Comparative Toxicity of Crude and Refined Coal Liquids and Analogous Petroleum Products: II. Chemical Characterization*

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Introduction

In Part I of this paper, the dermal tumorigenicity of crude and hydrogenated H-Coal Blends, a home heating oil and a reformed naphtha refined from the hydrotreated H-Coal Blend, and two analogous petroleum products is reported. This paper compares the tumorigenicity assay results with the chemistry of the samples.

Experimental

Samples: The crude and upgraded coal liquids consisted of a water-washed 60/40 (wt./wt.) blend of Light and Heavy Oils from the H-Coal Pilot Plant at Catlettsburg, KY) (H-Coal Blend-AWW, sample identification no. 931), the blend hydrotreated under "low severity" conditions resulting in 900 SCF/Bbl of hydrogen incorporation (H-Coal Blend-HDT/L, no. 934), the blend hydrotreated under "medium severity" conditions for 1400 SCF/Bbl of hydrogen consumption (H-Coal Blend-HDT/M, no. 933), and the blend hydrotreated under "high severity" conditions for 3000 SCF/Bbl hydrogen consumption (H-Coal Blend-HDT/H, no. 935). In addition, two products were prepared as petroleum product substitutes. No. 935 H-Coal Blend-HDT/H was devolatilized to meet most of the ASTM specifications for no. 2 fuel oil and was designated as H-Coal Home Heating Oil (no. 978). A 96 octane "gasoline" product (H-Coal Reformed Naphtha) was prepared by a high severity hydrogenation of the no. 931 H-Coal Blend, followed by hydrocracking and catalytic reforming. Blending, catalytic hydrogenation, and hydrocracking were conducted by the Chevron Research Corporation (Richmond, CA), and catalytic reforming was performed by Universal Oil Products, Inc. (Des Plaines, IL). Two petroleum products, API no. 2 Fuel Oil (no. 975) and API Light Catalytically Cracked Naphtha (no. 976) were supplied by the American Petroleum Institute (Washington, DC). Sample origin and processing are described in detail elsewhere (1,2).

Mouse Skin Dermal Tumorigenicity: (See Part I.)

Bacterial Mutagenicity: Bacterial mutagenicity was determined using the plate incorporation assay of Ames with strain TA-98 and Aroclor-induced S-9 metabolic activation.

Organic Chemical Characterization: Benzo(a)pyrene was measured using a sequential high performance liquid chromatography/high performance liquid chromatography (HPLC/HPLC) procedure and quinoline was estimated by direct injection of a diluted sample into a gas chromatograph (GC) equipped with a packed column and a nitrogen-compound-selective thermionic detector. The 5-ring polycyclic aromatic hydrocarbons (PAH) were estimated by capillary column GC following preparation of a PAH-enriched fraction using semi-preparative HPLC. Major organic compounds in the fuels were identified by capillary column GC-mass spectroscopy. The chemical class distribution was determined gravimetrically after acid/alkaline partitioning of the sample and gel chromatography of the neutral fraction. More detailed descriptions of these procedures are given in reference (1).

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Results and Discussion

The changes in bulk composition and properties of the H-Coal Blend as the severity of hydrogenation is increased are consistent with those found in other studies, and are not reported in detail here (see reference 1). Briefly, the heteroatomic content decreases while the hydrogen concentration increases, with S being reduced most readily and O least easily. The density and viscosity decrease, the boiling range is lowered, and both the flash point and pour point decrease with increasing severity of hydrotreatment.

The more toxicologically important compositional changes are compared in Table 1 with summaries of the mutagenicity and dermal tumorigenicity assays. It is evident that tumorigenicity and mutagenicity are dramatically reduced by hydrogenation. Mutagenicity is undetectable in the hydrogenated blends when the sample is assayed as a slurry in dimethylsulfoxide. Tumorigenicity is reduced by low severity hydrotreatment, but no further reduction is evident for the high severity hydrotreated sample. The concentrations of toxic components or chemical classes in the samples also decrease with increasing severity of hydrotreatment, but not in direct proportion to the reductions in toxicity. BaP, a classic PAH dermal tumorigen drops to less than 0.4% of its original level upon low severity hydrotreating of the blend. A more gradual decrease in concentration is noted for the polycyclic aromatics chemical class fraction, which includes the PAH dermal tumorigens. The PAH are associated with the tumorigenicity (3-5) of crude coal liquids.

Quinoline, one of the major N-heterocyclics, decreases in concentration with increasing hydrotreatment severity. The ether-soluble base chemical class fraction also decreases in concentration. This fraction includes the polycyclic aromatic primary amines, which are the determinant mutagens in crude coal liquids (6,7).

In contrast, phenol appears to resist reduction until high severity hydrogenation conditions are employed. This behavior parallels the relative difficulty in reducing the total O content as gauged by ASTM Ultimate Analyses of the crude and hydrotreated blends (1). This trend is not reflected in the ether-soluble acid fraction, which contains most of the oxygenates such as phenols and carboxylic acids.

