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Health Effects Research in Direct Coal Liquefaction

Studies of H-Coal Distillates: Phase I. PDU Samples—the Effects of Hydrotreatment

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HEALTH EFFECTS RESEARCH IN DIRECT COAL LIQUEFACTION

Studies of H-Coal Distillates:

Phase I. PDU Samples — the Effects of Hydrotreatment

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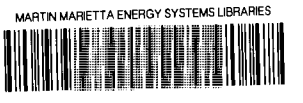


TABLE OF CONTENTS

TABLE OF CONTENTS (Cont'd.)

FIGURE LEGENDS

TABLE LEGENDS

TABLE LEGENDS (Cont'd.)

INTRODUCTION

H-COAL LIQUEFACTION

A multi-divisional effort (Life Sciences Synthetic Fuels Program, managed by K. E. Cowser) aimed at the integrated assessment of the health and environmental effects of various coal conversion and shale oil technologies is being carried out. The Biology Division's efforts with the H-Coal Process (Phase I: PDU Samples) are summarized below. Chemical fractions and analyses were provided by staff of the Analytical Chemistry Division.

The feasibility of using health effects bioassays to predict the potential biohazard of various H-Coal derived test materials will be examined in a coupled chemical and biological approach. The primary focus of the research will be the use of preliminary chemical characterizations and preparation for bioassay, followed by testing in short-term assays in order to rapidly ascertain the potential biohazard. Mammalian toxicological assays parallel the testing.

The biological work was, in many cases, carried out as a collaborative effort with the Analytical Chemistry Division. We specifically want to acknowledge M. R. Guerin, W. H. Griest, B. R. Clark, C. Y. Ma, and C. H. Ho for their role in the fractionation and biopreparation of the materials. Samples examined in this study were supplied by the USEPA/USDOE Synfuels Research Materials Facility for generic research into the chemical and biological properties of petroleum substitutes.

Research Approach

Using crude and/or fractionated materials, bioassay systems are being used to determine which materials or fractions thereof are biologically active, thus aiding in the assignment of priorities for further chemical separation and characterization. Additionally, secondary screening of partially defined constituents aids in determining which mixtures, classes, or specific compounds require testing in intact animal or plant systems. Conversely, complex materials that are known or prove to be active in higher organisms can be assessed with the short-term tests and, again, detailed chemical analyses can be guided by the display of biological (genetic) activity. The overall approach may validate the use of short-term genetic screening systems to predict mutagenicity and carcinogenicity for intact organisms and man. Implied in the coupled chemical-biological approach is the application and further development of bioassays, not only for detecting

hazardous materials in environmental effluents and process streams but also for measuring and monitoring these materials, via bioassays, in the general environment, in the work place, and during their storage (or disposal) and transport. Furthermore, methods for applying short-term tests to the monitoring of exposed individuals through cytogenetic assays or microbial screening assays utilizing body fluids are under development. Preliminary information concerning the metabolic mechanisms of activation, the definition of cellular and molecular mechanisms of damage, and the repair of damage caused by key compounds (from the major classes of chemical pollutants) is being accumulated along with the determination of potential genetic biohazard.

The H-Coal program will be carried out in two phases. Phase I assesses samples that are currently available from Process Development Unit scale operations; short-term mutagenesis, cytotoxicity along with mammalian toxicity, and skin carcinogenesis assays will be carried out with these materials. Phase II will assess samples developed when the H-Coal plant is under way. Phase I tests (summarized here) include the H-Coal raw distillate product, various stages of upgrading, and H-Coal products. The preliminary assays parallel existing efforts with other syncrudes. The information received should aid in selection of actual process samples for evaluating the Catlettsburg, Kentucky, H-Coal pilot plant. It may also provide useful comparison of any changes which occur in the biological characteristics of specific process liquids as a function of scale-up.

Information gained in the preceding integrated program will provide the assessor with specific information on specific process materials. The generic approach, coupled with the chemistry, health effects studies, and environmental studies, should place these materials in context with respect to the data base currently available. Direct information on the potential mutagenicity, carcinogenicity, and overall toxicity of the materials tested can be placed in perspective with results from other technologies. Comparative information and the published data on similar materials should permit some ordered estimate of the biohazards of each process.

Phase I: H-Coal Process Distillates

Phase I of the H-Coal project has involved comparative biological studies of two suites of samples. The first suite is composed of an H-Coal composite distillate before and after hydrotreatment. Samples were provided through the courtesy of Mobil Research and Development Corp. and represent material

obtained from the Hydrocarbon Research, Inc., Process Development Unit located in Trenton, New Jersey. The second suite is composed of representative H-Coal process distillates obtained from the Hydrocarbon Research, Inc. Process Development located in Trenton, New Jersey. Table I lists the two sample suites and their ORNL Repository Numbers. The second suite of distillates were obtained at similar locations but under two different operating modes. The first mode is designated the syncrude mode and these sample-location combinations are identified with the "S.C." prefix. The other operating mode is the fuel oil mode and this condition is indicated by the prefix "F.O." Available data from other direct liquefaction processes will be listed for comparison. However, process operating conditions at the time of sampling, sampling conditions, and sample histories, are not sufficiently defined to provide process-specific conclusions. See also Appendix A.

Table II summarizes the biological assays that have been carried out.

Table I

H-Coal Process Samples

Material	ORNL No.
H-coal distillate	1601
HDT distillate, low	1602
HDT distillate, med.	1603
HDT distillate, high	1604
S.C. atmospheric overhead	1308
S.C. atmospheric bottoms	1309
S.C. vacuum overhead	1310
F.O. atmospheric overhead	1312
F.O. atmospheric bottoms	1313
F.O. vacuum overhead	1314

Table II

"H-Coal" Liquefaction Samples

	Acute oral	Acute dermal	Skin irritation	Eye irritation	Skin sensitization	Carcinogenesis dermal	Mutagenesis microbial	Cytotoxicity	Analytical fractionation
H-Coal Distillate									
Raw	X	X	X	X	X	X	X	X	X
HDT--low severity	X	X	X	X	X	X	X	X	X
HDT--medium severity	X	X	X	X	X	X	X	X	X
HDT--high severity	X	X	X	X	X	X	X	X	X
Preproduct Materials									
A. (PDU No. 5) Sept./Oct. 1977 Syncrude mode/Illinois No. 6									
Atmospheric overhead	X	X	X	X	X	X	X	X	X
Atmospheric bottoms	X	X	X	X	X	X	X	X	X
Vacuum overhead	X	X	X	X	X	X	X	X	X
B. (PDU No. 7) Sept. 1978 Fuel oil mode/Illinois No. 6									
Atmospheric overhead	X	X	X	X	X	X	X	X	X
Atmospheric bottom	X	X	X	X	X	X	X	X	X
Vacuum overhead	X	X	X	X	X	X	X	X	X
Crude Oil (natural petroleum)	X	X	X	X	X	X	X	X	X

EXECUTIVE SUMMARY

Raw and hydrotreated product liquids from process development units of "H-Coal" and the pilot plant "solvent refined coal" process were examined for acute toxicity monitored as population growth impairment of Tetrahymena exposed to aqueous extracts and for mutagenic activity monitored as revertants of Salmonella exposed to metabolically activated chemical class fractions. With both systems deleterious effects are generally reduced as the severity of hydrotreatment is increased. However, medium to high severity hydrotreatment appears to be an effective means of reducing biological activity, presumably by reducing the aromaticity and heteroatom content.

Atmospheric still overhead and atmospheric still bottom samples from the fuel oil mode were weakly mutagenic.

The syncrude samples from atmospheric still bottoms, vacuum still overhead and vacuum still bottoms were strongly mutagenic.

The fuel oil samples from vacuum still overhead and vacuum still bottoms were also strongly mutagenic.

Five basic mammalian,acute toxicity tests have been conducted with selected H-coal samples and shale oil derivatives. The tests are: determination of acute toxicity (LD_{50}) following oral, intraperitoneal and dermal exposure of mice and rats, acute skin irritation and eye irritation in rabbits and skin sensitization in guinea pigs. The data show that H-Coal samples are moderately toxic (acute LD_{50} 0.5-5 g/kg) whereas the toxicity of shale oil derived products is slight (LD_{50} 5-15 g/kg) and comparable to samples obtained from naturally occurring petroleums. No overt skin or eye toxicity was found.

The present data reveal that coal-derived distillates generated by the H-coal process are highly carcinogenic to mouse skin. Wide differences due to the material composition were noted. Not surprisingly, the most carcinogenic samples were also the higher boiling materials in which it is assumed that the components most responsible for skin carcinogenicity, polynuclear aromatic hydrocarbons, are concentrated.

Completely unexpected was the observation of an extreme form of neurotoxicity associated with dermal exposure to one of the lighter, minimally carcinogenic, materials. While the basis of this response is unknown there

is precedent for neurotoxicity following skin and inhalation exposure to shale oils. It was suggested that non-volatile mono- and disubstituted phenols were responsible for neurobehavioral effects.

The carcinogenicity data indicate that substantial reduction in the skin carcinogenic potential of a composite H-coal distillate can be achieved at the lowest severity hydrotreatment used in this study. There is a further indication that greater systemic toxicity may result at higher levels of hydrotreatment. The most likely targets for systemic toxicity include, but cannot be assumed to be limited to, the exposed skin, the kidney and the gonads.

SECTION 1. SHORT-TERM BIOASSAYS — EVALUATION OF HYDROTREATMENT AS A MEANS OF REDUCING BIOLOGICAL ACTIVITY OF SYNFUEL RELATED MATERIALS

INTRODUCTION

During the past decade, with its declining petroleum reserves and escalating oil prices and shortages, coal conversion technologies have assumed greater importance as a potential solution to energy needs. Currently a variety of specific processes are being investigated by both private and public groups in an effort to generate clean and cost-competitive fuels from coal. Direct coal liquefaction is one of these technologies and involves several approaches including pyrolysis, hydrogenation, and solvent extraction. Regardless of the approach employed, however, there are differences between natural petroleum crude oils and synthetic crudes derived from coal. A major and important difference is the higher content of potentially hazardous aromatic and organic heteroatom (i.e., oxygen, nitrogen, and sulfur) compounds in synthetically-derived products (1). The quantity and type of these compounds depend on such factors as the engineering and operating conditions of the conversion plants and the constituents of the feed or parent coal. (For a review of the principle organic compounds found in coal conversion products see reference 2.)

Although the potential coal-derived liquid fuels are lower in sulfur and ash than their parent coals, the commercial use of such fuels requires additional treatment to bring them to a quality approaching natural petroleum fuels now used in power generation. A promising scheme for upgrading residual coal liquids is by the addition of hydrogen (3,4,5). Hydroprocessing results in at least two major improvements: the reduction of aromatic content by hydrogenation of unsaturated hydrocarbons and the reduction of heteroatom content by hydrogenolysis of heteromolecules. Acute toxicity studies using pure compounds associated with synfuel materials have shown that phenols, monoaromatic hydrocarbons, and nitrogen-containing cyclic compounds are acutely toxic (6,7). In addition, chemical and biological analyses of test materials from the liquefaction industry (8,9) have indicated mutagenic activity associated with the neutral and basic fractions. These mutagenic fractions are expected to contain mono- and fused-ring aromatic compounds as well as other heterocyclic compounds. Mutagenicity studies with such compounds have been reported by Ho et al. (10).

