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ORNL/TM-10070

## **Integrated Report on the Toxicological Mitigation of Coal Liquids by Hydrotreatment and Other Processes**

M. R. Guerin  
W. H. Griest  
C.-h. Ho  
L. H. Smith  
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Printed in the United States of America. Available from  
National Technical Information Service  
U.S. Department of Commerce  
5285 Port Royal Road, Springfield, Virginia 22161  
NTIS price codes—Printed Copy: A07 Microfiche A01

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ORNL/TM-10070  
Dist. Category UC-90d

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Date Published - June 1986

OAK RIDGE NATIONAL LABORATORY  
Oak Ridge, Tennessee 37831  
operated by  
MARTIN MARIETTA ENERGY SYSTEMS, INC.  
for the  
U.S. DEPARTMENT OF ENERGY  
under Contract No. DE-AC05-84OR21400



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## EXECUTIVE SUMMARY

Research here on the toxicological properties of coal-derived liquids focuses on characterizing the refining process and refined products. Principle attention is given to the potential tumorigenicity of coal-derived fuels and to the identification of means to further reduce tumorigenicity should this be found necessary. Hydrotreatment is studied most extensively because it will be almost certainly required to produce commercial products and because it is likely to also greatly reduce tumorigenic activity relative to that of crude coal-liquid feedstocks.

Two approaches are used. First, products of several levels of hydrotreatment made by others using realistic conditions are subjected to long-term bioassay and are chemically and physically characterized. Starting materials are compared with products, and products derived from coal are compared to nominally equivalent petroleum products. Second, laboratory-scale treatments and experiments are carried out to better understand the mechanisms of tumorigen removal and to scope the utility of alternate and supplemental treatments. Laboratory studies focus on the heavy oil component of coal liquids.

This report presents the results of a lifetime C3H mouse skin tumorigenicity assay of an H-Coal series of oils and considers the relationships between tumorigenicity, chemistry, and processing. Lifetime assay results are reported for an H-Coal syncrude mode light oil/heavy oil blend, a low severity hydrotreatment product, a high severity hydrotreatment product, a naphtha reformat, a heating oil, a petroleum-derived reformat, and a petroleum derived heating oil. Data are compared with those for an earlier study of an SRC-II blend and products of its hydrotreatment. Adequate data are presented to allow an independent qualitative assessment of the conclusions while statistical evaluation of the data is being completed. The report also documents the physical and chemical properties of the oils tested.

Results of the lifetime tumorigenicity assay clearly demonstrate that even low-severity hydrotreatment dramatically reduces tumorigenicity. The higher severity hydrotreatment examined led to no further reduction in tumorigenicity and may actually increase tumorigenicity slightly. The coal-derived naphtha reformat prepared by hydrocracking of the high

severity hydrotreated product followed by catalytic reforming exhibited the lowest (if any) tumorigenicity of any material tested in this study. Its tumorigenicity appears to be less than that of the petroleum reformat studied for comparison. The coal-derived heating oil is clearly more tumorigenic than is the petroleum heating oil tested for comparison. Except for the initial H-Coal blend and to a lesser degree the coal-derived heating oil, tumor incidence is very low and time-to-tumor is very long.

Results of laboratory studies reaffirm the utility of distillation for separating mutagens and tumorigens into the higher boiling fractions of coal-derived heavy oils. It is also shown that acid-wash treatment of heavy oils or vacuum gas oil material is very effective for reducing mutagenicity but not tumorigenicity. Alkaline-washing has no effect on mutagenicity but may decrease tumorigenicity slightly. None of the treatments examined was found as effective as hydrogenation for reducing tumorigenicity but evidence is presented that some treatments may improve the efficiency of tumorigen reduction when used prior to hydrogenation.

Chemical and biological data continue to suggest that polycyclic aromatic hydrocarbons (well-known complete tumorigens) are the primary tumorigenic agents of oils containing heavy oil constituents. Completely removing residual tumorigenicity may require treatments which can totally eliminate complete tumorigens, or which can alter tumor promoting agents in addition to reducing tumor initiators in the case of refined oils which exhibit low levels of tumorigenicity.

## 1.0 Introduction

This report summarizes the results of a lifetime mouse skin tumorigenicity study of oils produced by refining an H-Coal light oil/heavy oil blend and integrates the findings with those of chemical studies and of research into alternative refining approaches. Results are also compared with those of an earlier study of SRC-II oils. The origin, processing history, and physical/chemical properties of each of the oils studied is documented in detail for future reference.

The nature of the materials subjected to lifetime animal testing is discussed in Section 2.0 and detailed properties are itemized in Appendix A. Discussion centers upon the influence of hydrotreatment on the bulk and overall compositional properties of the oils. Oils used in laboratory studies and used in earlier skin painting studies are also described.

Results of the lifetime skin painting study of H-Coal products and of two comparative products of petroleum refining are summarized in Section 3.0. Cumulative percentage of animals developing tumors and the tumor latency are presented and compared with those observed in related studies. The relationship between lifetime testing, ten-animal dermal screening, and bacterial mutagenicity measurements is also discussed.

Observations concerning the relationship between tumorigenicity and chemistry as they are affected by hydrotreatment are presented in Section 4.0. Laboratory studies of the hydrogenative elimination of polycyclic aromatic hydrocarbon tumorigens are also described. Implications for predicting tumorigenicity from chemical measures and for approaches to improving tumorigenicity reduction are presented.

Laboratory surveys of non-hydrogenative methods for reducing tumorigenicity are discussed in Section 5.0. Using such processes as a pretreatment to hydrogenation is identified as a potentially important avenue of research.



## 2.0 STUDY MATERIALS ORIGIN AND PROPERTIES

Several suites of materials were examined chemically and toxicologically in this study. The primary study materials are listed in Table 2.1. Two suites of crude and upgraded coal liquids were derived from the H-Coal and Solvent Refined Coal (SRC-II) processes. A reformed naphtha and a home heating oil were refined only from the former. Comparative petroleum products were obtained from the American Petroleum Institute. The origin and processing of each of these sample suites is considered in detail below.

### 2.1 H-Coal Materials Origin and Processing History

The primary suite of samples used in this study was derived from the H-Coal process. Light and Heavy Oils were collected from the H-Coal pilot plant at Catlettsburg, Kentucky, on September 25, 1981 by personnel of Ashland Synthetic Fuels, Inc. Illinois No. 6 coal was being processed in the synfuel mode of operation in run no. 8. The oils were shipped to the Oak Ridge National Laboratory (ORNL), and two barrels of the Light Oil and one of the Heavy Oil were sent from ORNL to the Chevron Research Company, Richmond, California.

The sequence of blending and upgrading operations conducted on the Light and Heavy Oils and the relationships of the crude and refined samples are diagrammed in Figure 2.1. The Chevron Research Company blended the H-Coal Light and Heavy Oils in a 40/60 weight ratio because process engineers considered such a blend to be representative of the principal product of a scaled-up commercial plant. This blend is designated as H-Coal Blend-Before Water Washing (BWW) (Sample Number 930). The sample number in parenthesis following a sample name is the unique identifying number assigned to that sample.

Chevron performed a medium severity hydrogenation ("medium" severity only relative to the other hydrogenations conducted on the H-Coal blends) to meet a specification of a reduction of the total nitrogen content of the H-Coal Blend-BWW (No. 930) to ca. 500 ppm. This oil, designated as H-Coal Blend-Hydrotreated at Medium Severity (HDT/M) (No. 933), was prepared in a bench-scale downflow tubular reactor which contained a catalyst volume

Table 2.1  
LISTING OF PRIMARY STUDY MATERIALS

H-Coal Materials

H-Coal Blend - After Water Wash [AWW] (No. 931)  
H-Coal Blend - Hydrotreated at Low Severity [HDT/L] (No. 934)  
H-Coal Blend - Hydrotreated at Medium Severity [HDT/M] (No. 933)  
H-Coal Blend - Hydrotreated at High Severity [HDT/H] (No. 935)  
H-Coal Reformed Naphtha (No. 936)  
H-Coal Home Heating Oil (No. 978)  
H-Coal Heavy Oils (Nos. 695, 888, and 1334)

Petroleum Materials

American Petroleum Institute [API] Light Catalytically  
Cracked Naphtha (No. 976)  
American Petroleum Institute [API] No. 2 Fuel Oil (No. 975)

SRC-II Materials

SRC-II Blend - After Water Wash [AWW] (No. 916)  
SRC-II Blend - Hydrotreated at Low Severity [HDT/L] (No. 917)  
SRC-II Blend - Hydrotreated at Medium Severity [HDT/M] (No. 918)  
SRC-II Blend - Hydrotreated at High Severity [HDT/H] (No. 919)

