

CHEMICAL AND TOXICOLOGIC CHARACTERIZATION OF CO-PROCESSING AND TWO-STAGE DIRECT COAL LIQUEFACTION MATERIALS

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INTRODUCTION

Research and development of advanced coal liquefaction technology is being supported by the U.S. Department of Energy (DOE) as a means of utilizing domestic supplies of coal to produce petroleum-substitute fuels. As a component of this effort, the U.S. DOE has supported the chemical analyses and toxicological evaluations of coal conversion products and internal process materials to assess the potential health effects and industrial hygiene concerns associated with coal liquefaction technology.

Recent advances in coal liquefaction have included two-stage direct coal liquefaction processes and petroleum resid/coal co-processing technology. Two-stage coal liquefaction processes are generally comprised of a first-stage thermal or liquefaction reactor followed by a second-stage hydrogenation step. Petroleum resids and coal are simultaneously converted to liquefaction products in co-processing technology. The purpose of this paper is to report the preliminary results of the chemical analysis and toxicological testing of a coal liquefaction co-processing sample set, and to compare these results to those obtained from two-stage coal liquefaction materials.

SAMPLES

Samples for comparative chemical analysis and toxicological evaluation were provided from the proprietary UOP, Inc. co-processing technology (Des Plaines, Illinois) and the integrated, non-integrated, reconfigured integrated, and close-coupled reconfigured integrated two-stage coal liquefaction processes (ITSL, NTSL, RITSLS, and CCRITSLS respectively) from the Wilsonville Advanced Coal Liquefaction Research and Development Facility (Wilsonville, Alabama) operated by Catalytic, Inc. A summary is contained in Table 1 of the co-processing samples received from UOP, Inc. and the two-stage coal liquefaction materials analyzed for comparative purposes. Since the samples provided were from pilot plant or bench-scale advanced coal liquefaction origins, they may not necessarily be representative of materials produced on a commercial basis.

A description of the proprietary UOP, Inc. catalyzed, slurry, single-stage coal liquefaction co-processing technology has been given by Gatsis, *et al.* (1). ITSL and NTSL processes have been described by Later (2). For a brief overview of the RITSLS and CCRITSLS, see Gough *et al.* (3).

EXPERIMENTAL

Samples were chemically characterized by chemical class fractionation, gas chromatography, gas chromatography-mass spectrometry, and low-voltage probe-inlet mass spectrometry. Toxicological activity was measured using the standard histidine reversion microbial mutagenicity test and an initiation/promotion assay for mouse skin tumorigenesis. A brief description of these methods follow.

Chemical Class Fractionation

Samples were fractionated according to the method described by Later *et al.* (4) and Later and Lee (5) by sequential elution of standardized alumina (1.5% water, Later *et al.*, 6) with 20 ml hexane, 50 ml

Table 1. Samples Analyzed

PNL Number	Process	Description
51396-005	UOP	Lloydminster Petroleum Resid. Nominal boiling point (bp) >840°F, including non-distillables, no solids.
51396-004	UOP	Illinois No. 6 Coal and Lloydminster Petroleum Resid Slurry Feed. Nominal bp >840°F, including solids and non-distillables.
51396-001	UOP	Liquid Process Solvent (LPS). Nominal bp >212°F, including solids and non-distillables.
51396-003	UOP	Vacuum Fractionator Overhead Product. Nominal bp ~212-910°F.
51396-002	UOP	Vacuum Fractionator Bottoms Product. Nominal bp >910°F, including solids and non-distillables.
5226-059	ITSL	Hydrotreater (HTR) Distillation Column Bottoms. Nominal bp ~450-850°F. Run #242.
5226-022	NTSL	HTR Distillation Column Bottoms. Nominal bp ~450-850°F. Run #241.
50378-100	RITSL	HTR Heavy Distillate Product. Nominal bp >500°F, including resids and ash. Run #247.
50378-101	RITSL	HTR Heavy Distillate Product. Nominal bp >500°F, less resids and ash. Run #247.
50378-139	CCRITSL	HTR Heavy Distillate Product. Nominal bp >500°F. Run #249.

benzene, 70 ml chloroform:ethanol (99:1), and 50 ml methanol to produce aliphatic hydrocarbon (AH), polycyclic aromatic hydrocarbon (PAH), nitrogen-containing polycyclic aromatic compound (NPAC), and hydroxy-substituted PAH (hydroxy-PAH) fractions, respectively. The weight percent contribution of each fraction was determined gravimetrically after solvent removal by rotoevaporation at 40°C and drying under a stream of nitrogen.