The present study was undertaken to compare the mutagenicity of such chemical class fractions and the acute toxicity of aqueous extracts of raw

and hydrotreated residual and process liquids from two processes representing direct coal liquefaction technology. Both are processes in which pulverized coal is slurried with an organic solvent, mixed with hydrogen, and placed under a regime of heat and pressure (4,5). Our results show that indeed hydrotreatment of residual coal liquids from both processes does reduce the biological activity.

MATERIALS AND METHODS

An acute toxicity determination using the ciliate Tetrahymena pyriformis and a mutagenicity assay using Salmonella typhimurium were selected as short-term testing regimes to examine raw and hydrotreated samples.

Origin and description of test samples: Four samples of raw and hydrotreated process liquids and crude oils from H-coal and SRC-I liquefaction processes were used in these studies. (See Tables I and II for sample description and ORNL repository numbers; H-coal is a process development unit, SRC a pilot plant). They are not necessarily representative of coal liquids which will eventually be produced by a commercial facility. The test samples were acquired from the U.S. Environmental Protection Agency – U.S. Department of Energy Fossil Fuels Research Materials Facility located at Oak Ridge National Laboratory, Oak Ridge, Tennessee (11). The samples had been stored in tin plate cans in the dark at -20°C for 10 months prior to testing when 50 ml aliquots were transferred to brown glass bottles topped with teflon-lined caps and stored at -5°C. Samples from these substocks were used during the course of these investigations.

Acute Toxicity Studies - Tetrahymena

For acute toxicity testing, aqueous extracts of the samples were prepared by placing 30 ml of sterile Tetrahymena culture medium (proteose-peptone, see reference 7) into a 60-ml separatory funnel and adding 5 ml of the coal-derived sample. The mixture was agitated on a reciprocal shaker (208, 12 mm strokes/min) for 30 minutes, then allowed to stand for an additional 30 min to permit the separation of the aqueous and non-aqueous phases. The aqueous (culture medium) phase was then withdrawn and diluted appropriately for testing.

Acute toxicity was measured as population growth impairment of Tetrahymena. Population density was monitored spectrophotometrically as absorbance at 540 nm (12). Replicate test cultures were grown at 28°C in 2.5 x 15 cm tubes containing 10-ml aliquots of culture medium with various dilutions of extracts of the test materials. Cultures were inoculated with 0.2 ml of 72–80-hr-old, log-growth phase

Table I

72 Hr IGC_{50} of Medium Extracts of Raw and Hydrotreated (HDT) Coal Liquids in the Tetrahymena Assay

Sample Description	ORNL Repository No.	Toxicity Regression Model	Correlation Coefficient	72-Hr (%) IGC_{50} (95% Confidence Interval)
H-Coal Distillate				
Raw	1601	Y = - 0.041X + 0.300	- 0.976	3.7 (1.1 - 12.3)
HDT - Low Severity	1602	Y = - 0.126X + 1.260	- 0.997	8.7 (7.5 - 10.0)
HDT - Medium Severity	1603	Y = - 0.033X + 0.499	- 0.984	10.4 (6.5 - 16.5)
HDT - High Severity	1604	Y = - 0.023X + 1.209	- 0.987	45.5 (39.5 - 52.3)
SRC Light Organic Liquid				
Raw	1605	Y = - 0.110X + 0.247	- 0.962	0.8 (0.2 - 3.0)
HDT - Low Severity	1606	Y = - 0.130X + 0.258	- 0.971	0.8 (0.2 - 2.6)
HDT - Medium Severity	1607	Y = - 0.053X + 0.506	- 0.919	6.6 (4.6 - 9.4)
HDT - High Severity	1608	Y = - 0.007X + 0.394	- 0.944	34.1 (21.4 - 54.2)
SRC Wash Solvent				
Raw	1609	Y = - 0.013X + 0.585	- 0.979	3.3 (2.2 - 4.7)
HDT - Low Severity	1610	---	---	<0.5
HDT - Medium Severity	1611	Y = - 0.009X + 0.243	- 0.989	14.3 (6.2 - 33.0)
HDT - High Severity	1612	---	---	>100
SRC Recycle Solvent				
Raw	1613	Y = - 0.380X + 0.520	- 0.970	0.9 (0.6 - 1.5)
HDT - Low Severity	1614	Y = - 0.142X + 0.550	- 0.981	2.5 (1.7 - 3.7)
HDT - Medium Severity	1615	Y = - 0.014X + 0.576	- 0.996	27.4 (20.7 - 36.2)
HDT - High Severity	1616	Y = - 0.006X + 0.745	- 0.988	101.8 (94.3 -109.9)
H-Coal Distillates - Aqueous Extracts				
Atmospheric Still Bottoms Synthetic Crude Mode	1309	Y = - 0.8276X + 8.2708	- 0.982	3.95
Atmospheric Still Overhead Synthetic Crude Mode	1310	Y = - 0.6009X + 6.7549	- 0.978	2.92

Table I (Cont'd.)

72 Hr IGC_{50} of Medium Extracts of Raw and Hydrotreated (HDT) Coal Liquids in the Tetrahymena Assay

Sample Description	ORNL Repository No.	Toxicity Regression Model	Correlation Coefficient	72-Hr (%) IGC_{50} (95% Confidence Interval)
Atmospheric Still Bottoms Fuel Oil Mode	1312	Y = - 0.6348X + 6.6352	- 0.936	2.58
Atmospheric Still Overhead Fuel Oil Mode	1313	Y = - 0.5400X + 7.1275	- 0.986	3.94

Table II-A

Mutagenic Activities[a] of Fractionated Raw and Hydrotreated (HDT) Coal Liquids in the Salmonella Assay

Sample Description	ORNL Repository No.	% Wt. of Crude	Mutagenicity[b]	Correlation Coefficient	Weighted Mutagenic Activity[c]	Total Mutagenic Activity[d]
H-Coal Distillate						
Raw	1601					
Ether Soluble Base		1.54	3.90	0.973	0.060	
Polyaromatic		5.25	3.30	0.889	0.173	0.233
HDT - Low Severity Polyaromatic	1602	2.53	15.60	0.955	0.395	0.395
HDT - Medium Severity Polyaromatic	1603	1.59	5.44	0.953	0.087	0.087
HDT - High Severity	1604	---	0.0	---	0.0	0.0
SRC Light Organic Liquid						
Raw	1605	---	0.0	---	0.0	0.0
HDT - Low Severity	1606	NT[e]	NT	---	---	---
HDT - Medium Severity Polyaromatic	1607	0.17	0.82	0.945	0.001	0.001
HDT - High Severity	1608	---	0.0	---	0.0	0.0
SRC Wash Solvent						
Raw	1609	---	0.0	---	0.0	0.0
HDT - Low Severity	1610	NT	NT	---	---	---
HDT - Medium	1611	---	0.0	---	0.0	0.0
HDT - High Severity Polyaromatic	1612	0.09	0.49	0.979	<0.001	<0.001

Table II-A (Cont'd.)

Mutagenic Activities[a] of Fractionated Raw and Hydrotreated (HDT) Coal Liquids in the Salmonella Assay

Sample Description	ORNL Repository No.	% Wt. of Crude	Mutagenicity[b]	Correlation Coefficient	Weighted Mutagenic Activity[c]	Total Mutagenic Activity[d]
SRC Recycle Solvent						
Raw	1613					
Aliphatic		2.86	29.85	0.979	0.854	
Polyaromatic		19.36	9.44	0.982	1.827	
Residue		0.19	11.95	0.941	0.023	2.7
HDT - Low Severity	1614	---	---	---	---	---
HDT - Medium Severity	1615	---	0.0	---	0.0	0.0
HDT - High Severity	1616	---	0.0	---	0.0	0.0

[a]Determined from three to five independent experiments using the strain TA98 (with Aroclor-induced rat liver S-9).

[b]Slope of linear regression analysis of dose response data and given as rev/μg.

[c]% wt. X mutagenic activity and given as rev/μg.

[d]Summation of mutagenic activity (rev/μg) of individual fractions.

[e]NT = Not tested.

Table II-B

Mutagenicity of Class Fractionated Samples - Specific Mutagenicity[a] in Revertants per Milligram of Fraction

	V[b]	I	ESA	IA	ESB	IB	N-S	N-Ar	N-Ply	Resid
Petroleum Crude Oils										
Wilmington No.[c] 5301 Recluse No. 5305	0	-	0	0	0	0	0	20	15	0
Shale-Derived Substitute										
Paraho No. 4601	0	-	0	0	8,000	141	20	0	1,600	0
Coal-Derived Substitute										
SRC 11 FO Bld No. 1710	0	-	-	0	6,000	0	104	0	10,000	800
ZnCl Dist No. 1801	0	-	-	0	0	0	0	0	2,500	0
H-Coal ASB (Syn) No. 1309	0	-	1,200	0	22,500	643	12	0	5,000	3,000
H-Coal VSOH (Syn) No. 1310	0	-	700	200	40,000	600	40	0	6,000	1,800
H-Coal VSB (Syn) No. 1311	-	500	350	0	50,000	8,333	0	0	1,700	300
H-Coal ASOH (FO) No. 1312	0	-	0	0	0	0	0	0	0	0
H-Coal ASB (FO) No. 1313	0	-	0	0	7,000	1,750	0	0	0	0
H-Coal VSOH (FO) No. 1314	0	-	0	0	40,000	110	32	0	16,000	0
H-Coal VSB (FO) No. 1315	0	200	3,000	0	300,000	3,000	30	140	3,000	700
H-Coal Dist No. 1601	0	-	-	0	9,000	0	0	0	3,500	0
H-Coal Dist HDT/L No. 1602	0	-	-	0	0	0	0	0	18,000	0
H-Coal Dist HDT/M No. 1603	0	-	-	0	0	0	0	0	11,000	0
H-Coal Dist HDT/H No. 1604	0	-	-	0	0	0	0	0	0	0

[a] All tests using strain TA98 with Aroclor 1254-induced S9 activation.

[b] V = volatile; I = ether insolubles; ESA = ether soluble acids; IA = insoluble acids; ESB = ether soluble bases; IB = insoluble bases; N-S = neutral saturates; N-Ar = neutral aromatics; N-Ply = neutral poly-aromatics; Resid = Residual material.

[c] USEPA/USDOE Synfuels Research Materials designation.

[d] Dash, "-", indicates "not tested" or "unable to test due to toxicity or interference".

cultures. The growth (reproduction) of each culture was analyzed by the least-squares method of regression where Y is the 72-hr absorbance and X is the percent concentration of toxicant. The concentration which inhibited growth at 72 hr to 50% of the control (i.e., the 72-hr IGC_{50}) was determined from the linear regression model and the 95% confidence limits calculated following the procedure of Litchfield and Wilcoxon (13).