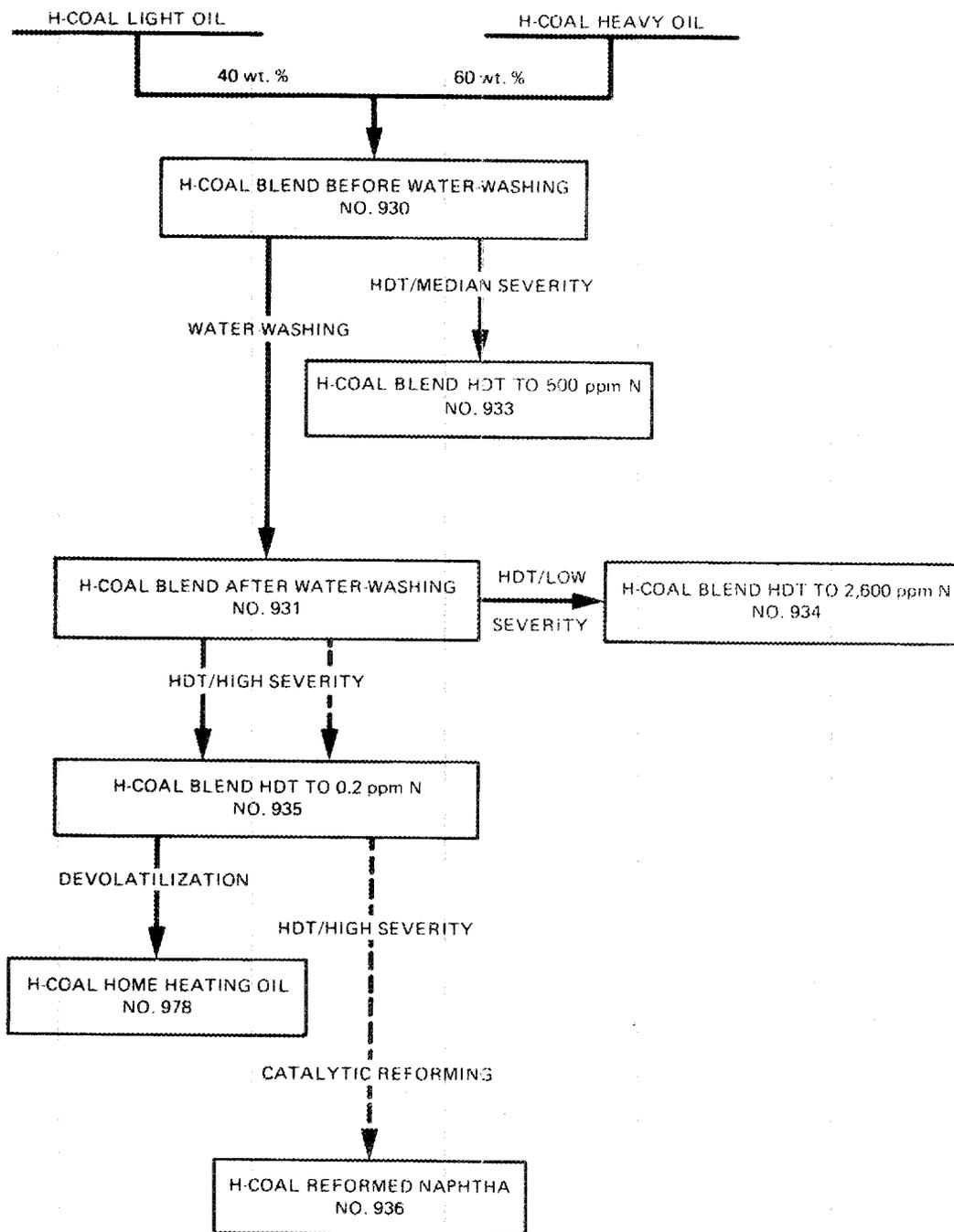


Figure 2.1. Diagram of H-Coal Blend Upgrading and Relationship of Samples.

of 130 cm<sup>3</sup>. The hydrotreatment was conducted in an isothermal mode with gas recycle and once-through flow of the coal liquid. Table 2.2 summarizes the run conditions.

Because of process line plugging problems from the ammonium chloride produced in the hydrotreatment of the H-Coal Blend-BWW (No. 930), this blend was washed twice with equal weights of water to reduce the chlorine content from 105 to 1.2 ppm (Sullivan, 1982). This washed blend is designated as H-Coal Blend-After Water Washing (AWW) (No. 931). It served as the crude coal liquid precursor of the finished products. Low and medium severity hydrotreatments were conducted on the H-Coal Blend-AWW (No. 931), as summarized in Table 2.2. The specifications were to reduce the total nitrogen content of the blend by 50% (low severity) and to produce a home heating oil of 30° API specific gravity (high severity). Chevron used their ICR 106 catalyst at temperatures of 338°-402°C (640-755°F) with ca. 2,300 psia of hydrogen for all three hydrogenations. The severity was varied from low to high by increasing the catalyst bed temperature and decreasing the liquid hourly space velocity through the reactor. The hydrotreated products are designated as H-Coal Blend-Hydrotreated at Low Severity (HDT/L) (No. 934), and H-Coal Blend-Hydrotreated at High Severity (HDT/H) (No. 935). The hydrogen incorporation for the three levels of severity were 900, 1,400, and 3,000 SCF/BBL. Properties of these materials are listed in Appendix A. Analytical methods are outlined in Appendix B.

The H-Coal Blend-HDT/H (No. 935) was intended to substantially meet the properties for a No. 2 fuel oil listed in ASTM D 396-80 Standard Specification for Fuel Oil. However, its flash point of 28°C (83°F) is too low to meet the specification of 38°C (100°F) minimum for a No. 2 fuel oil, which is used for home heating in oil-fired furnaces. The H-Coal Blend-HDT/H (No. 935) was devolatilized at ORNL using a Kontes-Martin MK IVB Fractionator (H. S. Martin, Inc., Vineland, New Jersey) equipped with a 30-plate, 25 mm ID Oldershaw column. Figure 2.2 shows the equipment set up in a California fume hood. This is a 4-l capacity, bench-scale apparatus which is much more relevant to industrial distillation than the usual laboratory-scale still. As indicated in Table 2.3, eight distillation cuts of 14°C (25°F) boiling range were distilled from 3.2 kg of the blend. The residue (distillate fraction no. 9) was found to have a flash point of 63°C (146°F), which met

TABLE 2.2

SUMMARY OF HYDROTREATING CONDITIONS FOR H-COAL BLEND<sup>a</sup>

Parameter	Severity of Conditions		
	"Low"	"Medium"	"High"
Catalyst	ICR 106	ICR 106	ICR 106
Average Catalyst Temp., °C (°F)	338 (640)	377 (710)	402 (755)
Total Pressure, psig	2,500	2,500	2,500
H <sub>2</sub> Partial Pressure, psia	2,300	2,300	2,300
LHSV, Vol. Feed/Vol. Catalyst/Hr.	1.0	1.0	0.5
Recycle Gas Rate, SCF/Bbl	15,000	15,000	15,000
Approx. H <sub>2</sub> Consumption, SCF/Bbl	900	1,400	3,000

<sup>a</sup>Data from Sullivan (1983)

TABLE 2.2

SUMMARY OF HYDRATE TREATING CONDITIONS FOR H-COAL BLENDS

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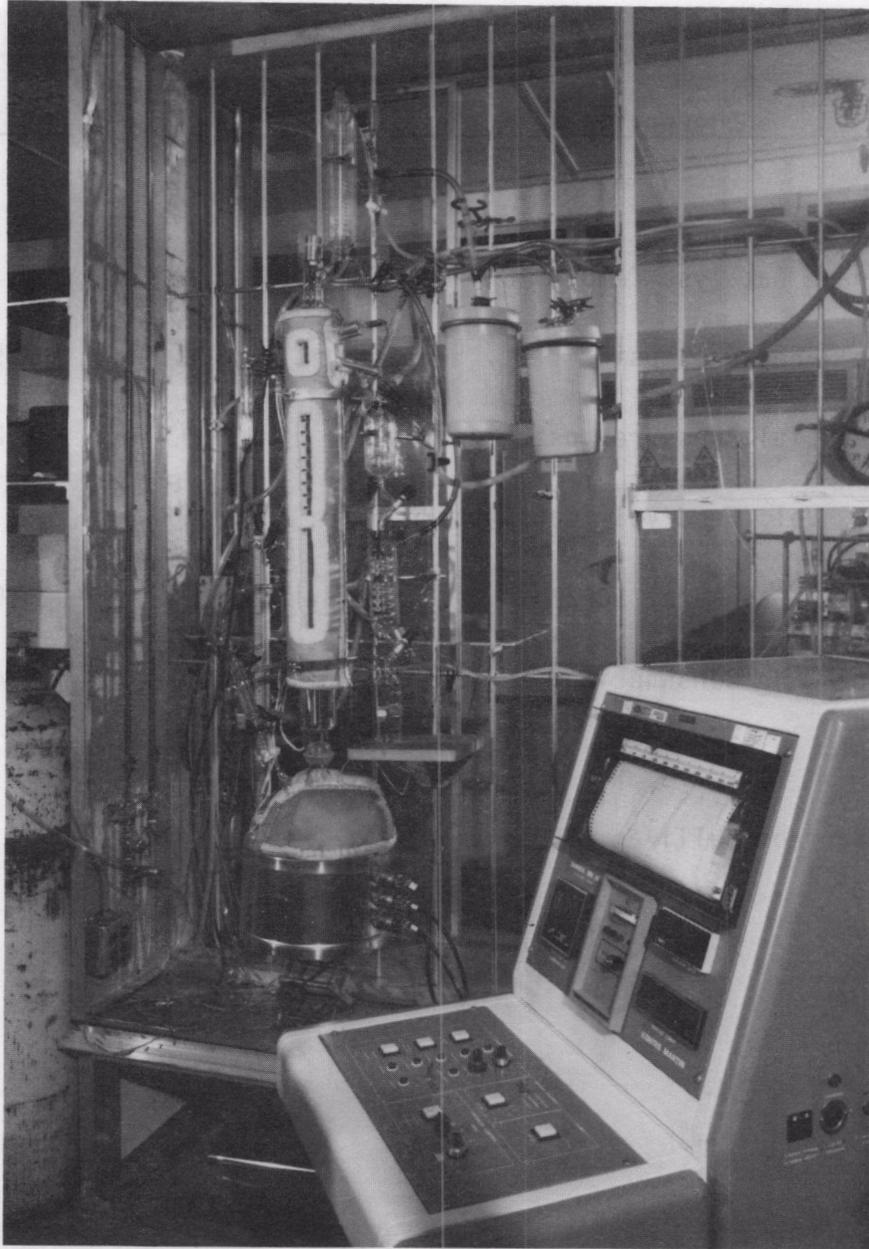


Figure 2.2. Kontes-Martin MK IVB Fractionator Used to Distill Coal Liquids.

TABLE 2.3

DISTILLATION OF VOLATILES FROM H-COAL BLEND-HDT/H (No. 935) TO INCREASE  
FLASH POINT TO MEET ASTM D396-80 SPECIFICATION FOR FUEL OILS

<u>Distillate Fraction</u>	<u>Distillation Range, °C (°F)</u>	<u>Wt. % of Sample</u>	<u>Flash Point of Sample With Fractions Re-Added, °C (°F)</u>
1	42-56 (108-133)	0.068	
2	56-70 (133-158)	0.056	
3	70-84 (158-183)	0.16	
4	84-98 (183-208)	0.61	
5	98-112 (208-234)	1.45	37 <sup>a</sup> (99) <sup>a</sup> 40 <sup>b</sup> (104) <sup>b</sup>
6	112-126 (234-259)	2.14	41 (105)
7	126-140 (259-284)	2.47	
8	140-149 (284-300)	1.45	49 (120)
9	>149 (>300)	91.6	63 (146)
-	Original sample	(100)	28 (83)

<sup>a</sup>After addition of one-third of Fraction 5 to residue.