Gas Chromatography

Selected fractions were analyzed by gas chromatography using a Hewlett-Packard (HP) 5880A gas chromatograph equipped with a 30-m x 0.25-mm-ID fused silica capillary column coated with 0.25- μ m film thickness DB-5 (J & W Scientific). The oven was temperature-programmed to 280°C at 4°C/min after 2 minutes isothermal at 50°C with a 5 minute isothermal period at the upper temperature limit. Splitless injection was used with hydrogen as carrier gas at 100 cm/sec linear velocity. The injection port and flame ionization detector were operated at 275 and 300°C, respectively. Fractions were analyzed at 5.0 mg/ml dilutions with 2-chloroanthracene added as an internal standard at a final concentration of 25 ng/ μ l.

Gas Chromatography/Mass Spectrometry (GC/MS)

GC/MS analyses were performed on an HP-5982A quadrupole mass spectrometer interfaced to an HP-5710 gas chromatograph equipped with a 15-m x 0.25-mm-ID DB-5 fused silica capillary column (J & W Scientific). Gas chromatographic conditions were similar to those described above, except the oven was temperature-programmed at 8°C/min. The MS was operated in the electron impact mode at 70 eV, and scan rates were typically 100 atomic mass units (amu)/sec.

Low-Voltage Probe-Inlet Mass Spectrometry (LVMS)

A VG ZAB 2-F double-focusing MS operated in the electron impact mode using ionizing electron energies of 10-12 eV was used for the LVMS analyses. Each sample (10 to 20 μ g) was loaded into a glass capillary tube, which was then inserted into the source affixed to the end of a direct insertion probe. The probe was heated in a linear fashion from ambient to 250-280°C while the MS scanned repeatedly throughout the desorption period. The MS was operated with an accelerating voltage of 6000 or 7000 V, a magnet scan rate of 2 to 3 sec/mass decade, a source temperature of 250°C, and a dynamic resolving power (as determined by the VG 2035 data system) of 1:2000. The intensities of each mass across the entire profile were summed, generating an average spectrum that was representative of the entire sample.

Microbial Mutagenicity

Standard agar-plate mutagenicity assays were performed as described by Ames *et al.* (7) using *Salmonella typhimurium*, TA98 microbial tester strain with S9 metabolic activation. Revertant colonies per petri plate were counted using a Biotran II automated colony counter. The specific mutagenic activities of samples are expressed as revertant colonies of *S. typhimurium*, TA98 per μg of test material as estimated by linear regression analysis of dose-response data. The following criteria were used for selecting the best dose range for estimating a linear dose response: at least a four-point dose range; approximate doubling of response for doubled dose concentration; a correlation coefficient of 0.8 or greater; and an intercept on the response (ordinate) axis within 20% of the negative control for the day.

Initiation/Promotion (I/P) Assay for Mouse Skin Tumorigenicity

The I/P mouse skin tumorigenicity assays were performed on selected samples as described by Mahlum (8) using female CD-1 mice (Charles River Laboratories, Portage, MI), approximately 6 to 8 weeks of age with 30 animals per test group. Each test material was diluted 1:1 with acetone or methylene chloride, and 50 μl of the diluted material was applied to the shaved backs of the mice (approximately 25 mg dose per mouse). Two weeks after initiation, 5- μg doses of phorbol myristate acetate (0.1 mg/ml acetone) were applied to the initiated area, twice weekly for 24 weeks. The mice were shaved as necessary throughout the study, usually weekly. Animals were observed regularly for tumor growth, and the number of tumors per animal was counted biweekly. The data are expressed as the total number of tumors per mouse normalized to groups of 30 mice.

RESULTS AND DISCUSSION

The results of the chemical class fractionation by alumina column chromatography are given in Table 2 for the advanced coal liquefaction products and internal process materials studied. The Lloydminster petroleum resid and the slurry feed from the UOP co-processing technology had low levels of AH compared to the other materials fractionated using these methods. The UOP slurry feed also gave a lower total recovery of material from the neutral alumina than did the other materials, indicating there was a high concentration of insoluble or intractable components in the slurry feed presumably due to the presence of

Table 2. Chemical Class Fractionation Data

Sample ^b	Process	Fraction Weight Percent ^a				
		AH	PAH	NPAC	Hydroxy-PAH	Total
51396-005	UOP	12	50	36	3	101
51396-004	UOP	8	26	22	2	58
51396-001	UOP	26	26	23	10	85
51396-003	UOP	53	27	8	6	94
51396-002	UOP	19	27	30	11	87
5226-059	ITSL	63	26	5	9	103
5226-022	NTSL	45	34	7	15	101
50378-100	RITSL	58	36	4	2	100
50378-101	RITSL	57	39	4	2	102
50378-139	CCRITSL	60	43	5	4	112

^aAverage of two determinations

^bFor description, see Table 1

the coal itself. The chemical composition of the UOP vacuum fractionator overhead product (51396-003) was comparable to an average composition of the two-stage coal liquefaction products, as determined by this chemical class fractionation. The UOP bottoms product had a decreased AH composition and an increased NPAC and hydroxy-PAH content compared to the lower boiling UOP overhead product. Similar results have been noted for both single- and two-stage coal liquefaction materials, namely, that higher boiling fractions have had decreased AH content and increased heteroatom content compared to their lower boiling counterparts (9).