Chemical Class Fractionation

Since the crude oils could not be tested for mutagenicity because of their potent toxicity, the test materials were chemically fractionated (Figures 1 & 2). The general fractionation procedure (Figure 2; reference 14) involved separation of acidic and basic fractions by use of liquid/liquid partitioning into ether soluble and insoluble acids and bases (water soluble fractions were generally found inactive in the mutagenicity assays). The neutral fraction was separated, using Sephadex LH-20, into aliphatic, aromatic, polyaromatic, and polar (residue) fractions by isopropanol elution. Solvents were removed by rotary evaporation; the material was dissolved in dimethylsulfoxide (DMSO) for mutagenicity assays.

Since the preliminary studies with H-coal HDT samples (Repository numbers 1602-1604) have indicated very little, if any, activity with acidic and basic subfractions, a modified fractionation procedure described in Figure 1 was used for the repository samples 1605 to 1616. The non-volatile residue of the crude samples was subjected to Sephadex LH-20 column chromatography and sequential elution with isopropanol, acetone and benzene. After removal of the solvent the residues were redissolved in DMSO. The acidic and basic fraction constituents are thus expected to be recovered in the aromatic fractions. In addition, data concerning boiling range and elemental characterization of each sample were analyzed. Note, however, that the two procedures cannot be directly compared.

Mutagenicity Assays

Mutagenicity assays of the chemical fractions were carried out with a frameshift strain of Salmonella typhimurium obtained through the courtesy of Dr. B. N. Ames. Choice of this strain for these studies is well established in this laboratory (15). The samples were tested with and without metabolic activation using Aroclor 1254 induced rat liver homogenates prepared according to the procedure of Ames et al. (16). Mutagenicity test procedures were described previously (17). The standard procedure (16) involved addition of

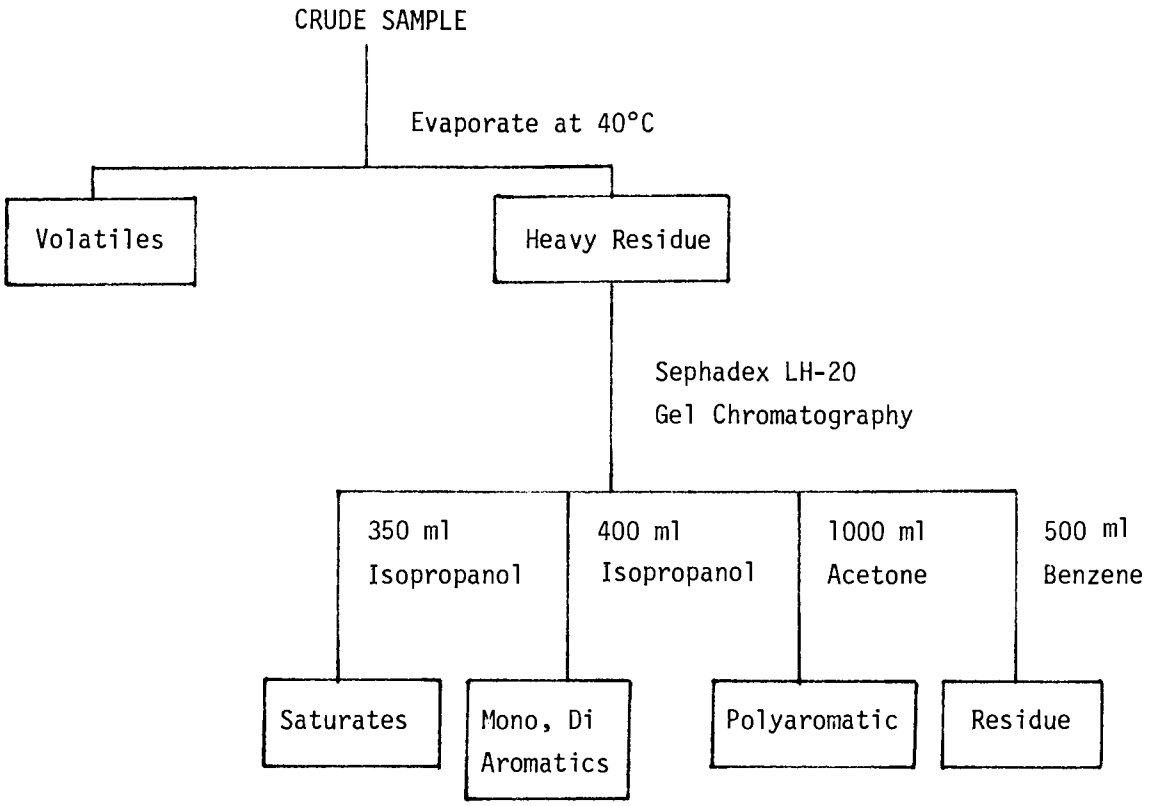
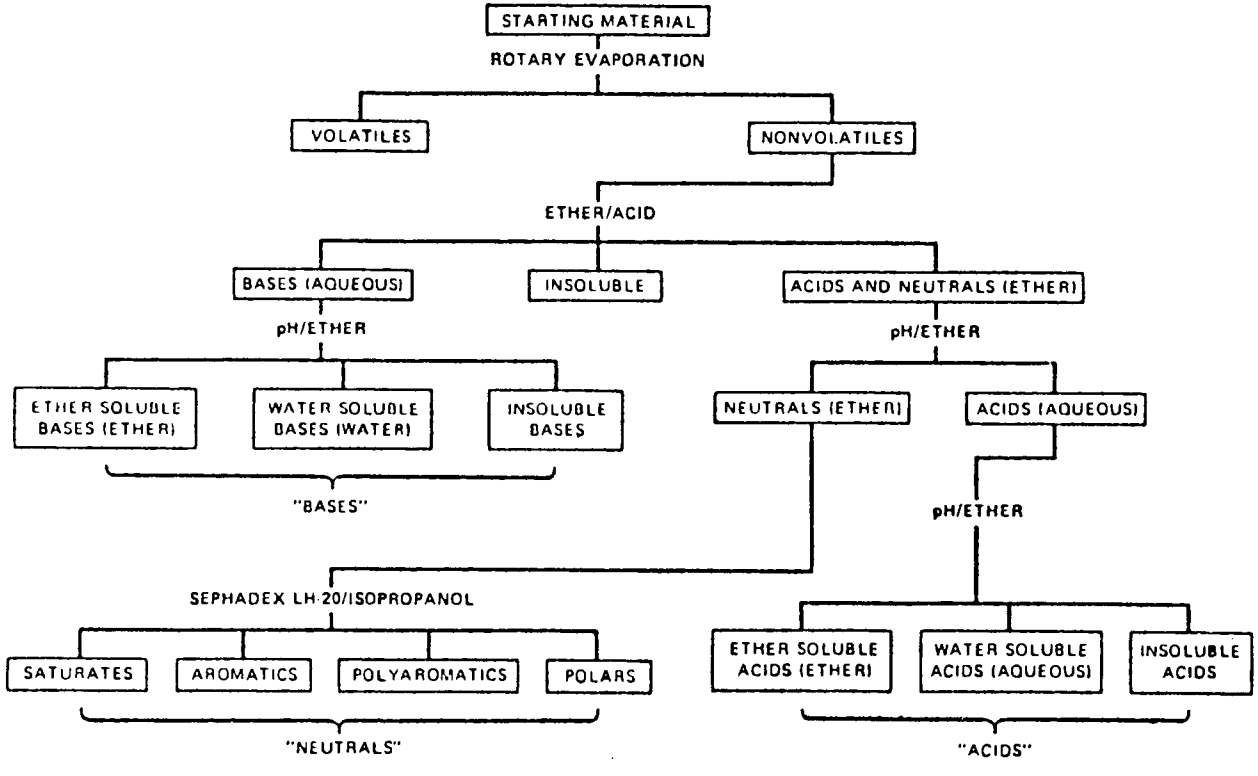


Figure 1. Fractionation of raw and hydrotreated coal liquids.



CHEMICAL CLASS FRACTIONATION FOR BIOTESTING
[MATERIAL], STEP, (PHASE)

Figure 2. Generalized fraction scheme.

bacterial cells (2×10^8) to soft agar containing the fraction being tested. Liver homogenate (S-9 mix) from Aroclor 1254 induced rats was incorporated into each plate to provide metabolic activation. Activity in revertants per unit weight (rev/mg) of test substance is derived from the slope of the linear portion of the induction curve. Total mutagenic activity of a starting material is computed from the activities of its subfractions following correction for the weight percentages contributed by the subfractions to the starting material.

EXPERIMENTAL RESULTS

Cytotoxicity

The linear acute toxicity model regression, correlation coefficients and calculated 72-hr IGC_{50} values and the 95% confidence levels for each sample are presented in Table I. The 72-hr IGC_{50} values for the low and high severity hydrotreated SRC-I wash solvent were estimated because the concentrations tested elicited insufficient differences in response for accurate regression analysis.

Investigations have also been completed in which the cell population growth impairment of the ciliate Tetrahymena pyriformis exposed to aqueous extracts (AEs) of four H-coal organic liquids was monitored. Aqueous (culture-medium) extracts were prepared by slow stirring from each of the coal-derived liquids and then diluting appropriately with fresh medium prior to testing to determine extract concentration levels that adversely affect population growth. The 48-hr IGC50 (inhibitory growth concentration for 50% of the cells) was calculated by the least-squares method of linear regression, where Y is the probit of the percent 48-hr control absorbance at 540 nm and X is the percent concentration of the extract.

The results of these studies are also presented in Table I. The no-observed-effects concentration for the AEs are 1.98%, 0.45%, 0.10%, and 0.85% for oils 1309, 1310, 1312, and 1313, respectively. The corresponding complete growth inhibition concentrations are 5.73%, 4.47%, 4.84%, and 6.94%, respectively.

In all four hydrotreatment suites tested toxicity decreased with increased severity of catalytic hydrotreatment. In general, low severity hydrotreatment does little to significantly reduce the toxicity of the soluble extracts compared to the raw, untreated samples. Medium severity hydrotreatment reduces

toxicity to a level which is intermediate between low and high severity hydrogenation, although the values remain close to those of the low severity extracts. A significant reduction in toxicity does occur, however, in those extracts derived from high severity hydrotreatment. This is especially outstanding in SRC-I wash and recycle solvent extracts where undiluted extracts are required to impair reproduction by 50%. Significant reduction in toxicity is also seen in severely hydrotreated SRC-I light organic liquid and H-coal distillate samples.