<sup>b</sup>After addition of one-third of Fraction 5 to residue, then devolatilization by bubbling air through sample for 15 min.

the specification but was too high to be typical for a home heating oil. Distillate fractions nos. 7, 6, and one-third of no. 5 were sequentially recombined with the residue to produce a sample with a flash point of 37°C (99°F), or just below the specification. Air was then gently bubbled through the sample to remove the most volatile components and raise the flash point to 40°C (104°F). In all, only ca. 0.7 wt % of the H-Coal Blend-HDT/H (No. 935) was removed in the distillation/devolatilization. The product is designated as H-Coal Home Heating Oil (No. 978).

A reformed naphtha product also was refined from the H-Coal Blend-AWW (No. 931). Chevron conducted two sequential hydrogenations on the blend, as summarized in Table 2.4. The first stage conditions were almost identical to those used in the high severity hydrotreatment for the H-Coal Blend-HDT/H (No. 935); thus, that sample might be considered as a precursor to the reformed naphtha. The naphtha resulting from the second stage hydrocracking was shipped by Chevron to the Universal Oil Products, Inc. (UOP, now Signal Research Center, Inc., Des Plaines, Illinois) for catalytic reforming. The exact conditions are proprietary, but the processing was conducted in a UOP pilot plant utilizing a UOP commercial Platforming® catalyst under conditions "typical of a high pressure, catalytic reforming operation. The high gas-to-oil ratio was chosen to ensure stable operation during the run" (Lambert, 1985). A target octane of 96 was met (actual 96.1-96.9). The resulting product is designated as H-Coal Reformed Naphtha (No. 936). Properties and compositional data for the products are listed in Appendix A.

Three other H-Coal Heavy Oil samples were used in the laboratory-scale studies. All of these heavy oils were collected at the H-Coal pilot plant during run no. 8 on Illinois No. 6 coal on the following dates: No. 695 - September 24, 1981, No. 888-October 29, 1981, and No. 1334 - October 30, 1981.

## 2.2 Comparative Petroleum Products

Petroleum-derived finished products were used in comparative studies alongside the coal-derived products. The main set of these samples was obtained from the American Petroleum Institute (API), Washington, DC. The

Table 2.4

SUMMARY OF CONDITIONS FOR PREPARATION OF  
HYDROCRACKED NAPHTHA FOR CATALYTIC REFORMING<sup>a</sup>

	<u>First Stage</u>	<u>Second Stage</u>
Run Conditions		
Average Catalyst Temperature, °C (°F)	406 (762)	313 (595)
Total Pressure, psig	2,500	1,400
H <sub>2</sub> Partial Pressure, psia (Approx.)	2,275	1,225
LHSV, Vol Feed/Vol Catalyst/Hr	0.5	1.1
Recycle Gas Rate, SCF/BBL	15,000	5,600
Mode of Operation	Once Through	Extinction Recycle
Recycle Cut Point, °C (°F)	-	177 (350)
Per Pass Conversion	-	60

<sup>a</sup>Data from Sullivan (1983).

API supplied two fuels, a no. 2 fuel oil composed of 70% straight run middle distillate (straight run diesel) and 30% light catalytic cracked distillate (FC light cycle gas oil), and a light catalytic cracked naphtha. These samples were assigned numbers 975 and 976, respectively. Other details of their origin and processing are available from the API. Properties of these products are listed in Appendix A.

### 2.3 SRC-II Materials Origin and Processing History

A suite of crude and upgraded materials derived from the SRC-II process also was included in this study. SRC-II Middle and Heavy Distillates were collected in the period of April 4-6, 1980, at the Ft. Lewis, Washington, Solvent Refined Coal Plant by the Pittsburgh and Midway Coal Mining Company. The plant was operating on Powhatan No. 6 coal (Pittsburgh seam) in the SRC-II mode. The distillates were shipped directly to Chevron.

The blending and upgrading operations for this suite also were conducted by Chevron. As indicated in Figure 2.3, the SRC-II Middle and Heavy Distillates were separately water-washed and then blended in a 63/37 (1.7/1) wt./wt. ratio to form the SRC-II Blend-AWW (No. 916). The SRC-II Blend BWW (No. 915) was not directly water-washed because its density was too close to that of water and severe emulsion formation was anticipated. The SRC-II Middle Distillate was washed twice with equal volumes of water each time. Some problems with emulsions were experienced in water-washing the SRC-II Heavy Distillate, and 50 ml of Oronite (a nonionic surfactant) were added to aid in breaking the emulsion. A second water-washing was not performed. These washings reduced the chlorine content of the SRC-II Blend from 205 to 50 ppm (Sullivan, 1981).

The SRC-II Blend-AWW (No. 916) was hydrotreated at three levels of severity, as summarized in Table 2.5, to yield products with ca. 5,000, 2,000, and 500 ppm total nitrogen. These products are designated as SRC-II Blend-HDT/L (No. 917), SRC-II Blend-HDT/M (No. 918), and SRC-II Blend-HDT/H (No. 919), respectively. The severity was adjusted by varying the liquid hourly space velocity through the reactor from 2.5 to 0.7. The catalyst for the low severity hydrotreatment (ICR 113) was different from that used for the medium and high severity treatments (ICR 106). In general, the

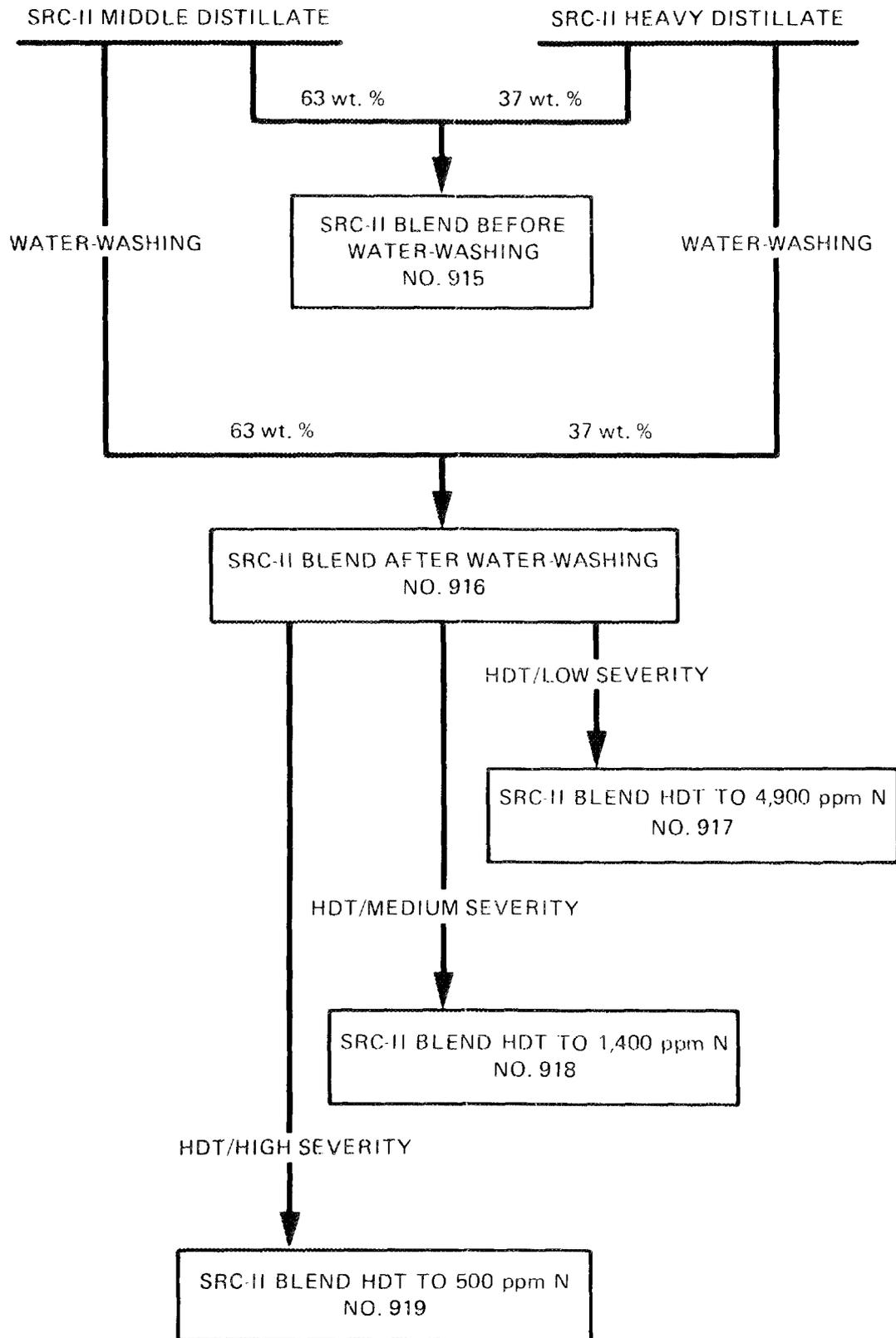


Figure 2.3. Diagram of SRC-II Blend Upgrading and Relationship of Samples.

TABLE 2.5

SUMMARY OF HYDROTREATING CONDITIONS FOR SRC-II BLEND<sup>a</sup>

Parameter	Severity of Conditions		
	"Low"	"Medium"	"High"
Catalyst	ICR 113	ICR 106	ICR 106
Average Catalyst Temp., °C (°F)	399 (750)	398 (748)	399 (750)
Total Pressure, psig	2,500	2,500	2,500
H <sub>2</sub> Partial Pressure, psia	2,250	2,250	2,250
LHSV, Vol. Feed/Vol. Catalyst/Hr.	2.5	1.0	0.7
Recycle Gas Rate, SCF/Bbl	15,000	15,000	15,000
Approx. H <sub>2</sub> Consumption, SCF/Bbl	975	1,450	1,850

<sup>a</sup>Data from Sullivan (1981)

conditions for the medium and high severity hydrotreatments of the SRC-II suite were very similar to those used for the corresponding H-Coal suite samples. The degree of hydrogen incorporation was similar in the two suites for the low and medium hydrotreatment severity, but quite different at the high severity: 1,850 SCF/BBL for the SRC-II Blend-HDT/H (No. 919) versus 3,000 SCF/BBL for the H-Coal Blend-HDT/H (No. 935). The properties of the products are listed in Appendix A, and are discussed below.

Table 2.6 lists the other samples used in this study. Included are crude and hydrogenated products from the H-Coal process demonstration unit (PDU), the Exxon Coal Liquefaction Plant (ECLP), and several additional petroleum-derived finished products.

