with high resolution mass spectral results from work at UOP (see Table 3.3), suggest that the feedstock contains significant amounts of four to six ring PAH material. The effectiveness of hydrotreatment in reducing mutagenicity may, in part, be explained by the degradation of high-molecular weight ring structures as well as the conversion of organic nitrogen to ammonia.

FIGURE 4.2. Relationship of Mutagenic Activity to Distillation Temperature

5.0 IMPLICATION OF FINDINGS TO DATE

The results which have been presented in this report reveal that hydrotreating of coal-derived liquids may greatly reduce or totally remove the microbial genotoxicity of the original distillate material. Fractional distillation also appears to be an operation that may be exploited to enhance the overall acceptability of the coal liquids. These conclusions are based on both chemical analyses and the biological assessment of the upgraded materials by Ames testing.

The specific effects of hydrotreating upon the chemical composition and biological activity of a given coal-derived fuel product will depend upon several factors (reaction conditions, catalysts and starting material composition). Nevertheless, it appears that hydrotreatment will, in general, result in products with reduced genetic activity. This is due to the fact that compound classes in coal liquids primarily responsible for inducing genetic damage, namely the nitrogen containing aromatics, especially the primary aromatic amines, and polynuclear aromatic hydrocarbons, are susceptible to alteration by hydrogenation. The marked reduction in microbial mutagenic activity in the hydrotreated products confirms this expectation. Each of the potentially hazardous compound classes known to be present in these liquids, namely the phenols, PAH's, and the nitrogen bases, have been substantially reduced in concentration by hydrotreatment.

The data obtained from mutagenesis assay of the laboratory distillation cuts of the SRC-II distillate blend may have important implications with respect to the planned boiling range of the demonstration product liquid. For example, it may be possible and desirable to adjust cut points to concentrate the bulk of the major mutagenically active compounds into a relatively small stream which might then receive special processing. However, the effects and implications of such trade-offs require further evaluation. The distillation cut assay results also suggest that heavy-end product and process streams should be of primary concern in the design and implementation of control technology aimed at protection of on-site workers.

The samples which were subjected to upgrading are generally representative of the distillates which will be produced by the demonstration plant, based upon its present design. The significance of the differences which are known cannot be assessed adequately with the present data base. This limitation highlights the need for biological and chemical characterization studies of processing effects.

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