Mutagenicity

Tables II-A (see Fig. 1), II-B and III (see Fig. 2) illustrate the mutagenicity results and chemical distribution. Significant mutagenic activities were noted with the raw H-coal distillate and the raw recycle solvent from the solvent refined coal process (SRC-I). The two other raw coal liquids, SRC light organic liquid and SRC wash solvent, were not mutagenic under the conditions used here. Hydrotreatment seems to have varying effects on mutagenic activity. In the case of the H-coal distillate suite low severity hydrotreatment eliminates the mutagenic activity of the ether soluble base fraction but the activity in the polyaromatic fraction doubles. Thus the total mutagenic activity is slightly greater in the low severity sample than in the raw distillate. Medium severity hydrotreatment reduces mutagenic activity in the polyaromatic fraction in comparison to the low severity and raw materials. High severity hydrotreatment eliminates all mutagenic activity from the H-coal distillate. With the SRC light organic liquid suite the raw liquid shows no mutagenicity, while the medium severity hydrotreatment causes a slight increase in mutagenic activity associated with the polyaromatic fraction. Again high severity hydrotreatment removes all activity. Similarly, the raw SRC wash solvent showed no mutagenicity. With this suite, however, medium severity hydrotreatment caused no increase while high severity hydrotreatment induced a very slight mutagenic activity in the polyaromatic fraction. The raw SRC recycle solvent is the most mutagenic sample examined. Mutagenicity was found associated with the aliphatic, polyaromatic and residue fractions. Hydrotreatment, no matter what the severity, eliminated this activity.

In Table IV are presented the boiling range, weight percent of H, O, N, and S and the percent of total carbon which is aromatic for each sample in the hydrotreatment suite. Within each suite the heteroatom content and aromaticity decrease and hydrogen content increases with increased severity of hydrotreatment.

Table III

Detailed Weight Distribution of Biotested Samples in Weight Percent

	Volatiles	Ether Insolubles	Ether Soluble Acids	Insoluble Acids	Ether Soluble Bases	Insoluble Bases	Neutral-Saturates	Neutral-Aromatics	Neutral-Poly-aromatics	Residue	Total[a]	Experimental	Summation	Recovery
	V	I	ESA	IA	ESB	IB	N-S	N-Ar	N-Ply	Resid	T	N_e	N_s	%
Petroleum Crude Oils														
Wilmington No.[b] 5301	7.2	-	0.3	2.2	0.2	0.6	55.7	16.5	9.8	6.2	98.8	90.2	88.2	97.7
Recluse No. 5305	19.6	-	0.2	<0.1	0.6	-	51.0	7.4	3.9	1.1	83.9	-	63.4	90.3
Shale-Derived Substitute														
Paraho No. 4601	0.3	-	0.4	0.3	3.3	0.5	55.6	27.4	7.0	2.2	96.9	95.4	92.1	96.5
Coal-Derived Substitute														
SRC II FO Bld No. 1710	3.0	-	3.8	0.1	5.6	0.1	5.0	59.2	7.3	0.2	84.2	78.5	71.5	91.1
ZnCl Dist No. 1801	0.8	-	0.5	0.4	4.9	0.1	11.8	64.0	21.2	0.6	104.2	96.8	97.6	100.8
H-Coal ASB (Syn) No. 1309	0.6	-	0.4	-	2.0	0.8	20.2	62.6	10.3	<0.1	96.9	97.1	93.1	95.9
H-Coal VSOH (Syn) No. 1310	0.2	-	0.6	-	2.5	0.4	10.2	63.7	22.8	<0.1	100.4	97.6	96.7	99.1
H-Coal VSB (Syn) No. 1311	-	65.1	2.0	0.6	2.1	3.6	0.8	5.8	20.0	0.5	98.4	28.9	27.1	94.0
H-Coal ASOH (FO) No. 1312	34.7	-	0.9	-	1.1	0.5	11.9	24.6	0.5	<0.1	74.2	54.9	37.0	67.4
H-Coal ASB (FO) No. 1313	0.8	-	0.6	0.1	2.1	-	22.9	55.8	6.9	<0.1	89.2	94.1	85.6	91.0
H-Coal VSOH (FO) No. 1314	0.3	-	1.2	0.3	2.6	-	13.9	58.5	19.7	<0.1	96.5	95.1	92.1	96.8
H-Coal VSB (FO) No. 1315	-	59.5	0.2	0.8	1.8	9.6	1.3	8.0	18.4	0.3	99.9	27.7	28.0	101.1
H-Coal Dist No. 1601	4.2	-	1.4	0.1	1.5	0.1	12.7	48.9	6.3	0.2	75.5	83.9	68.1	81.1
H-Coal Dist HDT/L No. 1602	9.3	-	0.2	1.0	1.2	1.0	13.9	47.6	3.0	-	77.1	84.0	64.5	76.8
H-Coal Dist HDT/M No. 1603	9.7	-	<0.1	1.0	0.8	0.9	15.8	47.9	1.9	-	77.8	82.1	65.6	79.9
H-Coal Dist HDT/H No. 1604	12.8	--	<0.1	1.1	0.3	1.0	18.5	42.3	1.4	-	77.3	79.0	62.2	78.7

[a]Using summation of neutral subfractions.

[b]USEPA/USDOE Synfuels Research Materials designation.

Table IV

Boiling Range and Elemental Characterization of Raw and Hydrotreated (HDT) Coal Liquids

Sample Description	Boiling Range °C	Weight Percent H	O	N	S	Percent C_A[a]
H-Coal Distillate						
Raw	135-360	9.65	1.62	0.39	0.107	57
HDT - Low Severity	-	9.87	0.95	0.20	0.002	52
HDT - Medium Severity	-	10.5[b]	0.39	0.13	<0.002	45
HDT - High Severity	80-330	10.9[b]	0.21	0.09	<0.002	39
SRC Light Organic Liquid						
Raw	50-220	11.2[b]	4.22	0.23	0.550	40
HDT - Low Severity	-	12.14	3.08	0.13	0.046	30
HDT - Medium Severity	-	13.11	0.62	0.04	0.138	23
HDT - High Severity	50-220	13.66	0.26	0.001	0.057	17
SRC Wash Solvent						
Raw	160-345	7.97	4.22	0.31	0.330	71
HDT - Low Severity	-	8.73	4.08	0.19	0.010	67
HDT - Medium Severity	-	10.28	0.22	0.09	0.021	53
HDT - High Severity	65-230	12.93	0.16	0.005	<0.002	16
SRC Recycle Solvent						
Raw	160-360	7.86	3.97	0.61	0.330	71
HDT - Low Severity	-	8.95	2.35	0.37	0.029	57
HDT - Medium Severity	-	10.13	0.57	0.10	<0.010	46
HDT - High Severity	65-315	11.12	<0.10	0.03	<0.010	33

[a]Aromatic carbon as percent of total carbon.

[b]Estimated.

Correlation with Chemical Content

As noted earlier, one of the major differences between natural petroleum crude oils and coal-derived liquids is the higher organic heteroatom and aromatic content of the latter. Due to the complex chemical composition of coal liquefaction products, molecular characterization is usually facilitated by chemical fractionation into acidic, basic and neutral fractions (8). The acid fraction is composed primarily of phenol and short-chain-alkyl-substituted phenols while the basic and neutral fractions consist in the main of aromatic amines, azaarenes and aromatic and aliphatic hydrocarbons, respectively (18, 19,20).

The solubility of toxicants in water (or culture medium) is an important consideration in acute toxicity studies since the toxicity of the extracts is directly related to the solubility of the compounds present in the coal-derived liquid samples used. Until a definitive chemical analysis of these samples is available, no precise evaluation can be made regarding specific molecular species responsible for the observed acute toxic effects. However, some general considerations and implications can be stated. For example, Schultz et al. (6,7) have demonstrated relationships between solubility and toxicity, boiling point and molecular weight for certain heteroatom and aromatic compounds common to liquids from a variety of fossil energy technologies. Based on the boiling point alone one would suspect that the recycle solvent, which has the highest boiling point (see Table IV) of any of the sample groups tested, would be the most toxic. This is not the case, however, and suggests that potentially toxic components in the light organic liquid are more soluble than those present in the recycle solvent. Although the toxic component(s) have not been identified, this observation does point to the important role solubility plays in considering acute toxic effects.

Based on partition coefficient, the water solubility of compounds is enhanced by the addition to the parent compound of heteroatoms such as nitrogen and oxygen, while sulfur substitution generally decreases solubility (21). Leo has also suggested that water solubility increases as hydrogen saturation decreases from the alkanes to the alkenes to the aromatics. While no data are currently available concerning the toxicity of oxygen or sulfur ring segment substitution, it has been shown that the nitrogen substituted primary aromatic amines, azaarenes, neutral nitrogen-containing heterocyclic compounds and phenols exhibit acute toxicity as do their aromatic hydrocarbon analogs (6,7).

Distribution of Activity

The chemical class distribution (see Figure 2 and Tables II, III, V, and VI) of mutagenic activity for synfuel related materials has been more precisely determined (8,9,10,17,22-26). Both basic and neutral class fractions contribute to mutagenicity. The neutral constituents, led by the polyaromatic subfraction, generally are the most important contributor to the total mutagenic activity of synfuel materials (27). Subfractionation studies (9,25) have revealed that mutagenicity within the neutral fraction resides not only with the polyaromatic hydrocarbons but also with the polycyclic aromatic nitrogen and polycyclic aromatic polar components. Since the latter two contain heteroatoms their percent weight contribution would be sharply reduced with hydrotreatment.

Mutagenic activity of basic fraction components is concentrated in the ether soluble base subfraction (8), containing the polycyclic primary aromatic amines and, to a lesser extent, the azaarenes. Both groups have been shown to contribute a mutagenic potential (8,9) but the content of both would be diminished by hydrotreatment.

Based on our previous work on the toxicity of a variety of unsubstituted and substituted aromatic compounds (6,7) and on the fact that hydrotreatment dramatically reduces heteroatom and aromatic hydrocarbon content (4,5), we feel that the acute toxicity of the non-hydrotreated samples is due primarily to the presence of mono- and diaromatic hydrocarbons whose toxicity is sharply enhanced by nitrogen, oxygen substitution. Further, we feel that the loss of toxicity after hydrotreatment is almost exclusively due to the removal of toxic heteroatom hydrocarbons. Reduction in mutagenicity following hydrotreatment is also most likely due to removal of heteroatoms and concomitant reduction in polyaromatic content. Thus the upgrading of synfuel materials by hydrotreatment reduces both acute toxicity and mutagenicity, probably by the reduction of heteroatom content and aromaticity of the material.