#### 2.4 Influence of Hydrogenation on Bulk Composition and Properties

Hydrogenation is conducted in petroleum refining to reduce the heteroatom content of high sulfur crude oils, to minimize catalyst poisoning and generally improve the suitability of the oils for further refining into useable finished products. The application of hydrotreatment to crude coal liquids likewise is accompanied by a decrease in heteroatom content, and an increase in hydrogen content, as shown in Table 2.7. A 50 percent decrease in the nitrogen content of the H-Coal Blend-AWW (No. 931) (this was the specification for the production of its low severity hydrotreated product, No. 934) required ca. 900 SCF/BBL of hydrogen incorporation. It may be significant to note that very similar levels of hydrogen incorporation, 975 and 920 SCF/BBL, were required for similar reductions of total nitrogen in the SRC-II Blend-AWW (No. 916) and in the H-Coal Distillate (No. 1601). However, these two starting materials contain 69% more and 29% less (respectively) total nitrogen than does the H-Coal Blend-AWW (No. 931), and conceptually, more and less hydrogen (respectively) should be required. However, further reductions of nitrogen content require different levels of hydrogen incorporation for the three sample sets. To reduce the total nitrogen level of the H-Coal Blend-AWW (No. 931) to < 0.1 ppm, 3,000 SCF/BBL of hydrogen was required. This is a greater incorporation of hydrogen than achieved in any other study which included tumorigenicity measurements of the upgraded fuel.

TABLE 2.6

## DESCRIPTION OF OTHER SAMPLES INCLUDED IN STUDY

Sample	Origin	Source
-- Coal-Derived Liquids --		
H-Coal Distillate - Raw (No. 1601)	Produced at H-Coal PDU Hydrotreated by Mobil Under EPRI contract	Mobil Research and Development Corporation, Paulsboro, NJ
H-Coal Distillate - HDT/L (No. 1602)		
H-Coal Distillate - HDT/M (No. 1603)		
H-Coal Distillate - HDT/H (No. 1604)		
EDS Spent Solvent (No. 1658)	Produced at EDS ECLP. Texas Lignite processed in Bottoms and VGO Recycle Mode on 8/17/82	Exxon Research and Engineering Company, Baytown, TX
EDS Recycle Solvent (No. 1659)		
Vacuum Still Overheads (No. 1314)	H-Coal PDU Run No. 7, Fuel Oil Mode, III. No. 6 Coal, 9/78	Hydrocarbon Research Inc. Lawrenceville, NJ
Vacuum Still Overheads (No. 1310)	H-Coal PDU Run No. 5, Syncrude Mode, III. No. 6 Coal, 11/77	
Atmospheric Still Bottoms (No. 1313)	H-Coal PDU Run No. 7, Fuel Oil Mode, III. No. 6 Coal, 9/78	
Atmospheric Still Bottoms (No. 1309)	H-Coal PDU Run No. 5, Syncrude Mode, III. No. 6 Coal, 11/77	
Atmospheric Still Overheads (No. 1312)	H-Coal PDU Run No. 7, Fuel Oil Mode, III. No. 6 Coal, 9/78	
Atmospheric Still Overheads (No. 1308)	H-Coal PDU Run No. 5, Syncrude Mode, III. No. 6 Coal, 11/77	
-- Petroleum-Derived Liquids --		
UOP Reformed Light Arabian Naphtha (No. 973)	Purchased in Knoxville, TN area	Universal Oil Products, Inc. Des Plaines, IL Commercial purchase Commercial purchase
UOP Hydrocracked Light Arabian Vacuum Gas Oil (No. 974)		
Petroleum Home Heating Oil (No. 984)		
Unleaded Gasoline (No. 977)		

Table 2.7

## INFLUENCE OF HYDROTREATMENT ON THE ULTIMATE COMPOSITION OF CRUDE COAL LIQUIDS

Sample Number	Description	Hydrotreatment Conditions <sup>a</sup>				Ultimate Composition				
		Temp., °C(°F)	H <sub>2</sub> , psia	LHSV <sup>b</sup>	H <sub>2</sub> Cnsptn. <sup>c</sup> , SCF/BBL	C, %	H, %	N, ppm	S, ppm	O, %
931	H-Coal Blend - AWW	-	-	-	-	88.67	10.12	5,200	1,100	0.58
934	H-Coal Blend - HDT/L	338(640)	2,300	1.0	900	88.16	11.19	2,600	<10	0.39
933	H-Coal Blend - HDT/M	377(710)	2,300	1.0	1,400	88.81	11.64	500	<10	<0.01
935	H-Coal Blend - HDT/H	402(755)	2,300	0.5	3,000	87.77	13.53	<100	<10	<0.01
936	H-Coal Blend - HDT/2X + Cat. Ref.	406(762) 313(595)	2,725 1,225	0.5 1.1	NA	87.5	12.2	<100	<1	0.3
916	SRC-II Blend - AWW	-	-	-	-	85.36	8.74	8,800	2,600	4.76
917	SRC-II Blend - HDT/L	399(750)	2,250	2.5	975	86.74	9.90	4,900	83	2.86
918	SRC-II Blend - HDT/M	398(748)	2,250	1.0	1,450	87.87	10.78	1,400	26	1.21
919	SRC-II Blend - HDT/H	399(750)	2,250	0.7	1,850	88.25	11.46	500	<10	0.24
1601	H-Coal Distillate Raw	-	-	-	-	88.75	9.84	3,700	990	0.94
1602	H-Coal Distillate - HDT/L	357(675)	2,500	4.0	ca. 240 <sup>d</sup>	88.67	10.52	2,600	770	0.47
1603	H-Coal Distillate - HDT/M	357(675)	2,500	2.0	ca. 920 <sup>d</sup>	89.08	10.54	1,800	440	0.16
1604	H-Coal Distillate - HDT/H	385(725)	2,500	2.0	ca. 1,000 <sup>d</sup>	88.40	11.17	600	400	0.33

<sup>a</sup>Data from Sullivan (1981 and 1983).

<sup>b</sup>Liquid Hourly Space Velocity - vol. feed/vol. catalyst/hr.

<sup>c</sup>Hydrogen consumption

<sup>d</sup>Estimated in Maruhnich et al. (1982).

The oxygen content appears to be the most difficult to reduce while the sulfur content is most readily reduced. The latter dropped by > 99% vs the 50% for nitrogen and 33% for oxygen in H-Coal Blend HDT/L (No. 934). Hydrogen content increases steadily with increasing hydrogenation severity but by two or three % to a total of 11 to 13%. The catalytic reforming step performed on the H-Coal Naphtha has decreased the total hydrogen content slightly, as expected from the formation of aromatic compounds in this operation.

Increasing severity of hydrogenation also is accompanied by regular changes in the physical properties of the samples. The results listed in Table 2.8 demonstrate that increases in the severity of hydrogenation result in decreases in density and viscosity, and in a lowering of the boiling range and flash point of the sample. In general, density decreases by five to 10%, viscosity drops by six to 73% and the initial boiling point diminishes by 30 to 100°C (54 to 180°F) as polar, heteroatomic functional groups are removed, aromatic rings are cracked, and as the degree of saturation increases. The final and average boiling points do not change as drastically as do the initial boiling points, suggesting a resistance of the higher-boiling material to hydrogenation and cracking. The influence of hydrogenation upon pour point is not clear. However, this property is difficult to measure precisely, and the results may reflect the lack of precision in the determination.

The H-Coal Home Heating Oil (No. 978) was processed to represent a coal-derived oil suitable for home-heating in oil-fired furnaces. An equivalent petroleum product, the API No. 2 Fuel Oil (No. 975), was provided by the American Petroleum Institute for direct comparison. ASTM specifications for a No. 2 Fuel Oil (included in D 396-80) are compared with the measured properties of these two oils in Table 2.9. Both samples meet these specifications, with the possible exception of the temperature at the 90% distillation point for the H-Coal Home Heating Oil (No. 978). The datum shown for this sample was determined using simulated distillation, instead of true distillation, but for highly refined samples such as this, the two procedures generally yield equivalent results. The H-Coal Home Heating Oil (No. 978) is slightly lighter in nature than is the API No. 2 Fuel Oil (No. 975), and exhibits a lower flash point and pour point.

Table 2.8

## INFLUENCE OF HYDROTREATMENT ON PHYSICAL PROPERTIES OF CRUDE COAL LIQUIDS

Sample Number	Description	Density g/cm <sup>3</sup> @ 25°C	Viscosity, cSt @ 25°C	Boiling Range, °C (°F)			Flash Point °C (°F)	Pour Point °C (°F)
				IBP	ABP	FBP		
931	H-Coal Blend - AWW	0.968	7.05	193(379)	260(500)	396(745)	96(205)	-25(-13)
934	H-Coal Blend - HDT/L	0.934	4.82	125(257)	256(493)	388(730)	66(151)	-18(0.4)
933	H-Coal Blend - HDT/M	0.916	3.74	107(225)	249(480)	387(729)	48(118)	-25(-13)
935	H-Coal Blend - HDT/H	0.867	2.68	84(183)	241(466)	363(685)	-40(-40)	-28(-18)
936	H-Coal Blend - HDT/2X + Cat. Ref.	0.781	0.60	78(172)	102(216)	198(389) <sup>a</sup>	<-10(14)	<-30(<-22)
916	SRC-II Blend - AWW	0.989	9.39	147(297)	243(469)	401(754)	88(190)	-39(-38)
917	SRC-II Blend - HDT/L	0.942	4.93	76(169)	241(466)	385(725)	35(95)	-45(-49)
918	SRC-II Blend - HDT/M	0.913	2.76	75(167)	228(442)	375(707)	25(77)	-40(-40)
919	SRC-II Blend - HDT/H	0.901	2.54	75(167)	225(437)	373(703)	24(75)	-27(-17)
1601	H-Coal Distillate Raw	0.956	3.89	107(225)	190(374)	338(640)	-	-
1602	H-Coal Distillate - HDT/L	0.926	2.97	75(167)	187(369)	331(628)	-	-
1603	H-Coal Distillate - HDT/M	0.921	2.73	74(165)	181(358)	323(613)	-	-
1604	H-Coal Distillate - HDT/H	0.908	2.56	74(165)	183(361)	321(610)	-	-

<sup>a</sup>Data point from Lambert (1982).