The PAH fractions isolated from the samples were analyzed in greater detail since this chemical fraction has historically been the most tumorigenic fraction isolated from coal liquefaction products and internal process materials when analyzed using these methods. High-resolution gas chromatograms of the PAH fractions isolated from the UOP, ITSL, and NTSL distilled products are shown in Figure 1. Many of the major components in each of these fractions are labelled with their identifications from retention time and GC/MS data. The major components identified in the UOP vacuum fractionator overheads were similar to the major components identified in both the ITSL and NTSL hydrotreater distillation column bottoms; PAH compounds were present ranging from two to four aromatic rings in size. Alkyl-substituted PAH and some hydroaromatics (particularly of m/z 168 and 182, the parent and methyl-substituted dihydrofluorenes or dihydrophenalenes) were also detected in all three products. The components identified in the RITSL and CCRITSLPAH fractions were similar to those detected in the UOP, ITSL, and NTSL PAH fractions of Figure 1, except they were of a higher molecular weight range; the methylchrysene isomer was the component of highest concentration in both the RITSL and CCRITSL distilled products.

The LVMS spectra from the analyses of the PAH fractions isolated from the UOP, ITSL, and NTSL distilled products are shown in Figure 2. The UOP product PAH fraction was more complex than either of the two-stage coal liquefaction PAH fractions shown. For example, there were signals for a greater number of masses representing 40% or more of the total ion current (TIC) in the UOP product PAH fractions than there were for the ITSL and NTSL PAH fractions. There was also relatively more materials that gave rise to the series including masses 232, 246, 260, and 274 amu in the UOP distilled product PAH fractions as compared to the ITSL and NTSL distilled product PAH fractions, showing some differences in the composition of the co-processing and two-stage coal liquefaction samples.

Table 3 contains the results of microbial mutagenicity testing of the crudes and chemical class fractions isolated from some of the advanced coal liquefaction samples studied. No mutagenic activity was detected in any of the AH or PAH fractions isolated from the UOP petroleum resid/coal co-processing materials, as was also the case for the distilled two-stage coal liquefaction products. Regardless of process, the majority of the microbial mutagenicity was expressed by the isolated NPAC fractions, with

Table 3. Microbial Mutagenicity Data

Sample ^a	Process	Response (rev/ μ g); Chemical Class Fraction				
		Crude	AH	PAH	NPAC	Hydroxy-PAH
51396-004	UOP	0	0	0	0	<1
51396-001	UOP	6	0	0	10	4
51396-003	UOP	4	0	0	48	2
51396-002	UOP	3	0	0	6	6
5226-059	ITSL	0	0	0	3	0
5226-022	NTSL	6	0	0	65	<1
50378-100	RITSL	0	0	0	22	3
50378-101	RITSL	4	0	0	32	0

^aFor description, see Table 1

some mutagenic response also expressed by the hydroxy-PAH fractions (particularly in the UOP vacuum fractionator bottoms product, 51396-002). The microbial mutagenic response of the UOP vacuum fractionator overhead product more closely resembled the response of the NTSL and RITSL distilled products, showing increased mutagenic activity as compared to the ITSL distilled product.

Initiation/promotion results, given as total number of tumors per mouse \pm standard error, for the ITSL and NTSL hydrotreater distillation column bottoms were 1.3 ± 1.2 and 1.1 ± 1.4 , respectively.