Table V

Mutagenicity of Class Fractionated Samples - Weighted Mutagenicity[a] in Revertants per Milligram of Original Sample

	V[b]	I	ESA	IA	ESB	IB	N-S	N-Ar	N-Ply	Resid	T
Petroleum Crude Oils											
Wilmington No.[c] 5301 Recluse No. 5305	0	-[d]	0	0	0	0	0	4	2	0	6
Shale-Derived Substitute											
Paraho No. 4601	0	-	0	0	265	1	11	0	111	0	388
Coal-Derived Substitute											
SRC II FO Bld No. 1710	0	-	0	0	349	0	5	0	748	1	1,070
ZnCl Dist No. 1801	0	-	0	0	0	0	0	0	530	0	530
H-Coal ASB (Syn) No. 1309	0	-	4	0	445	5	2	0	513	1	970
H-Coal VSOH (Syn) No. 1310	0	-	4	1	988	3	4	0	1,367	1	2,368
H-Coal VSB (Syn) No. 1311	-	325	7	0	1,040	298	0	0	340	2	2,012
H-Coal ASOH (FO) No. 1312	0	-	0	0	0	0	0	0	0	0	0
H-Coal ASB (FO) No. 1313	0	-	0	0	141	<2	0	0	0	0	143
H-Coal VSOH (FO) No. 1314	0	-	0	0	1,048	<1	4	0	3,155	2	4,210
H-Coal VSB (FO) No. 1315	-	119	5	0	5,340	288	<1	11	551	2	6,317
H-Coal Dist No. 1601	0	-	-	0	129	0	0	0	217	0	346
H-Coal Dist HDT/L No. 1602	0	-	-	0	0	0	0	0	544	0	544
H-Coal Dist HDT/M No. 1603	0	-	-	0	0	0	0	0	212	0	212
H-Coal Dist HDT/H No. 1604	0	-	-	0	0	0	0	0	0	0	0

[a] All tests using strain TA98 with Aroclor 1254-induced S9 activation.

[b] See Table II-B for names of fractions.

[c] USEPA/USDOE Synfuels Research Materials designation.

[d] Dash, "-", indicates "not tested" or "unable to test due to toxicity or interference".

Table VI

Summary - Approximate Mutagenicity and Weight Distributions by Chemical Class

Sample	Mutagenic Activity					Weight Distribution				
		Percentage Contribution				Percentage of Total				
	Total Rev/mg	Acids %	Bases %	Neutrals %	Other %	Acids %	Bases %	Neutrals %	Other %	Total Recovered %
Petroleum Crude Oils										
Composite No. 5107	150	2	3	95	0	1	2	85	1	89
Wilmington No. 5301	5	0	0	100	0	2	1	90	7	99
Recluse No. 5305	5	0	0	100	-	<1	<1	65	20	85
LMS No. 5101	75	0	0	100	0	2	1	80	3	86
Shale-Derived										
LETC No. 4101	180	2	42	54	2	2	7	85	1	95
Paraho No. 4601	390	0	69	31	0	1	4	95	0	100
Coal-Derived										
Synthoil No. 1202	4,200	3	80	10	8	8	10	65	20	103
COED HDT No. 1106	530	0	11	89	0	4	7	85	1	97
SRC II FO Bld No. 1701	1,100	0	35	65	0	4	5	80	3	92
ZnCl Dist No. 1801	530	0	0	100	0	1	1	95	1	98
H-Coal ASB (Syn) No. 1309	970	1	46	53	0	<1	3	95	<1	99
H-Coal VSOH (Syn) No. 1310	2,400	0	42	58	-	1	3	95	1	100
H-Coal VSB (Syn) No. 1311	2,000	0	66	17	16	2	5	30	65	102
H-Coal ASOH (FO) No. 1312	0	0	0	0	-	1	2	55	35	93
H-Coal ASB (FO) No. 1313	140	0	100	0	-	1	2	95	1	99
H-Coal VSOH (FO) No. 1314	4,200	0	25	75	-	1	2	95	1	99
H-Coal VSB (FO) No. 1315	6,300	0	89	9	2	1	10	30	60	101
H-Coal "Dist" No. 1601	350	0	37	63	0	1	1	85	4	91
H-Coal "Dist" HDT-L No. 1602	540	0	0	100	0	1	2	85	10	98
H-Coal "Dist" HDT-M No. 1603	210	0	0	0	0	1	2	80	10	93
H-Coal "Dist" HDT-H No. 1604	0	0	0	0	0	1	1	80	13	97

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SECTION 2. TOXICOLOGY

ACUTE TOXICITY

Samples from several different coal liquefaction processes have been studied in acute toxicity tests. Such tests are useful in two ways: to obtain some overall idea on the toxic potential of a given sample and to obtain information which might be helpful in assessing health hazards in the case of acute accidents (spills, inadvertent exposure).

The tests can be grouped into 5 categories: determination of acute oral or interperitoneal toxicity, dermal toxicity, skin irritation and corrosion, eye irritation and corrosion and delayed type hypersensitivity.

Acute Lethality

The acute lethality of coal conversion products from H-coal (Table I) SRC I and SRC II coal conversion processes and of samples collected at the UMD gasifier have been determined in mice. To date, all compounds have been found to be moderately to slightly toxic (LD_{50} ranging from 2 to 10 g/kg). As a general rule, however, the acute lethal doses for coal conversion products was somewhat lower than the acute toxicity of natural petroleum products or of shale-oil derived products.

In view of the limited information value of acute LD_{50} determinations with pharmacologically inactive compounds and in view of the fact that all agents tested had LD_{50} in the range of g/kg, the biological significance of the findings need not be overinterpreted. Suffice to say that they do not appear to represent an acute toxic hazard, even if handled in large amounts.

Skin Toxicity

None of the compounds evaluated, from any process, has been capable of producing acute lethality in rats if applied onto the skin at a dose of 2 g/kg. This corroborates our conclusion arrived at by determining overall toxicity, discussed above. The data can be interpreted to mean that these products can be handled without any undue concern for acute effects.

Skin Irritation/Corrosion

If applied directly onto the skin of rabbits, some, but not all, of the compounds evaluated produced some slight redness and swelling of the skin within 24-72 hours. However, no sample was capable of producing serious

Table I

Acute Toxicity of H-Coal Distillates[a]

Material	ORNL No.	LD_{50} (g/kg)	95% Limits
H-Coal Distillate	1601	3.6	(2.8-4.5)
HDT Distillate, Low	1602	4.0	(3.4-4.7)
HDT Distillate, Medium	1603	-	-
HDT Distillate, High	1604	5.5	(3.8-7.2)
S.C. Atmospheric Overhead	1308	-	-
S.C. Atmospheric Bottoms	1309	3.6	(2.4-5.2)
S.C. Vacuum Overhead	1310	2.5	(1.7-3.1)
F.O. Atmospheric Overhead	1312	5.8	(4.7-7.2)
F.O. Atmospheric Bottoms	1313	2.3	(1.9-2.6)
F.O. Vacuum Overhead	1314	2.6	(2.2-3.2)
Wilmington Crude	5301	>16.0	-
Recluse Crude	5305	>16.0	-

[a]Test method: Male mice, BALB/c strain, 6-8 weeks old were used. Products were diluted with corn oil and administered orally. The animals were observed for two weeks and the acute LD_{50} was estimated with the help of Weil's Tables (Biometrics 8, 249, 1952).

skin lesions such as necrosis of the living tissue or deep ulcerations. Acute dermal exposure is thus without any practical consequence. While this can be taken as some information which indicates that the sample may be safe for acute handling and shipping, this should not be construed to mean that repeated skin exposure will be without any untoward consequence.

Acute Eye Irritation/Corrosion

When dropped into the eyes of rabbits, samples obtained from the UMD gasifier produced some damage to the cornea (superficial abrasions). However, the changes were essentially reversible within one week. Other samples (H-coal, SRC process) were less active in this particular test. While these observations alert us to the possibility that acute spills might cause some ocular discomfort, at the same time they provide some assurance that no serious permanent damage is likely to occur. Nevertheless, prudence would dictate that attention be paid to eye protection in all activities where coal conversion products are handled.

Skin Sensitization

Only a few samples could be evaluated in this test which involves repeated intradermal treatment of guinea pigs with test agents, followed by a challenge with the test agent. Surprisingly, 3 shale-oil derived samples were capable of eliciting delayed-type hypersensitivity responses, whereas coal-derived samples were negative. Too little information is still available to interpret these observations in a meaningful way. More work in this area will be needed, since the development of allergic reactions to certain products, particularly if handled in large amounts over extended time periods, may become a nuisance to the worker.

In summary, acute toxicity tests have not shown any findings which would raise undue concern, even in the case of substantial accidental exposure. Good industrial hygiene practices should prevent most, if not all, undesirable effects.

SUBCHRONIC AND CHRONIC TOXICITY

Practically no information is available on the chronic toxicity of coal conversion products, with the exception of findings from long-term skin painting studies.

The lack of such data is of considerable concern since, in one experiment, it was found that intratracheally instilled products from the $ZnCl_2$

hydrocracking process persisted in the lung for up to one year after acute administration. This points out that isolated material might have an equally long retention time and also makes it likely that regionally deposited material may become translocated to different organs (1).

The data base on subchronic and chronic toxicity, toxicokinetics and eventual target system toxicity of coal liquefaction products is extremely meager and, for risk assessment, inadequate.

Risk Assessment

Some risk assessment can be and has been done by relying on data obtained with model compounds, particularly benzo(a)pyrene, modeling systems, environmental transport data and some other information. By inference, some conclusions can also be drawn from human epidemiologic studies which relate to similar processes and operations as occurred in coal liquefaction.

Nevertheless, both the epidemiologic and experimental data on which risk assessment is based are weak to non-existent. In view of the complexity of the chemical composition of the samples one is concerned with, it seems unwise to arrive at a risk assessment solely based on one or a few model compounds. The data base on the toxicology of mixtures is not well explored. Moreover, the problem is compounded by the fact that, by necessity, many experimental studies have been done with samples which ultimately may not be representative of the final industrial process.

While it is realized that, for the time being, the only way to arrive at some kind of risk assessment may be to work with model compounds and systems, it must not be overlooked that the acquisition of a broader experimental and epidemiological data base is highly desirable.

Summary

The Toxicology Group has conducted 5 basic acute toxicity tests with selected H-coal samples and shale oil derivatives. The tests are: determination of acute toxicity (LD_{50}) following oral, intraperitoneal and dermal exposure of mice and rats, acute skin irritation and eye irritation in rabbits, and skin sensitization in guinea pigs. In addition, selected compounds have been evaluated for carcinogenicity in the mouse lung tumor assay. The data show that H-coal samples are moderately toxic (acute LD_{50} 0.5-5 g/kg), whereas the toxicity of shale oil derived products is slight (LD_{50} 5-15 g/kg) and comparable to samples obtained from naturally occurring petroleums. No overt skin or eye toxicity was found. Shale oil derivatives

have, however, the potential to produce skin sensitization in guinea pigs. In the lung tumor assay, hydrotreated residues from shale oil have been found to produce a significantly increased number of lung tumors in mice.

In future work the acute toxicity of selected H-coal samples will be evaluated with the same assays. It is anticipated that studies on subchronic toxicity, with emphasis on histopathology, will soon be initiated. Research in the Toxicology Group studies pathogenic mechanisms causing acute and chronic lung damage as well as principles underlying interactions between chemicals in complex mixtures.

REFERENCE

1. W. M. Haschek, M. E. Boling, M. R. Guerin, and H. P. Witschi, "Pulmonary toxicity of a coal liquefaction distillate product," in Pulmonary Toxicology of Respirable Particles, pp. 338-355, Proc. 19th Ann. Hanford Life Sciences Symposium (C. L. Sanders, F. T. Cross, G. E. Dagle, J. A. Mahaffey, eds.). Technical Information Center, U.S. Department of Energy, 1980.