Table 2.9

COMPARISON OF PROPERTIES OF H-COAL HOME HEATING OIL (NO. 978) AND API NO. 2 FUEL OIL (NO. 975) WITH ASTM D396-80 STANDARD SPECIFICATION FOR FUEL OILS

<u>Parameter, unit</u>	<u>Specification for No. 2 Fuel Oil</u>	<u>H-Coal Home Heating Oil (No. 978)</u>	<u>API No. 2 Fuel Oil (No. 975)</u>
Flash Point, °C (°F)	38 (100) Min.	40 (104)	65 (149)
Pour Point, °C (°F)	-6 (20) Max.	-33 (-27)	-17 (1.4)
Distillation Temperature at 90% Point, °C (°F)	282 (540) Min. 338 (640) Max.	254 (490) <sup>b</sup>	299 (570) <sup>a</sup>
Kinematic Viscosity at 40°C (104°F), cSt	1.9 Min. 3.4 Max.	2.19	2.16 <sup>a</sup>
Specific Gravity at 60/60°F (°API)	0.8767 Max. (30 min.)	0.8756 (30)	0.835 <sup>a</sup> (38) <sup>a</sup>
Sulfur, %	0.5 Max.	<0.001 <sup>c</sup>	0.03

<sup>a</sup>Data provided by the API.

<sup>b</sup>Estimated using simulated distillation.

<sup>c</sup>Data for H-Coal Blend-HDT/H (No. 935).

Table 2.10 compares the bulk physical and chemical properties of the coal- and petroleum-derived finished products. The H-Coal Home Heating Oil (No. 978) is seen to have a slightly lower boiling range than does the API No. 2 Fuel Oil (No. 975), consistent with the results presented in Table 2.9. Other properties, including the distribution of aromatics and saturates (as determined by the fluorescent indicator assay, FIA) are quite similar.

The bulk organic composition of the two fuel oils are compared by capillary column gas chromatography (GC) in Figure 2.4. The nature of these differences is listed in detail in Appendix Tables A.8 and A.13, and will be discussed in Section 4. Experience has indicated that the fuel can be quantitatively accounted for using GC. The main conclusion of importance here is that the bulk organic matrix of these two fuel oils is quite different, even though they are very similar in bulk physical properties and gross compositional parameters. This point illustrates that specifications based upon end use and engineering performance do not necessarily have a relationship to organic composition when comparing fuels refined from different fossil sources.

The sample matrix of the petroleum-derived API No. 2 Fuel Oil (No. 975) appears for all practical purposes to consist of a No. 2 diesel fuel. Figure 2.5 compares the high resolution capillary column GC profiles of this sample with both Phillips Reference No. 2 Diesel Fuel (No. 1910) and a locally-purchased home heating oil (No. 984). All three are remarkably similar in composition, considering the diversity in sources. The differences among the samples are mainly quantitative, not qualitative.

A reason for this similarity of composition of the fuels refined from petroleum is suggested by the comparison of ASTM Specifications for No. 2 Fuel Oil (D 396-80) and No. 2 Diesel Fuel (957-81) listed in Table 2.11. It is seen that a fuel meeting the specifications for a No. 2 diesel fuel also could meet those for a No. 2 fuel oil if its viscosity is not at the upper limit allowed for the No. 2 diesel fuel, and if its specific gravity is low enough. The reverse is true if the fuel oil does not have a flash point at the minimum allowed for the No. 2 fuel oil, and its cetane number is high enough.

TABLE 2.10

## COMPARISON OF PHYSICAL AND BULK CHEMICAL PROPERTIES OF PETROLEUM AND COAL-DERIVED FINISHED PRODUCTS

Parameter	Naphtha		Home Heating Oil		
	H-Coal (No. 936)	API, Petroleum (No. 976)	H-Coal (No. 935)	H-Coal (No. 978)	API, Fuel Oil (No. 975)
<b>-Ultimate Analysis-</b>					
C%	87.5	85.2	87.77	-	85.9
H%	12.2	13.8	13.53	-	13.6
N%	<0.01	0.03	<0.01	-	0.02
S%	<0.001	0.01	<0.001	-	0.03
Pour Point, °C (°F)	<-30 (-22)	<-40 (-40)	-40 (-40)	-33 (-27)	-17 (1.4)
Flash Point, °C (°F)	<-10 (14)	<-35 (-31)	28 (82)	40 (104)	65 (149)
Density, g/cc at 25°C	0.781	0.730	0.867	0.876 (@ 16°C)	0.827
Viscosity, cSt at 25°C	0.60	0.57	2.68	2.2 (@ 38°C)	3.13
Specific Gravity, °API	50	60	30	30.0	38.0
<b>-ASTM Simulated Dist.-</b>					
IBP, °C (°F)	78 (172)	148 (298)	84 (183)	156 (313)	180 (356)
ABP, °C (°F)	102 (216)	154 (309)	241 (466)	234 (453)	261 (502)
FBP, °C (°F)	198 (389) <sup>a</sup>	197 (387)	363 (685)	333 (631)	351 (664)
<b>-FIA Analysis<sup>a</sup>-</b>					
Aromatic, Vol. %	58.4	20.3	18.5	-	21.0
Olefin, Vol. %	0.9	29.6	-	-	7.0
Saturated, Vol. %	40.7	50.0	81.4	-	72.0

<sup>a</sup>Data supplied by Chevron, the American Petroleum Institute, and UOP, Inc.

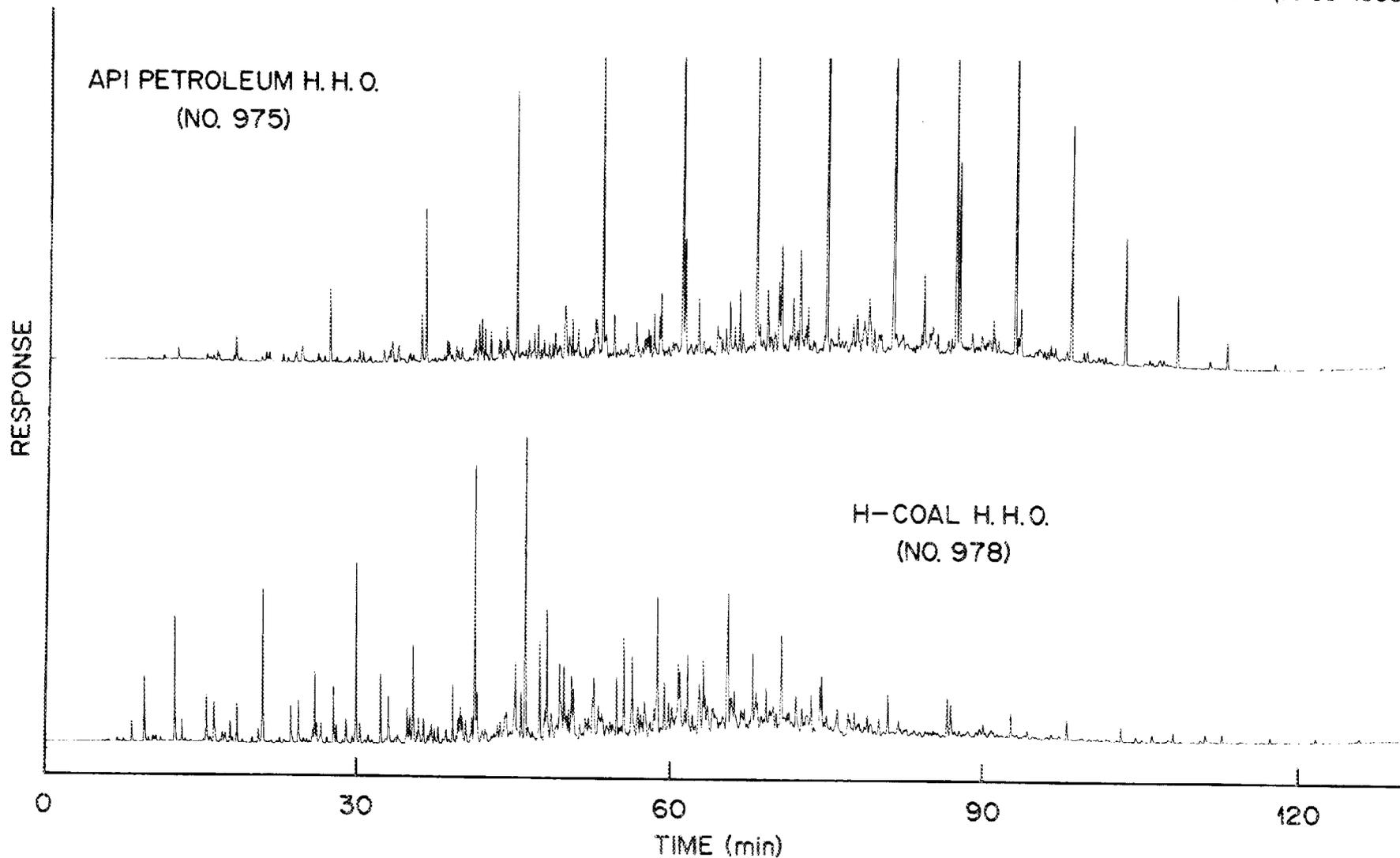


Figure 2.4. Comparison of Major Organic Compound Composition of API No. 2 Fuel Oil (No. 975) and H-Coal Home Heating Oil (No. 978).