The PAH content and dermal tumorigenicity of the refined products derived from coal liquids and petroleum are compared in Table 2. It is evident that the further refining (hydrocracking and catalytic reforming) to produce the H-Coal Reformed Naphtha has eliminated the tumorigenicity of the original crude H-Coal Blend. The API Light Catalytically Cracked Naphtha is only slightly tumorigenic. The home heating oils are somewhat more tumorigenic than the naphthas, with the H-Coal Home Heating Oil being more tumorigenic than the API No. 2 Fuel Oil. It also is apparent that the least tumorigenic product (the H-Coal Reformed Naphtha) has the highest BaP and 5-ring PAH concentrations. The fuel oils have lower BaP and PAH content than does the H-Coal Reformed Naphtha, but much higher tumorigenic activities.

One hypothesis for this apparent disparity between PAH content and tumorigenicity is that there are differences in tumor promoting activity among the samples. This hypothesis is being tested. An alternate hypothesis is that the expression of tumorigenicity by the PAH is mediated by differences in the sample matrix composition. The capillary column GC separations shown in Figure 1 illustrate that major compositional differences do exist between the H-Coal Home Heating Oil and the API No. 2 Fuel Oil. Mass spectral analysis of the samples confirmed these differences. The API No. 2 Fuel Oil is composed mainly of C_7-C_{24} n-alkanes and alkylated 1-3 ring aromatic hydrocarbons (in order of decreasing concentration: C_0-C_5-naphthalenes, C_0-C_4-benzenes, C_1-C_4-indanes, and C_0-C_1-phenanthrenes). In contrast, the H-Coal Home Heating Oil is comprised mainly of cycloparaffins (in order of decreasing concentration): decahydronaphthalene, C_1-C_4-decahydronaphthalenes, C_0-C_4-cyclohexanes, and C_0-C_4-tetralins. Aromatic and partially saturated aromatic hydrocarbons

and alkanes also are present, but at much lower levels (in order of decreasing concentration): C_1-C_4-indanes, C_7-C_{25} n-alkanes, and C_0-C_4-benzenes.

The chromatograms of the naphthas (Figure 2) show that they are quite different as a group from the home heating oils. The two naphthas share many components, such as C_4-C_7-alkanes and C_0-C_3-benzenes. However, the H-Coal Reformed Naphtha is more aromatic than the API Light Catalytically Cracked Naphtha, having 7-fold more benzene, 4.5-times more toluene, and 2-fold greater levels of C_2-benzenes. In contrast, the API Light Catalytically Cracked Naphtha is more olefinic, being more enriched in partially unsaturated C_5-C_8 hydrocarbons. The fluorescent indicator assay results reported by the Universal Oil Products, Inc., and the American Petroleum Institute reflect these compositional differences: H-Coal Reformed Naphtha (58.4% [vol./vol.] aromatic, 0.9% olefin, 40.7% saturate) and API Light Catalytically Cracked Naphtha (20.3% aromatic, 29.6% olefin, 50.0% saturate). It is possible that these compositional differences among the samples affects the absorption, metabolism, and uptake of PAH tumorigens, and modifies or potentiates their tumorigenic activities.

Conclusions

The decrease in tumorigenicity of the crude H-Coal Blend by catalytic hydrogenation is associated with the reduction of tumorigens. Comparison of the composition and residual tumorigenicity in refined products derived from the H-Coal Blend and from petroleum suggests that the tumorigenicity associated with PAH is modified by the presence of tumor promoting agents, by matrix composition differences, or both.

Acknowledgement

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References

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Table 1. Influence of Hydrotreatment on Chemical Parameters, Mutagenicity, and Tumorigenicity of Coal Liquids (1)

Sample Number	Description	Chemical Class Fraction, wt. %					Quinoline, µg/g	Phenol, mg/g	Benzo(a)pyrene, µg/g	Mutagenicity[b], rev/µg	Animals w/Skin Tumors[c], % Dose (wt./vol. %)	
		ESB	ESA	Sat.	Aro.	Polyaro.					100	50
931	H-Coal Blend - AWW	3.3	1.5	30.8	56.7	5.8	164	0.15	50	4.9	82	90
934	H-Coal Blend - HDT/L	2.4	0.8	38.3	46.5	1.3	6	0.13	<0.2	<0.1	14	12
933	H-Coal Blend - HDT/M	0.6	0.6	35.9	46.7	0.8	<1	0.13	<0.2	<0.1	-	-
935	H-Coal Blend - HDT/H	0.7	0.5	58.9	8.3	0.5	<1	<0.1	<0.1	<0.1	20	34

[a]ESB = ether-soluble bases, ESA = ether-soluble acids, Sat. = saturates, Aro. = mono/di-aromatics, Polyaro. = polycyclic aromatics.

[b]TA-98 + S-9 activation.

[c]Data for 104 weeks of three-times weekly treatment of 25 male plus 25 female C3H mice per dose group/substance. Male and female mice data combined.