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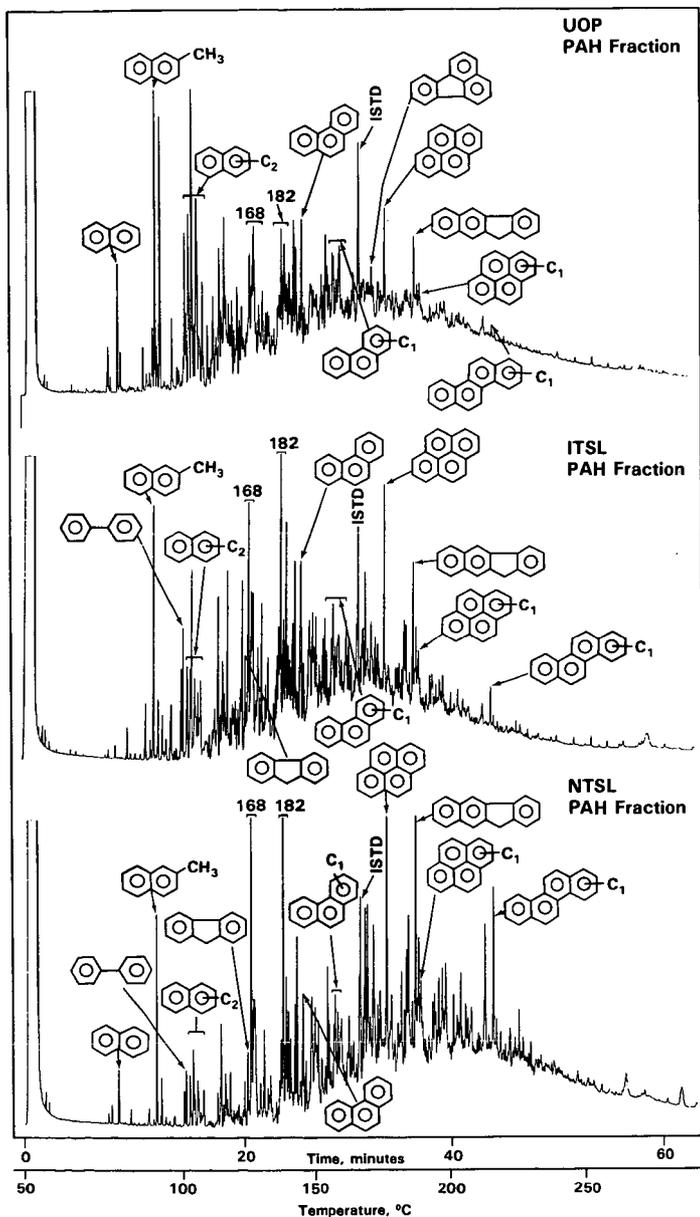


Figure 1. High Resolution Gas Chromatograms of the PAH Fractions Isolated from the UOP Vacuum Fractionator Overhead Product (top), ITSL (middle) and NTSL (bottom) Hydrotreater Distillation Column Bottoms. See Text for Conditions.

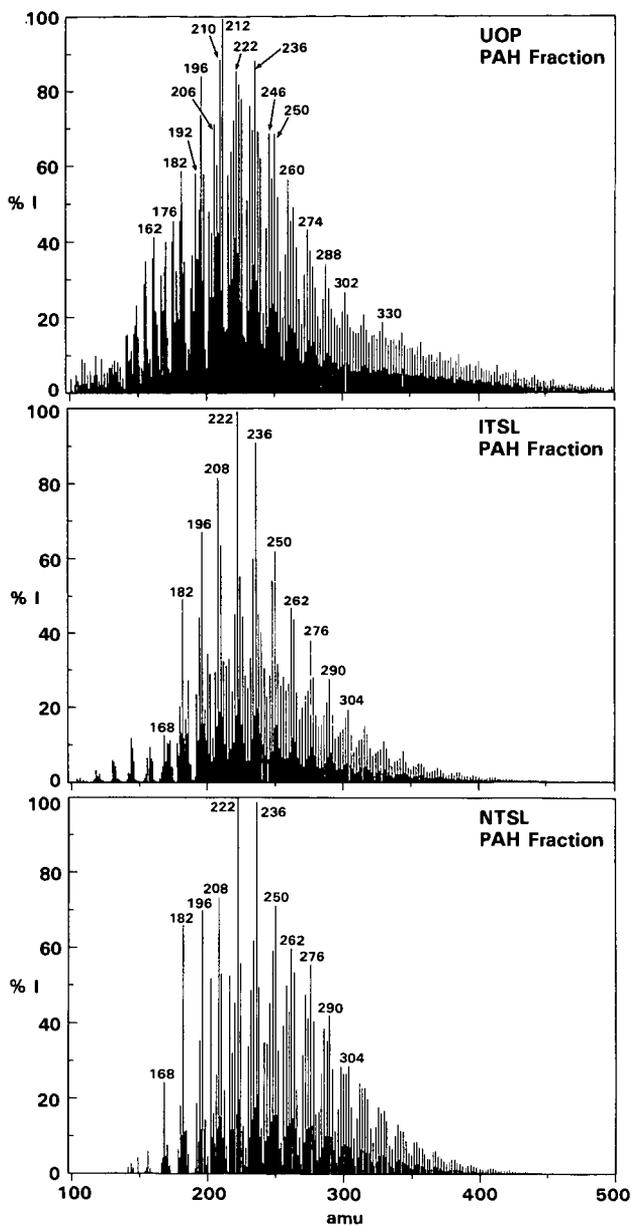


Figure 2. LVMS Spectra. See Figure 1 for Sample Descriptions. See Text for Conditions.