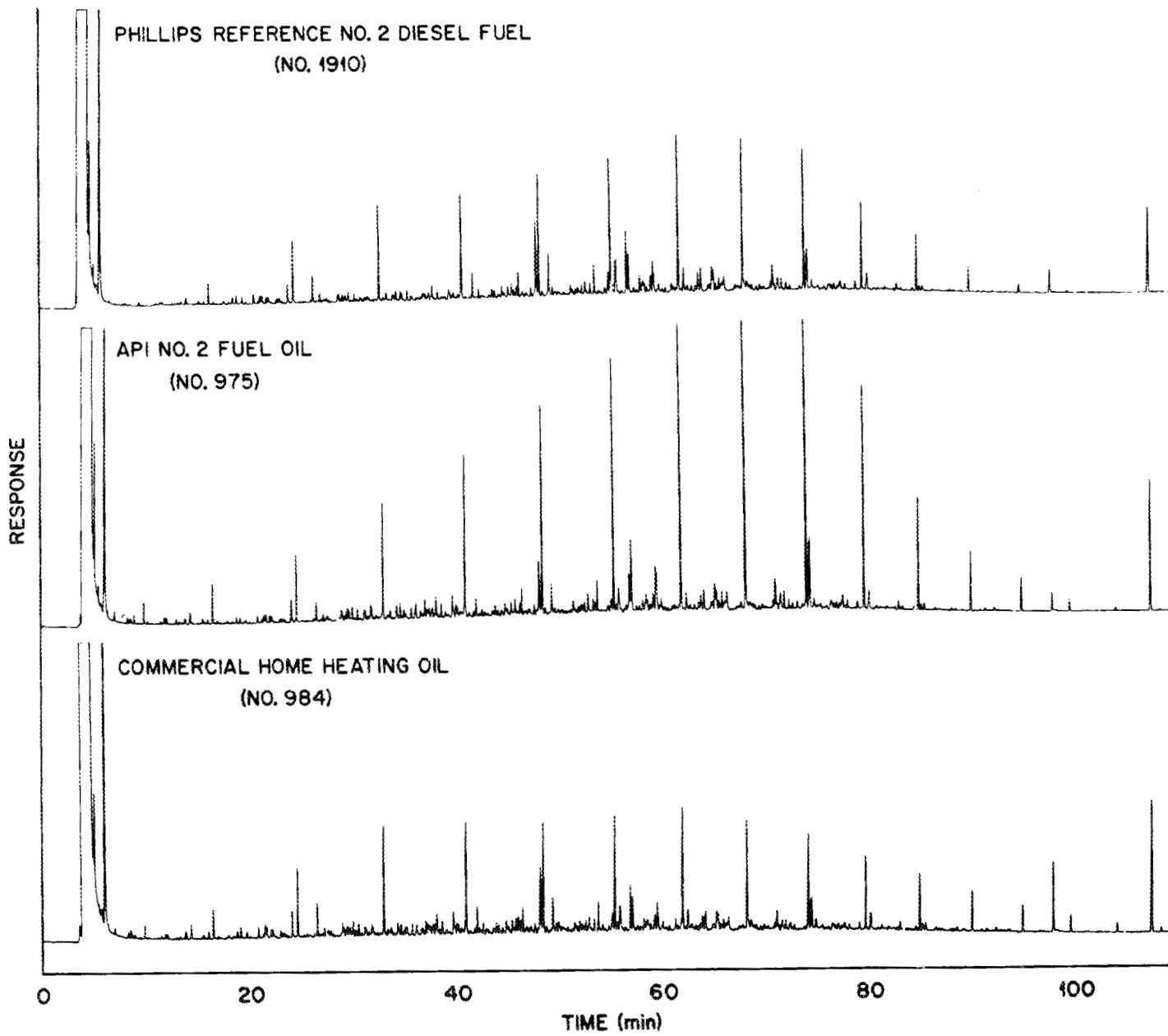


Figure 2.5. Comparison of Major Organic Compounds in API No. 2 Fuel Oil with Phillips Reference No. 2 Diesel Fuel and A Commercial Home Heating Oil (No. 984).

TABLE 2.11

COMPARISON OF ASTM SPECIFICATIONS FOR NO. 2 FUEL OIL  
AND NO. 2 DIESEL FUEL

Parameter, Units	Min. or Max.	Requirement	
		No. 2 Fuel Oil ASTM 396-80	No. 2 Diesel Fuel ASTM 957-81
Flash Point, °C (°F)	Min	38(100)	52(125)
Pour Point, °C (°F)	Max	-21 (-6)	-
Water & Sediment, Vol %	Max	0.05	0.05
C residue on 10% bottoms, %	Max	0.35	0.35
Ash, wt. %	Max	-	0.01
Distillation Temp. @ 90% Point, °C (°F)	Min	282(540)	282(540)
	Max	338(640)	338(640)
Seybolt Viscosity, SUS @ 100°F	Min	32.6	32.6
	Max	37.9	40.1
Kinematic Viscosity, cSt @ 104°F	Min	1.9	1.9
	Max	3.4	4.1
Sulfur, wt. %	Max	0.5	0.5
Specific Gravity @ 60°/60°F	Max	0.8762	-
Cu Strip Corrosion	Max	No. 3	No. 3
Cetane No.	Min	-	40

Physical and gross compositional parameters of the coal- and petroleum-derived naphthas are compared in Table 2.10. Some differences in properties are evident, such as the greater specific gravity and lower boiling range of the H-Coal Reformed Naphtha (No. 936) than for the API Light Catalytically Cracked Naphtha (No. 976). The former also is considerably more aromatic than the latter. This difference is at least partly mirrored in their capillary column GC profiles, shown in Figure 2.6. The two fuels are much more alike than are the fuel oils, but they also exhibit some compositional differences (see Appendix Tables A.6 and A.10). These will be explored in more detail in Section 4.

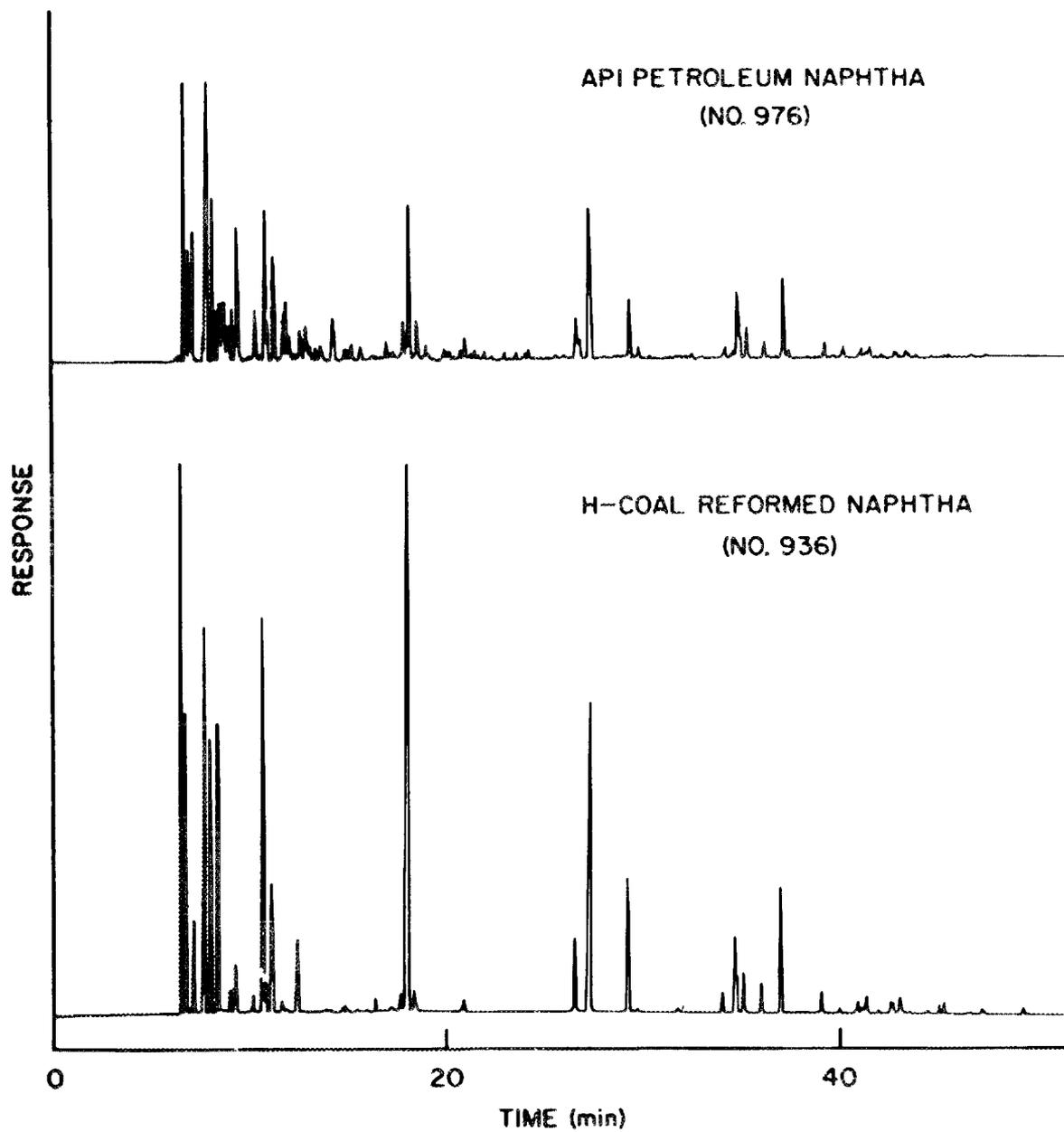


Figure 2.6. Comparison of Major Organic Compounds in API Light Catalytically Cracked Naphtha (No. 976) and H-Coal Reformed Naphtha (No. 936).



### 3.0 Comparative Tumorigenicity

The tumorigenicities of the primary samples examined in this program have been determined using a lifetime mouse skin painting study. This includes a blend of light oil and heavy oil produced at the Catlettsburg, Kentucky H-Coal Pilot Plant, four refined oils produced from the blend, and two petroleum-derived nominally equivalent products. Laboratory studies of hydrogenation and of alternative or supplemental treatments for reducing tumorigenicity have relied upon less costly biological measures and chemical measures of potential tumorigenicity. These include *Salmonella* mutagenicity, ten-animal mouse dermal testing, and measures of benzo(a)pyrene.

Results of the lifetime testing are presented here in terms of gross cumulative tumor incidence and, for some samples, in terms of median time to tumor. Histological classification of the tumors, biostatistical evaluation of the data, and miscellaneous observations related to systemic toxicity are beyond the scope of this report. Sufficient data are presented to illustrate trends and to allow independent evaluation of the conclusions.

#### 3.1 Experimental Conditions

The origin and properties of the oils tested are described in detail in Section 2 of this report. Oils subjected to long-term testing were (a) a water washed H-Coal Light Oil/Heavy Oil Blend (Sample No. 931), (b) a low severity hydrotreated product (Sample No. 934) of the blend, (c) a high severity hydrotreated product (Sample No. 935) of the blend, (d) a home heating oil (Sample No. 978) produced by laboratory devolatilization of the high severity hydrotreated oil, (e) a naphtha reformat (Sample No. 936) produced by a second stage hydrogenation and catalytically reforming the high severity hydrotreated product, (f) a petroleum-derived cracked naphtha (Sample No. 976), and (g) a petroleum-derived number 2 fuel oil (Sample No. 975). Laboratory studies of hydrogenation and alternative treatments were supported by 10-animal skin tumor screening. Two heavy oils (Sample No. 888 and 1334) produced at the Catlettsburg Kentucky H-Coal pilot plant, vacuum gas oil (>650°F/343°C boiling range) cuts of the heavy oils, and the H-Coal blend (No. 931) studied in the lifetime assay were tested using the 10-animal procedure. A middle distillate (<650°F/343°C) of Heavy Oil No. 888 was also tested.