Table 2. Comparison of PAH Content and Tumorigenicity of Final Products Refined from Coal Liquids and Petroleum

Sample Number	Description	Benzo(a)pyrene µg/g	Sum of 5-Ring PAH[a], µg/g	Animals w/Skin Tumors[b], % Dose (wt./vol. %)		Median Time-To-Tumor[c], Wks
				100	50	
936	H-Coal Ref. Nap.	1.4	35	0	0	155-ND
976	API Lt. Cat. Cr. Nap.	<0.002	<0.5	6	8	125-143
978	H-Coal Home Ht. Oil	0.08	3	28	24	97-112
975	API No. 2 F. O.	0.04	0.09	12	14	120-144

[a]Benzo(b/j)fluoranthenes + benzo(e)pyrene + benzo(a)pyrene + indeno(1,2,3-cd)pyrene + benzo(ghi)perylene.

[b]Data for 25 months of three-times weekly application to 25 male + 25 female C3H mice per dose group/substance. Acetone solvent for 50% dose.

[c]Range including all dose groups and both sexes. ND = none detected (for zero tumor incidence).

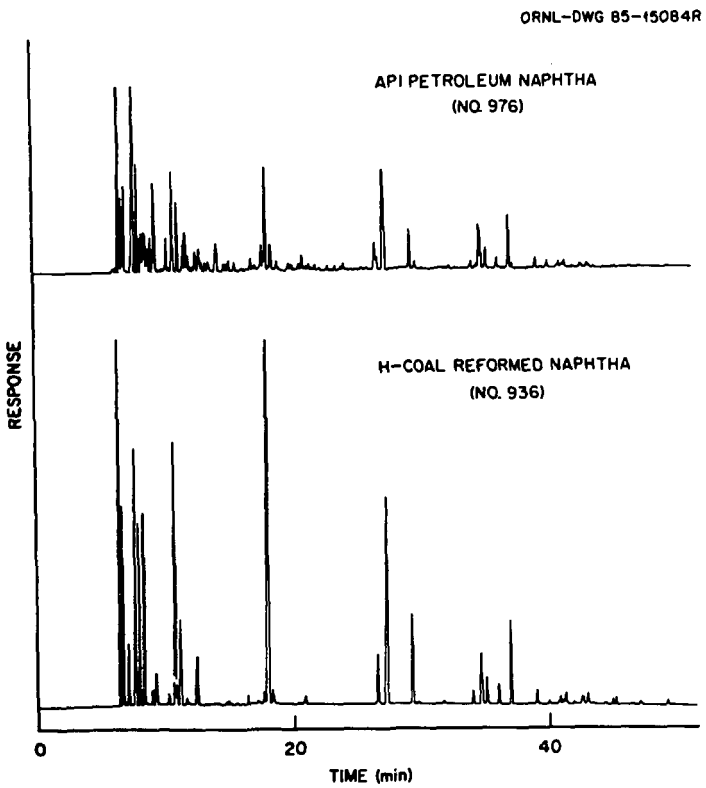

Figure 1. Capillary Column GC Comparison of Major Organic Compounds in Coal- and Petroleum-Derived Naphthas.

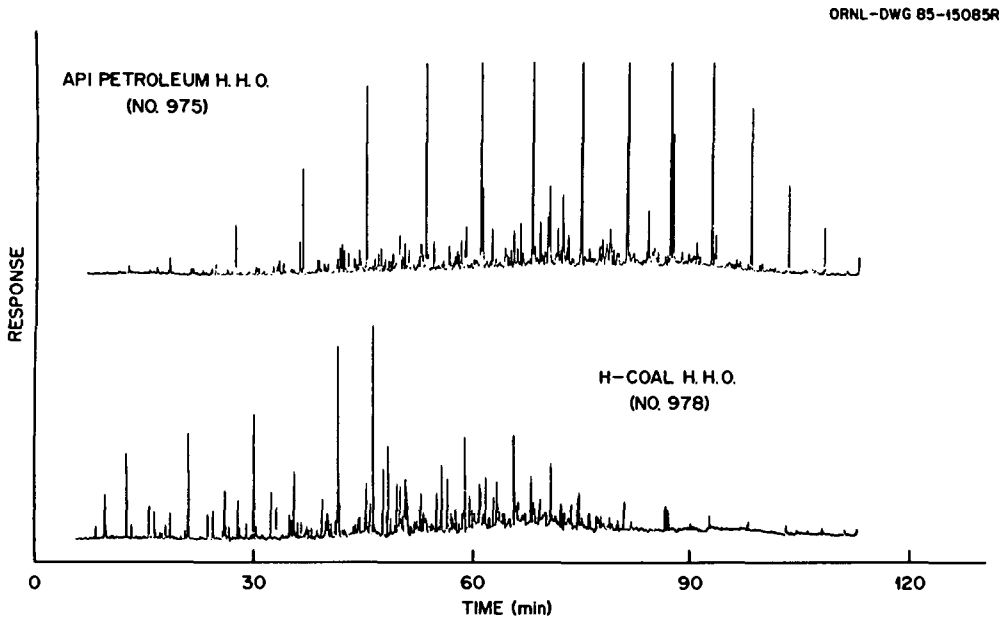

Figure 2. Capillary Column GC Comparison of Major Organic Compounds in Coal- and Petroleum-Derived Home Heating Oils.