SECTION 3: THE EFFECT OF HYDROTREATMENT ON THE CHRONIC DERMAL TOXICITY OF A BLENDED H-COAL PILOT PLANT DISTILLATE

INTRODUCTION

In general, it is anticipated that hydrotreatment will reduce the skin carcinogenicity of a given sample of oil. However, the degree of hydrotreatment necessary to achieve reduction to levels comparable to that of natural petroleum is unknown. Also, there is little experimental data concerning those factors which could conceivably influence the cutaneous toxicity of petroleum as a result of hydrotreatment. Among factors that could be important are initial sample composition, generation of new toxicants, and alteration of the chemical matrix in which toxic components are distributed. Any or all of these sample dependent factors could influence the type and degree of biological response.

The purpose of the present investigation was to determine the chronic dermal toxicity and carcinogenicity of an H-coal composite distillate before and after hydrotreatment. Samples were provided through the courtesy of Mobil Research and Development Corp. and represent material obtained from the Hydrocarbon Research, Inc. H-coal pilot plant located in Trenton, N. J.

MATERIALS AND METHODS

Materials were applied to the shaved back of male and female C3Hf/Bd mice, thrice weekly, commencing at 11 weeks of age. Animals were monitored at each exposure for signs of ill health, dermatitis and skin neoplasms arising in the area of application. Duration of exposure was determined by the response to a sample of Recluse natural petroleum.

A composite solvent consisting (by volume) of 70% acetone and 30% cyclohexane was used as a diluent. The volume per application was 50 µl and the indicated concentrations are in weight/volume percent.

Test Materials

Material identity and ORNL repository numbers are provided, together with other pertinent chemical and physical data, in Table I. These data were provided by Mobil and are gratefully acknowledged. Prior to commencing animal exposure the test materials were placed in scintillation vials, one vial for each week of the experiment, in an amount which would yield the highest concentration after addition of the solvent. At the beginning of

each week solvent was added, the contents sonicated and serial dilutions made for application. Before use the vials were kept in the dark at 4°C.

Clinical Observations

The effect of each material was evaluated on the basis of time to occurrence of each treatment-related skin tumor, skin irritation, death and several quantitative measures including body weight, organ weight and water consumption as a function of treatment and dose.

RESULTS

Chemical Composition

Data provided by Mobil Corp. (Table I) show clearly the major effects of hydrotreatment. The raw distillate, sample 1601, shows substantially reduced oxygen, sulfur and nitrogen content, coupled with a reduced aromaticity and lower boiling range with increasing hydrotreatment severity. Benzo(a)pyrene content was determined by ORNL's Analytical Chemistry group. As a specific indicator PAH the benzo(a)pyrene concentration was dramatically reduced at all levels of hydrotreatment.

Skin Toxicity and Carcinogenicity

The data in Table II provide a summary and comparison of the effects of these materials associated with exposure for 65 weeks. Differences are readily apparent that correlate well with the reduced B(a)P content. It is important to note that the activity of even the lowest severity hydrotreated sample is less than that of Recluse natural petroleum. It would be of interest to evaluate the minimum quantity of hydrogen necessary to satisfy both engineering requirements as well as reduction in dermal toxicity. It is possible that significant reduction in long term dermal exposure risk could be achieved at much less cost in terms of quantity of hydrogen required.

Systemic Toxicity

Systemic toxicity may also occur as a result of skin absorption. As an indicator of toxicity.mortality in excess of that observed in animals exposed to the vehicle alone was observed in groups exposed to the raw distillate as well as the highest severity hydrotreated sample. Tissue samples taken from animals at the time of death will reveal whether deaths were related to the presence of a skin tumor in groups exposed to the raw

distillate. Deaths in the group exposed to the high severity hydrotreated sample are less likely the result of skin neoplasia.

In addition to mortality, a quantitative measure of systemic toxicity can be obtained from body and organ weights. The data in Table III are average weights at the time of death at the highest dose levels of each material. Values underlined in Table III are significantly different than vehicle control at the 0.05 level (Student's T). The data indicate that body weight is depressed in direct proportion to increasing levels of hydrotreatment, especially in males. Kidney specific weights also varied with some groups above and others below vehicle control. Water intake, a sensitive measure of damage to both the skin and kidney, was also increased. Again, the greatest increase was noted in the highest severity hydrotreated sample.

Summary and Conclusions

Taken together these data indicate that substantial reduction in the skin carcinogenic potential of a composite H-coal distillate can be achieved at the lowest severity hydrotreatment used in this study. There is a further indication that greater systemic toxicity may result at higher levels of hydrotreatment. The most likely targets for systemic toxicity include, but cannot be assumed to be limited to, the exposed skin, the kidney and the gonads.

Table I

Physical-chemical Properties of H-coal Distillate Before and After Hydrotreating[a]

Property	Material and Degree of Hydrotreatment			
	Raw Distillate (ORNL 1601)	Low (1602)	Medium (1603)	High (1604)
Hydrotreat. Temp., °F	-	675	675	725
Space velocity, hr^{-1}	-	4	2	2
Hydrotreat. Pres., psig.	-	2500	2500	2500
Wt. % hydrogen	9.65	9.87	10.5	10.9
Wt. % oxygen	1.62	0.95	0.39	0.21
Wt. % nitrogen	0.39	0.20	0.13	0.09
Wt. % sulfur	0.107	0.002	<0.002	<0.002
% aromatic carbon	57	52	45	39
Boiling range, °F	300-700	-	-	200-650
Benzo(a)pyrene, μg/gm[b]	57	9	3	2

[a]Mobil Research and Development Corporation.

[b]ORNL, Analytical Chemistry Division.

Table II

Skin Tumorigenicity of H-coal Distillates

Material	Concentration (w/v%)	No. with Skin Tumor (%)[a]		Average Latency (days±SE)		Deaths	
		Female	Male	Female	Male	Female	Male
H-coal raw	50	5(50)	4(40)	301(37)	342(54)	2	1
Distillate	25	0	7(70)	-	336(30)	1	0
	12.5	1(10)	1(10)	434	390	0	0
	6.25	0	0	-	-	0	0
Hydrotreat.	50	1(10)	0	450	-	0	1
Low severity	25	0	0	-	-	1	1
	12.5	0	0	-	-	0	0
	6.25	1(10)	0	412	-	0	1
Hydrotreat.	50	0	0	-	-	0	0
Med. severity	25	0	0	-	-	0	0
	12.5	0	0	-	-	0	0
	6.25	0	0	-	-	0	0
Hydrotreat.	50	1(10)	0	462	-	1	0
High severity	25	0	0	-	-	2	0
	12.5	0	0	-	-	2	1
	6.25	0	1(10)	-	405	0	0
Recluse	50	0	3(30)	-	381(25.4)	0	0
Petroleum	25	0	0	-	-	0	0
	12.5	0	0	-	-	0	0
	6.25	0	0	-	-	1	0
Acetone:Cyclohexane	100	0	0	-	-	1	1

[a]10 male and 10 female mice per dose group.

Table III

Systemic toxicity associated with long term dermal exposure to hydrotreated H-coal distillates[a]

Material	Body wt. (gm)		Kidney wt. (mg)		Kidney sp. wt.		Water intake
	Female	Male	Female	Male	Female	Male	ml/mouse/day
Raw distillate	29.9(.7)	32.7(.9)	262(7)	351(12)	17.6(.4)	21.4(.8)	7.3(.3)
Low severity	27.5(.6)	30.8(.8)	243(5)	347(8)	17.9(.6)	23.1(.5)	7.3(.2)
Med. severity	27.8(.7)	29.2(.4)	338(7)	398(10)	23.7(.5)	27.2(.5)	9.3(.4)
High severity	23.7(1.4)	28.3(1)	335(9)	385(15)	25.4(1.8)	27.8(.4)	8.5(.3)
Recluse Petrol.	28.3(0.8)	32.7(1)	217(4)	347(14)	15.5(.5)	21.3(.7)	4.4(.2)
Solvent	28.1(0.9)	35.4(1.1)	294(6)	447(13)	21.1(.5)	24.7(.7)	4.6(.2)

[a]Values underlined differ significantly from solvent control ($p < .05$).

SECTION 4: TOXICITY AND CARCINOGENICITY ASSOCIATED WITH CHRONIC DERMAL EXPOSURE TO H-COAL PROCESS DISTILLATES

INTRODUCTION

These studies were intended to evaluate the relative carcinogenic potency of representative H-coal distillates obtained from the Hydrocarbon Research, Inc. Process Development Unit located in Trenton, N. J. Since one of the primary routes of occupational exposure to these materials will be skin, the dermal route was selected for the materials. In addition to local effects of the materials there was interest as well as opportunity to monitor the animals for evidence of systemic toxicity as a result of skin absorption of toxic components.

MATERIALS AND METHODS

Animal Exposure

Groups of 25 male and 25 female C3HF/Bd mice were exposed to H-coal distillate materials commencing at 11 weeks of age. Duration of exposure, as well as post exposure follow-up, differed for each material and, in some cases, dose groups. This was necessary due to the wide difference in skin irritation and carcinogenic potency among these materials and, in one case, the limited quantity of material available for test.

Test Materials

Samples were obtained through the courtesy of Hydrocarbon Research, Inc. and represent process conditions prevailing at the time. It cannot be assumed that the data necessarily predict the activity of the same or similar distillates obtained under different process conditions or derived from different coal feed.

Material identification, ORNL No. and densities are given in Table I together with the calculated dose, in mg per week, applied to each animal in 3-50 μl fractions. Density was determined by placing 0.2 ml aliquots of each material on preweighed pieces of filter paper which were weighed immediately. This procedure most closely approximates the manner in which samples are prepared and also applied to animals. The solvent used to dilute the materials was acetone. Material preparation and storage was the same as for the hydrotreated materials (see Section 3).

Table I

H-coal Distillates Tested for Chronic Dermal Toxicity

Material	Run Mode	ORNL No.	Density (gm/ml)	Concentration (wt. vol. %)	Dose (mg/wk)
Atmospheric overhead	Syncrude	1308	0.905	100	136
				50	71
				25	36
Atmospheric bottoms	Syncrude	1309	1.050	100	157
				50	77
				25	38
Vacuum overhead	Syncrude	1310	0.935	100	140
				50	72
				25	36
Atmospheric overhead	Fuel oil	1312	0.825	100	124
				50	68
				25	34
Atmospheric bottoms	Fuel oil	1313	1.050	100	157
				50	77
				25	38
Vacuum overhead	Fuel oil	1314	0.975	100	146
				50	74
				25	37

Potency Determination

Statistical analyses of the time-to-skin-tumor distributions for test material and the reference carcinogen benzo(a)pyrene [B(a)P] were compared using parameters of a Weibull model fit to the data for each dose of a test material. Details concerning these methods can be found elsewhere(1-3).