For the lifetime study, groups of 25 female and 25 male inbred Specific Pathogen Free C3Hf/Bd mice were assigned to test groups at 10-11 weeks of age. The animals were maintained five per cage. Each material was tested at three doses [100% (neat) oil, 50% oil, and 25% oil] by applying 50 microliters of the material to the shaved backs of the mice three times per week. Acetone was used as the diluent to prepare the 50% and 25% test dosage. Skin painting continued for each surviving animal until it was found dead. Animals exhibiting a tumor remained on test for two weeks after tumor appearance and were then sacrificed to acquire tissue for histopathology. All major organs were also taken for later examination. Body weight, water consumption, and evidence of dermatitis were monitored throughout the experiment.

Experimental controls for the lifetime study included three groups of 25 female and 25 male mice (for a total of 75 female and 75 male mice) each exposed to benzo(a)pyrene in acetone at concentrations of 0.1%, 0.05%, and 0.025% benzo(a)pyrene. Multiple positive control groups were required because various groups of oils were placed on test at different times. In addition, 50 female and 50 male mice were exposed to acetone using the same regimen as used for the test oils to provide a vehicle control. A total of 100 male and 92 female animals served as untreated room controls.

For the 10-animal screening, groups of five female and five male C3Hf/Bd were painted two times per week with the neat (100%) oil and/or a 50% suspension of the oil in acetone again using 50 ul applications. Highly viscous samples such as some vacuum gas oils and some products of chemical treatment could not be tested neat. The animals remained on test for up to 11 months depending on the study or until tumors were observed. The animals remained alive for two weeks following tumor appearance and were then sacrificed. Time to tumor appearance was the only data taken.

### 3.2 Observations and Data from the Lifetime Study

The lifetime skin painting test protocol used here was initially designed as an 18-month study to compare with earlier work by Holland et al. (Holland et al. 1979, 1981, 1984) on other hydrotreated coal and shale oils. The test was extended (to lifetime) when it was observed that many of the oils were likely to exhibit very low tumorigenicity and that the previous

work by Holland indicated the first appearance of tumors for some related samples to occur at approximately 50 weeks. Practices common to true "lifetime" studies such as replacing animals dying early in the study, weekend surveillance to acquire tissue of unexpected deceased animals for histopathology, and serial sacrifice groups were not included in this testing. Special attention must therefore be given to survival and to tumor incidence of control groups. For very weakly tumorigenic samples (those yielding tumors only very late in the testing), tumor incidence must be carefully compared to the number of animals surviving, (i.e., to mortality).

Results for the positive controls (benzo(a)pyrene), vehicle (acetone) control group, and room (untreated) control group are summarized in Table 3.1. The tumor incidence for animals treated with benzo(a)pyrene is in good agreement with that observed by Holland (in Griest et al. 1983). Animals exposed to the acetone vehicle (diluent) and those maintained in the same environment without exposure to any test agent (room controls) exhibited no skin tumors. The median lifespan of untreated C3H mice is approximately 23 months and the maximum lifespan is approximately 32 months. This is in general agreement with the mortality data (Table 3.1) for both the vehicle and room control groups. Approximately 80% of the animals on test lived to 20 months, approximately 50% to 23 months, and approximately 20% survive at 24-25 months. The test period beyond 20 months is accompanied by a rapid depletion of the number of animals available for test as they die of natural causes. The insult provided by exposure to the test oils can increase the natural mortality rate resulting in an even smaller number of animals on test for the exposure groups.

The cumulative percentage of mice with skin tumors as a function of time is summarized in Tables 3.2 and 3.3. The data in Table 3.2 compare the starting H-Coal blend with the products of hydrotreatment and catalytic reforming. Table 3.3 summarizes the results for coal-derived and petroleum-derived products of refining. The convention used is to begin with the month in which the first tumor is observed in either sex and to continue to the month in which a change in incidence is observed or when the number of animals at risk (on test) is insufficient to meaningfully influence the results. It should be noted that with a total of 25 animals of each sex on test, a cumulative incidence of 4% in either sex group corresponds to only one animal exhibiting a tumor.

Table 3.1  
EXPERIMENTAL CONTROL DATA FOR H-COAL OILS MOUSE SKIN TUMORIGENICITY STUDY

Dose (%) Study Month	Cumulative Percentage Animals with Skin Tumors <sup>a</sup>									Cumulative Percentage Mortality				Study Month		
	Benzo(a)pyrene Control <sup>b</sup>						Vehicle			Room		Vehicle			Room	
	0.1%		0.05%		0.025%		Control <sup>c</sup>			Control <sup>c</sup>		Control <sup>d</sup>			Control <sup>d</sup>	
	F	M	F	M	F	M	F	M	F	M	F	M	F		M	
1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1
2	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	2
3	1	0	3	0	0	0	0	0	0	0	0	0	0	0	0	3
4	9	1	23	0	1	3	0	0	0	0	0	0	0	0	0	4
5	83	43	67	20	16	8	0	0	0	0	0	0	0	0	0	5
6	97	91	100	67	55	21	0	0	0	0	0	0	0	0	0	6
7	97	97	100	89	89	69	0	0	0	0	0	0	0	0	0	7
8			100	97	96	93	0	0	0	0	0	0	0	0	0	8
9					97	97	0	0	0	0	0	0	0	0	0	9
10							0	0	0	0	2	0	0	0	0	10
11							0	0	0	0	2	0	0	0	0	11
12							0	0	0	0	2	0	0	0	0	12
13							0	0	0	0	2	2	0	0	0	13
14							0	0	0	0	2	2	0	0	0	14
15							0	0	0	0	2	2	0	0	0	15
16							0	0	0	0	2	4	4	4	4	16
17							0	0	0	0	4	4	4	10	4	17
18							0	0	0	0	4	10	6	10	6	18
19							0	0	0	0	8	16	10	12	10	19
20							0	0	0	0	8	22	22	16	22	20
21							0	0	0	0	36	34	36	32	36	21
22							0	0	0	0	42	38	48	44	48	22
23							0	0	0	0	50	48	62	58	62	23
24							0	0	0	0	76	62	74	58	74	24
25							0	0	0	0	88	74	82	74	82	25
26							0	0	0	0	92	76	84	78	84	26
27							0	0	0	0	94	92	96	88	96	27
28							0	0	0	0	96	98	96	96	96	28
29							0	0	0	0	98	100	100	100	100	29
30							0				98 <sup>e</sup>					30

<sup>a</sup>The last number in each column is the cumulative percentage of mice with skin tumors at the time all animals were sacrificed or had died in the study. <sup>b</sup>Combined data for total of 75 male and 75 female animals per dose group. <sup>c</sup>For 50 male and 50 female animals. <sup>d</sup>Combined data for total of 100 male and 92 female animals. <sup>e</sup>One animal is still alive at thirty months.

Table 3.2

CUMULATIVE PERCENTAGE OF MICE WITH SKIN TUMORS - HYDROTREATMENT SERIES<sup>a</sup>

Study Month	H-Coal LO/HO Blend (No. 931)						Low Severity HDT of 931 (No. 934)						High Severity HDT of 931 (No. 935)						Naphtha Reformat of 935 (No. 936)						Dose (%) Study Month
	100		50		25		100		50		25		100		50		25		100		50		25		
	F	M	F	M	F	M	F	M	F	M	F	M	F	M	F	M	F	M	F	M	F	M	F	M	
1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1
2	0	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2
3	0	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3
4	0	8	0	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	4
5	0	8	4	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	5
6	4	36	4	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	6
7	36	40	12	4	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	7
8	48	40	20	4	4	4	0	0	0	0	0	0	0	4	0	0	0	0	0	0	0	0	0	0	8
9	56	48	32	8	8	8	0	0	0	0	0	0	0	4	0	0	0	0	0	0	0	0	0	0	9
10	68	52	44	32	12	8	0	0	0	0	0	0	0	4	0	0	0	0	0	0	0	0	0	0	10
11	72	56	52	40	16	16	0	0	0	0	4	0	0	4	4	0	0	0	0	0	0	0	0	0	11
12	80	64	72	52	28	20	0	0	0	0	4	0	0	4	4	0	0	0	0	0	0	0	0	0	12
13	84	68	80	64	40	28	4	0	4	0	4	0	0	4	4	0	0	0	0	0	0	0	0	0	13
14	88	76	84	72	40	48	4	0	4	0	4	0	0	4	4	0	0	0	0	0	0	0	0	0	14
15	88	76	96	76	64	64	4	0	4	0	4	0	0	4	8	0	0	0	0	0	0	0	0	0	15
16			96	84	84	76	4	0	4	8	4	0	0	4	12	0	0	0	0	0	0	0	0	0	16
17			96	84	88	80	4	4	4	8	4	0	8	4	16	0	0	0	0	0	0	0	0	0	17
18			96		92	84	4	4	8	12	4	0	12	4	16	4	4	0	0	0	0	0	0	0	18
19					84		8	12	8	12	4	0	16	8	16	12	8	8	0	0	0	0	0	0	19
20							8	12	8	12	4	0	16	12	16	24	8	8	0	0	0	0	0	0	20
21							12	16	12	12	4	0	20	16	20	28	16	12	0	0	0	0	0	0	21
22							12	16	12	12	4	0	20	16	20	32	16	12	0	0	0	0	0	4	22
23							12	16	12	12	4	0	20	24	44	16	12	0	0	0	0	0	0	4	23
24							12		12		4	0	20	24	44	16	16	0	0	0	0	4	4	4	24
25									12		4	0		24	44		16	0	0	0	0	4	4	4	25
26											0				44			0	0	0	0	4	4	4	26
27											0							0	0	0	0	4	4	4	27
28																				0	4				28
29																					0	4			29

<sup>a</sup>The last number in each column is the cumulative percentage of mice with skin tumors at the time all animals were sacrificed or had died in the study.  
<sup>b</sup>25 female (F) plus 25 male (M) C3H mice per dose group, 3 applications per week.