RESULTS

Skin Tumor Response

Table II summarizes the number of animals that developed treatment related skin neoplasms during the period of exposure or within two weeks following cessation of exposure. A three parameter model was fit to the observed distribution of time to onset of skin tumor, corrected for mice dying from other causes, either natural, accidental or treatment related. From the resultant fit the estimated median time to tumor was obtained as a summary measure of the overall tumorigenicity of a given material/dose/sex combination.

In order to compare materials in this experiment with those tested in other experiments and at other times the data were further evaluated to estimate relative potency, that is, the relative effect of the test material to that of benzo(a)pyrene at equal doses or the ratio of dosages required to elicit a comparable median response. These data are given in Table III. Differences among the materials are readily apparent with the order of potency being, 1310>1314>1309>1313>>1308 = 1312. Of interest is the observation that males tend to be more sensitive to hydrocarbon skin carcinogenesis than females. The chi square values for the difference in the response of the two sexes (Log rank test) together with the exact two-sided P indicates the difference was significant in the case of material 1309 and 1310. Significant differences in the sensitivity of male and female were not demonstrated for material 1313 and 1314, but the trend of the data was also in the same direction.

Systemic Toxicity

Mortality is a crude summary measure of the potential systemic toxicity associated with long term dermal exposure. Based on the log rank test of a comparison of the proportion of mice alive in treated versus vehicle control groups the data in Table IV indicate significantly greater treatment related mortality in those groups in which skin neoplasms were induced at high frequency. The most likely interpretation of this is that death was the indirect result of the skin tumor rather than systemic toxicity. Evaluation of gross and microscopic tissue lesions will, in the majority of cases, permit a determination of cause of death, or at the very least, the exclusion of skin neoplasia as a possible cause of death. The amount of material 1308 available for test precluded evaluation of systemic toxicity.

Table II

Frequency of skin tumors and estimated median time to tumor following long term exposure to H-coal distillates

Material	Dose mg/wk	Duration of exposure and (follow-up) in wks.	No. with Tumors[a] Female	Male	Median Time to Tumor, Days (±SE) Female	Male
1308	136	16(16)	0	0	-	-
	71	16(16)	0	0	-	-
	36	16(16)	0	0	-	-
1309	157	28(0)	25	25	132(4)	104(4)
	77	36(0)	22	23	199(7)	185(8)
	38	50(0)	16	17	324(13)	308(14)
1310	140	6(24)	10	16	60(3)	55(2)
	72	28(0)	23	24	135(8)	106(4)
	36	28(0)	24	25	169(6)	142(5)
1312	124	60(0)	0	0	-	-
	68	60(0)	0	0	-	-
	34	60(0)	0	0	-	-
1313	157	54(0)	21	17	291(11)	301(15)
	77	54(0)	13	17	382(18)	350(17)
	38	54(0)	2	5	569(70)	503(45)
1314	146	6(24)	3	7	73(7)	63(3)
	74	28(0)	25	25	129(4)	123(3)
	37	30(0)	22	24	178(5)	167(5)
Acetone	119	60(0)	0	0	-	-
Benzo(a)pyrene	0.015	(0)	44	48	319(7)	316(7)
	0.0075	88(0)	45	50	500(10)	465(10)
	0.00375	106(0)	16	26	778(26)	711(19)
	0.001875	106(0)	2	2	1037(99)	1084(108)

[a]10 per dose and sex for Material 1308; 25 per dose and sex materials 1309-1314 and acetone and 50 per dose and sex for benzo(a)pyrene.

Table III

Relative potency estimation for H-coal distillates applied to the skin of C3H mice

Material	Dose	Relative potency^{-1} (95% lower CL) Female	Male	Sex Effect χ^2	P
1309	157	2770(2330)	1900(1530)	10.39	0.0013
	77	2690(2390)	2270(1980)	2.16	0.1419
	38	2610(2350)	2700(2380)	0.46	0.4963
1310	140	1420(1080)	766(584)	2.11	0.1463
	72	1240(1020)	757(619)	4.47	0.0345
	36	1070(903)	747(628)	4.95	0.0261
1313	157	9370(8370)	10200(8970)	0.21	0.6480
	77	7300(6580)	7260(6550)	1.39	0.2387
	38	5710(4710)	5170(4350)	1.50	0.2201
1314	146	1390(1070)	943(731)	1.46	0.2274
	74	1210(1020)	923(776)	0.82	0.3647
	37	1050(907)	904(779)	0.87	0.3500

Table IV

Mortality in mice associated with chronic skin application of H-coal distillates

Material	Dose	No. of Deaths		χ^2		P	
		Female	Male	Female	Male	Female	Male
1309	157	2	3	3.09	3.66	0.08	0.06
	77	2	4	3.06	4.21	0.08	0.04
	38	4	2	4.26	2.29	0.04	0.13
1310	140	7	8	8.44	9.49	0.004	0.002
	72	6	4	8.26	7.49	0.004	0.006
	36	2	2	3.09	2.04	0.08	0.15
1312	124	1	0	1.00	-	0.32	-
	68	3	1	3.13	1.00	0.08	0.32
	34	4	0	1.00	-	0.32	-
1313	157	9	8	10.74	21.86	0.001	0.0001
	77	4	6	4.75	13.95	0.03	0.0002
	38	1	0	1.67	1.25	0.2	0.26
1314	146	5	3	5.97	4.78	0.01	0.03
	74	2	2	2.04	11.13	0.15	0.001
	37	0	1	-	1	-	0.32
Acetone	119	0	0	-	-	-	-
Benzo(a)pyrene	0.015	9	7	7.12	4.03	0.008	0.04
	0.0075	33	15	0.34	0.70	0.56	0.4
	0.00375	23	16	0.69	0.00	0.41	1.00
	0.001875	28	16	0.00	0.34	1.00	0.56

Body and organ weight comparisons between treated and vehicle control groups provide another measure of systemic toxicity. These data are presented in Table VA for female and VB for male mice.

Table VA

Body and organ weights in female C3H mice exposed chronically to H-coal process distillates

Material	Dose (mg/wk)	Body (gm)	Average Weight at Necropsy[a] Liver (gm)	Spleen (mg)	R. Kidney (mg)	L. Kidney[b] (mg)
1308	136	29(0.8)	-	-	-	-
	71	29.8(0.4)	-	-	-	-
	36	30.6(0.9)	-	-	-	-
1309	157	28(0.3)	1.901(.6)	171(12)	276(6)	261(6)
	77	28.1(0.6)	1.893(.4)	-	506(10)	
	38	28.8(0.6)	2.003(.5)	-	518(17)	
1310	140	27.2(0.9)	1.976(.5)	-	506(15)	
	72	26.1(0.6)	1.783(.4)	-	470(11)	
	36	26.3(0.6)	1.974(.1)	-	519(11)	
1312	124	28.6(0.3)	1.712(.4)	127(6)	252(6)	239(6)
	68	27.8(0.5)	1.589(.4)	133(9)	264(7)	238(6)
	34	30.4(0.7)	1.606(.4)	140(10)	271(4)	257(4)
1313	157	25.8(0.8)	1.719(0.8)	241(49)	275(10)	261(8)
	77	27.2(0.7)	1.743(0.7)	152(9)	261(8)	252(7)
	38	28.7(0.5)	1.648(0.4)	168(22)	246(6)	228(6)
1314	146	26.3(1.4)	-	-	-	-
	74	26.2(.5)	2.125(.7)	-	510(15)	
	37	27.8(.4)	1.883(.5)	-	484(12)	
Acetone	-	29.1(0.6)	1.458(0.4)	131(5)	230(5.5)	217(5.2)

[a]Values underlined were significantly different than acetone control ($P < 0.05$).

[b]A single number means both the kidneys were weighed together.

Table VB

Body and organ weights in male mice exposed chronically to H-coal process distillates

Material	Dose (mg/wk)	Body (gm)	Average Weight at Necropsy[a] Liver (gm)	Spleen (mg)	R. Kidney (mg)	L. Kidney[b] (mg)
1308	136	34.7(0.7)	-	-	-	-
	71	34(0.9)	-	-	-	-
	36	35.7(0.8)	-	-	-	-
1309	157	29.7(0.7)	2.292(0.9)	-	687(17)	
	77	28.3(0.7)	2.118(0.6)	-	686(19)	
	38	31.3(0.3)	2.207(0.6)	163(12)	399(10)	381(8)
1310	140	29.4(1.1)	2.041(0.8)	-	661(27)	
	72	30.1(0.8)	2.399(0.1)	-	669(27)	
	36	30.8(0.6)	2.341(0.9)	-	704(23)	
1312	124	30.9(0.4)	1.735(0.4)	103(2)	382(7)	358(7)
	68	33.8(0.5)	1.828(0.3)	116(8)	366(7)	347(7)
	34	33.6(0.4)	1.668(0.4)	103(7)	379(10)	350(9)
1313	157	28.1(0.8)	1.771(0.7)	230(45)	355(12)	341(15)
	77	30.8(0.8)	1.809(0.1)	261(46)	346(13)	328(8)
	38	35.4(0.6)	1.924(0.3)	132(16)	399(19)	395(12)
1314	146	33.5(0.7)	1.80(0.1)	-	736(54)	
	74	29.7(0.7)	2.245(0.1)	-	663(12)	
	37	30.4(0.4)	2.214(0.4)	-	703(17)	
Acetone	-	35.2(0.8)	1.764(0.3)	105(3)	389(11)	372(10)

[a]Values underlined were significantly different than acetone control ($P < 0.05$).

[b]A single number means both the kidneys were weighed together. Kidney weights were not statistically analyzed.

Water intake was also monitored periodically throughout the experiment. Slight but statistically significant ($P < 0.05$) increased water consumption was noted in all groups (Table VI). The basis for this small increase is unknown but we have obtained evidence that it is due in part to skin alteration caused by exposure to the test materials. There is no evidence that kidney function is affected in these animals.

Table VI

Average daily water consumption in mice exposed dermally to H-coal process materials

Material	Weekly Dose (mg)	Average Daily Water Intake (ml)	
		Females	Males
1308	136	5.7±0.7	5.5±0.5
	71	5.0±0.1	5.5±0.4
	36	5.4±0.3	5.8±0.2
1309	157	6.2±0.09	8.2±0.2
	77	6.0±0.2	5.6±0.1
	38	5.6±0.1	5.3±0.2
1310	140	n.t.[a]	n.t.
	72	5.9±0.1	7.4±0.2
	36	5.3±0.1	5.4±0.1
1312	124	6.0±0.2	5.2±0.1
	68	5.5±0.1	5.1±0.1
	34	5.2±0.1	5.0±0.2
1313	157	5.6±0.1	5.8±0.2
	77	5.4±0.2	5.0±0.1
	38	5.0±0.1	5.4±0.4
1314	146	n.t.	n.t.
	74	5.4±0.1	6.6±0.2
	37	5.2±0.2	5.2±0.2
Acetone	-	4.5±0.1	4.5±0.1

[a]Not tested.

Commencing at approximately the eighth month of exposure and with increasing frequency thereafter neurotoxicity was observed in mice exposed to the two highest dose levels of material 1312. The response was elicited within 10-30 seconds following application. Clinically, the animals displayed a stereotypic behavior commencing with an arched back and tail held rigid and erect. This was followed immediately by prostration, tonic-clonic convulsions with transition to a hyperactivity state with rapid and coordinated body movement. The hyperexcitement stage was followed by collapse and exhaustion. The animals appear dazed with rapid and shallow respiration. After a few moments the affected animal began moving around the cage and soon thereafter could not be distinguished from unaffected cage mates. A movie (16 mm) has been made to document the effect.

While the overall frequency of this syndrome was both dose and treatment related not all animals on a given day exhibited the response, and an individual affected one or more times may remain unaffected on a given day. It may be important to note that relatively fewer animals in a given dose group were affected on Monday than either the Wednesday or Friday exposure. We conjecture that this is due to a longer recovery time between the Friday and Monday exposure. If this is true it implies that, whatever the components of material 1312 responsible for this effect, physiologic recovery is rapid following cessation of exposure. To date, light microscopic evaluation of the spinal cord and brain have failed to reveal any microscopic lesion consistent with this syndrome. Our current working hypothesis is that the effect is due to a sudden release of neurostimulatory, or block of neuroinhibitory, chemicals in the brain induced by rapid percutaneous penetration of components of the test material. Whatever the eventual explanation, it is of utmost importance to determine the neurophysiologic basis of the response and from this the chemical components most likely responsible. From this it should be possible to evaluate the significance of these findings to human health.

SUMMARY AND CONCLUSIONS

The present data reveal that coal derived distillates generated by the H-coal process are highly carcinogenic to mouse skin. Wide differences due to material composition were noted. Not surprisingly, the most carcinogenic samples were also the higher boiling materials in which it is assumed that the components most responsible for skin carcinogenicity, polynuclear aromatic hydrocarbons, are concentrated.

Completely unexpected was the observation of an extreme form of neurotoxicity associated with dermal exposure to one of the lighter, minimally carcinogenic, materials. While the basis of this response is unknown there is precedent for neurotoxicity following skin and inhalation exposure to shale oils (4).

In the case of shale oil it was suggested that non-volatile mono and disubstituted phenols were responsible for neuro behavioral effects. To date, the analysis of sample 1312 is incomplete; however, a more extensive analysis, with particular attention to the phenolic components, is in progress.

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APPENDIX A

CHARACTERISTICS OF COAL-DERIVED LIQUIDS

Mobil Research and Development Corporation (MRDC) has provided information[1] on nineteen coal-derived liquid samples that were shipped to Oak Ridge National Laboratory. These samples were obtained and/or upgraded by MRDC under contract RP 361-2 with the Electric Power Research Institute (EPRI). However, the properties of these samples do not correspond to properties reported for specific material balance periods from the EPRI-sponsored MRDC work.[2-5] We presume[6] the samples provided by MRDC to Oak Ridge National Laboratory were composite samples. MRDC advises[1] "These samples were obtained by bench-scale and pilot unit preparations. They are not necessarily representative of coal liquids which will eventually be produced in a commercial facility."

The information provided on these samples is reproduced as Table 1, Table 2,[7] and Table 3.[8]

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[1] P. J. Angevine, personal communication to L. E. McNeese (March 16, 1981).

[2] J. G. Bendoraitis et al., Upgrading of Coal Liquids for Use as Power Generation Fuels, EPRI 361-1, Phase I Report (January 1976).

[3] T. R. Stein et al., Upgrading of Coal Liquids for Use as Power Generation Fuels, EPRI AF-444, Annual Report (October 1977).

[4] T. R. Stein et al., Upgrading of Coal Liquids for Use as Power Generation Fuels, EPRI AF-873, Annual Report (December 1978).

[5] P. J. Angevine et al., Upgrading of Coal Liquids for Use as Power Generation Fuels, EPRI AF-1225, Final Report (December 1979).

[6] P. J. Angevine, personal communication to H. D. Cochran (April 20, 1981).

[7] R. F. Kimball and N. B. Munro, A Critical Review of the Mutagenic and Other Genotoxic Effects of Direct Coal Liquefaction, ORNL-5721.

[8] W. L. Goldman, Hydrocarbon Research, Inc., Lawrenceville, NJ, personal communication to K. Cowser (October 25, 1978).

Table 1

Properties of Coal Liquid Samples Shipped to Oak Ridge National Laboratory (ORNL)

Coal Liquid Number	ORNL Repository Number	Sample	T[a]	SV[b]	P[c]	H[d]	O[e]	N[f]	S[g]	Boiling Range, °F	% C_A[h]
1	1601	H-Coal Distillate (raw)				9.65	1.62	0.39	0.107	300-700	57
2	1602	HDT at low severity	675	4.0	2500	9.87	0.95	0.20	0.002		52
3	1603	HDT at medium severity	675	2.0	2500	10.5[i]	0.39	0.13	<0.002		45
4	1604	HDT at high severity	725	2.0	2500	10.9[i]	0.21	0.09	<0.002	200-650	39
5	1605	SRC Light Organic Liquid (raw)				11.2[i]	4.22	0.23	0.55	150-450	40
6	1606	HDT at low severity	600	4.0	500	12.14	3.08	0.13	0.046		30
7	1607	HDT at medium severity	625	2.0	1000	13.11	0.62	0.04	0.138		23
8	1608	HDT at high severity	625	1.0	500	13.66	0.26	0.0012	0.057	150-450	17
9	1609	SRC Wash Solvent (raw)				7.97	4.22	0.313	0.33	350-675	71
10	1610	HDT at low severity	675	2.0	500	8.73	4.08	0.19	0.010		67
11	1611	HDT at medium severity	725	1.0	500	10.28	0.22	0.085	0.021		53
12	1612	HDT at high severity	725	0.5	2000	12.93	0.16	0.0051	<0.002	175-475	16
13	1613	SRC Recycle Solvent (raw)				7.86	3.97	0.61	0.33	350-700	71
14	1614	HDT at low severity	675	1.0	1500	8.95	2.35	0.37	0.029		57
15	1615	HDT at medium severity	775	1.0	1500	10.13	0.57	0.10	<0.01		46
16	1616	HDT at high severity	775	0.5	2500	11.12	<0.10	0.03	<0.01	175-625	33
		H-Coal Fuel Oil (raw								375-1000	58
17	1617	HDT at low severity	675	0.5	2000	9.17	0.94	0.58	0.059		52
18	1618	HDT at medium severity	725	0.5	2000	9.22	0.74	0.55	0.039		51
19	1619	HDT at high severity	775	0.5	2000	9.67	0.44	0.30	0.011	375-1000	44

[a] T = hydrotreat temperature, °F.
[b] SV = hydrotreat space velocity, h^{-1} (volume oil per hour per volume catalyst).
[c] P = hydrotreat pressure, psig.
[d] H = wt % hydrogen.
[e] O = wt % oxygen.
[f] N = wt % nitrogen.
[g] S = wt % sulfur.
[h] % C_A = aromatic carbon as percent of total carbon.
[i] Estimated.

Source: P. J. Angevine, personal communication to L. E. McNeese (March 16, 1981).

Table 2

Additional Data on HRI H-Coal PDU Samples[a]

	Volumetric Distillation (°F)												
	Initial Boiling Point	10%	30%	50%	70%	90%	End Boiling Point	API Gravity	C[b] (W%)	H[b] (W%)	N[b] (W%)	S[b] (W%)	Phenols[b] (V%)
Atmospheric Overhead (ASOH) LO-1414, 1308	146	232	316	395	455	525	590	32.0	88.1	11.8	0.17	0.07	5.4
Atmospheric Bottoms (ASB) LO-1415, 1309	458	519	570	616		66%/650		10.5	90.9	9.4	0.37	<0.03	
Vacuum Overhead (VSOH) LO-1416, 1310	492	570	640		34%/650			4.6	90.8	8.7	0.42	<0.03	
Atmospheric Overhead (ASOH) LO-1418, 1312	172	249	315	388	424	476	565	30.8					
Atmospheric Bottoms (ASB) LO-1419, 1313	410	475	516	556	608		81%/650	13.1					
Vacuum Overhead (VSOH) LO-1420, 1314	462	517	592		46%/633			6.0					

Vacuum Bottoms (VSB)	Toluene Solubles (%)	Toluene Insolubles (%)	Ash (%)	Unconverted Coal (%)	Insoluble Resid (%)					
LO-1417, 1311	52.5	19.7	27.8	12.0	7.8	63.8	4.3	0.90	3.0	
LO-1421, 1315	47.5	32.1	20.4	11.3	20.8					

[a]Samples 1308 through 1311 from PDU Run No. 5 processing Illinois No. 6 coal. In the syncrude mode of operation during September and October of 1977.

Samples 1312 through 1315 from PDU Run No. 7 processing Illinois No. 6 coal in the fuel oil mode of operation during September of 1978.

[b]These values are from a sample run the preceding day with similar operating characteristics.

Table 3

Description of Hydrocarbon Research, Inc., Samples[a,b]

Sample Description	Sample No.	Period	PDU	Quantity (gms)
Atmospheric Overhead (ASOH)	LO-1414	130-82-5A	5	3069
Atmospheric Bottoms (ASB)	LO-1415	130-82-5A/B	5	3819
Vacuum Overhead (VSOH)	LO-1416	130-82-5A/B	5	3913
Vacuum Bottoms (VSB)	LO-1417	130-82-5B	5	3091
Atmospheric Overhead (ASOH)	LO-1418	130-86-5A	7	3430
Atmospheric Bottoms (ASB)	LO-1419	130-86-5A	7	3005
Vacuum Overhead (VSOH)	LO-1420	130-86-5A	7	2640
Vacuum Bottoms (VSB)	LO-1421	130-86-5B	7	3539

[a]PDU 5 processed Illinois No. 6 coal in the syncrude mode of operation during September and October of 1977 and PDU 7 processed Illinois No. 6 coal in the fuel oil mode of operation during September of 1978.

The blending ratios for a syncrude product from PDU 5 are: ASOH, 86.0 wt. %; ASB, 12.6 wt. %; VSOH, 1.4 wt. %.

The blending ratios for a $400^{+\circ}$F fuel oil product from PDU 7 are: ASOH, ($400^{+\circ}$F)*, 23.8 wt. %; ASB, 21.4 wt. %; VSOH, 5.0 wt. %; VSB (only oil)*, 49.8 wt. %. (*Please note that 23.8 wt. % ASOH refers to $400^{+\circ}$F material and 49.8 wt. % VSB refers to oil only. The VSB sample contains approximately 20 wt. % ash and 11 wt. % coal, which must be removed before a fuel oil product can be obtained.)

[b]William L. Goldman, Hydrocarbon Research, Inc., Lawrenceville, NJ, personal communication to K. Cowser (October 25, 1978).

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