Table 3.3  
 CUMULATIVE PERCENTAGE OF MICE WITH SKIN TUMORS - COAL AND PETROLEUM PRODUCTS<sup>a</sup>

Dose (%) <sup>b</sup>	H-Coal Home Heating Oil (No. 978)						Petroleum No. 2 Fuel Oil (No. 975)						Petroleum Cracked Naphtha (No. 976)						Naphtha Reformate of 935 (No. 936)						Dose (%)
	100		50		25		100		50		25		100		50		25		100		50		25		
	F	M	F	M	F	M	F	M	F	M	F	M	F	M	F	M	F	M	F	M	F	M	F	M	
Study Month																									Study Month
1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1
2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2
3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3
4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	4
5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	5
6	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	6
7	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	7
8	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	8
9	0	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	9
10	0	4	0	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	10
11	4	8	0	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	11
12	4	12	0	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	12
13	4	16	0	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	13
14	12	16	0	4	0	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	14
15	12	16	0	8	8	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	15
16	12	20	0	8	8	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	16
17	12	20	0	12	12	4	0	0	0	0	0	0	0	0	0	4	0	0	0	0	0	0	0	0	17
18	12	32	8	16	16	12	4	0	0	0	0	0	0	0	0	4	0	0	0	0	0	0	0	0	18
19	20	32	16	28	16	12	4	16	4	4	0	4	0	0	0	4	0	0	0	0	0	0	0	0	19
20	20	36	20	28	16	16	4	16	12	8	0	4	8	0	0	12	0	0	0	0	0	0	0	0	20
21	20	36	20	28	16	16	4	16	12	16	0	4	12	0	0	12	16	4	0	0	0	0	0	0	21
22	20	36	20	28	16	16	4	20	12	16	4	4	12	0	4	12	16	4	0	0	0	0	0	4	22
23		36	20	28	16	16			12	16	4	4	12	0	4	12	16	8	0	0	0	0	0	4	23
24		36	20	28	16	16			12		4	4	12	0	4	12	16	12	0	0	0	0	4	4	24
25				28		16					4	4	12	0	4	12	16	16	0	0	0	0	4	4	25
26													12	0		12	16	16	0	0	0	0	4	4	26
27													12	0		12	16		0	0	0	0	4	4	27
28													12			12			0	0	0	0	4		28
29																12					0	4			29

<sup>a</sup>The last number in each column is the cumulative percentage of mice with skin tumors at the time all animals were sacrificed or had died in the study.

<sup>b</sup>25 female (F) plus 25 male (M) C3H mice per dose group, 3 applications per week.

A generally accepted indicator that the experimental tumorigenicity observed is due to the test agent applied is that there be a clear dose-response relationship (that animals exposed to a greater quantity of the agent exhibit a greater incidence of tumors than those exposed to lesser quantities). A clear dose-response relationship is observed for the H-Coal blend (No. 931) early (e.g., 2-11 months) in the study and to a lesser extent early in the tests of several other oils. This relationship decays later in the study of the H-Coal blend (931) because the animals exhibiting tumors are sacrificed to obtain tissue for histopathology analysis. Fewer animals remain in this group to be at risk to develop tumors relative to those groups which exhibit tumors later in the study.

Many of the test groups exhibit very low levels of tumor incidence very late in the testing schedule. We currently view any incidence of tumors in any dose group as indicating potential tumorigenicity because of the complete absence of tumors in both vehicle and room control groups. This conclusion remains to be confirmed by statistical evaluation of the data.

### 3.3 Product Comparisons

Table 3.4 summarizes tumor incidence results for the 100% (neat oil) dose group of all the oils tested in the lifetime study. Median time to tumor results were calculated using the Weibull distribution (see e.g., Holland et al. 1981) corrected for non neoplastic mortality for each sex at each dose group. The largest and smallest result for each oil is given in Table 3.4.

The H-Coal light oil/heavy oil blend (931) is found clearly and significantly tumorigenic with 72% of the animals exposed to the neat oil for 12 months exhibiting tumors. The median time to tumor of 46-63 weeks is well within the normal median lifetime (approximately 98 weeks) of C3H mice. This result is very similar to that previously reported (discussed below) for a blend of middle and heavy distillate from the SRC-II process. It is also consistent with the previously reported (Munro et al. 1985) tumorigenicity of heavy oils from the H-Coal process since the blend tested consists of approximately 60% heavy oil.

Table 3.4

## COMPARATIVE MOUSE SKIN TUMORIGENICITY OF H-COAL OILS AND PETROLEUM COMPARATIVE OILS

Material	Sample Code	Percentage <sup>a</sup> Animals with Tumor After Month Number										Median Time to Tumor in Weeks <sup>b</sup>
		6	8	10	12	14	16	18	20	22	24	
H-Coal Light Oil/Heavy Oil Blend	931	20	44	60	72	82	- <sup>c</sup>	-	-	-	-	46-63
Low Severity Hydrotreated Blend 931	934	0	0	0	0	2	2	4	10	14	-	109-ND
High Severity Hydrotreated Blend 931	935	0	2	2	2	2	2	8	14	18	-	96-116
Naphtha Reformate from H-Coal 935	936	0	0	0	0	0	0	0	0	0	0	156-ND
Home Heating Oil from H-Coal 935	973	0	0	2	8	14	16	22	28	28	-	91-111
Petroleum No. 2 Fuel Oil from API	975	0	0	0	0	0	0	2	10	12	-	104-ND
Petroleum Cracked Naphtha from API	976	0	0	0	0	0	0	0	4	6	6	116-ND
Benzo(a)pyrene Positive Control <sup>d</sup>	-	84	99	-	-	-	-	-	-	-	-	19-33
Vehicle (Acetone) Control	-	0	0	0	0	0	0	0	0	0	0	ND
Room (Untreated) Control	-	0	0	0	0	0	0	0	0	0	0	ND

<sup>a</sup>Total of male plus female animals for 100% (neat oil) dose group, 25 male plus 25 female C3H mice, 3 applications per week.

<sup>b</sup>Range including all dose groups and both sexes. ND = none detected (for zero tumor incidence).

<sup>c</sup>Dash indicates all test animals dead or insufficient number remaining alive to significantly influence result.

<sup>d</sup>Pooled results from three experiments with total of 75 male plus 75 female C3H mice, 0.05% BaP in acetone, 3 applications per week.

The low severity hydrotreated (50% reduction in total nitrogen content with an approximately 900 SCF/BBL hydrogen consumption) product (No. 934) yielded no tumors until the 13th month at the 100% dose level and reached a final incidence of 14% (7 of 50 animals) at the 21st month. The high severity hydrotreated (a home heating oil product requiring approximately 3000 SCF/BBL hydrogen consumption) hydrotreated product (No. 935) exhibited a similar to slightly greater tumorigenicity than did the low severity hydrotreatment product. The relationship between the chemistry and tumorigenicities of these products is discussed in Section 4 of this report.

Results for the coal- and petroleum-derived naphtha reformates and heating oils are summarized in Tables 3.4 and 3.5. The coal-derived naphtha (No. 936) produced the lowest tumor incidence of any of the oils tested. One animal in the low dose group exhibited a skin tumor in the 22nd month of the study. The petroleum naphtha (No. 976) exhibited a slightly greater tumorigenicity with the 100% dose group containing 6% (3 of 50) animals with tumor at 21 months and the 25% dose group containing 16% (8 of 50) animals with the tumor by the 25th month. The fuels oils exhibited a similar trend except that the coal-derived oil (No. 978) is clearly tumorigenic and is more so than the petroleum-derived oil (No. 975). The coal-derived oil produced one animal with a tumor in the 9th month of the study and showed a good dose-response relationship to the end (20th month) of the test. The final tumor incidence for the coal-derived heating oil 100% dose group was 28% at 20 months while the petroleum fuel oil yielded 12% animals with tumor at the 22nd month of the study in its 100% dose group. The median time to tumor for the coal-derived heating oil (No. 978) was found similar to that of the high severity hydrotreated product (No. 935) and approximately equal to the expected median lifetime of C3H mice. Results of the lifetime study are summarized as follows:

- a) The starting blend (No. 931) of H-Coal light oil/heavy oil is clearly and significantly tumorigenic as would be predicted from the well-documented tumorigenicity of coal-derived heavy oils.
- b) Low severity hydrotreatment (in this study, a 50% reduction of total nitrogen content achieved by a hydrogen consumption of 900 standard cubic feet per barrel for the starting blend 931) reduces tumorigenicity to a level similar to that of the refined petroleum oils studied.

Table 3.5

COMPARATIVE TUMORIGENICITY<sup>a</sup> OF H-COAL AND PETROLEUM PRODUCTS

Parameter	No. 936 H-Coal Ref. Nap.		No. 976 API Lt. Cat. Cr. Nap.		No. 978 H-Coal Home Heating Oil		No. 975 API No. 2 Fuel Oil	
	F	M	F	M	F	M	F	M
Cumulative Tumor Incidence <sup>a</sup> , % Animals								
at 25% Dose	4	4	16	16	16	16	4	4
at 50% Dose	0	0	4	12	20	28	12	16
at 100% Dose	0	0	12	0	20	36	4	20

<sup>a</sup>Data for lifetime of three-times weekly application to 25 male and 25 female C3H mice per dose group/substance. Acetone solvent for 50% and 25% doses. F = female and M = male.

- c) High severity hydrotreatment (to produce a home heating oil product from 3000 SCF/BBL of hydrogen consumption) of the starting blend also greatly reduces tumorigenicity but to no greater degree than did low severity hydrotreatment. The high severity hydrotreated product may be slightly more tumorigenic than is the product of low severity hydrotreatment.
- d) Further hydrogenation and catalytic reforming of the high severity hydrotreated product (No. 935) produced a coal-derived naphtha reformat (No. 936) exhibiting the lowest (if any) tumorigenicity of the materials tested. Only two of the 150 animals on test developed a tumor and that occurred after 21 months. The petroleum cracked naphtha (No. 976) exhibited a detectable tumorigenicity and clearly greater than that produced by the coal-derived naphtha (No. 936).
- e) The coal-derived heating oil (No. 978) exhibited a clearly detectable tumorigenicity and its' tumorigenicity is greater than that exhibited by the petroleum fuel oil (No. 975). The petroleum fuel oil yields a tumorigenicity very similar to that of the petroleum catalytically cracked naphtha.

#### 3.4 Comparison with Related Materials and Tests

Results of the lifetime H-Coal study as of 12 months are compared (Table 3.6) with those of a previous (Griest et al. 1983) 50 week skin painting study of similar SRC-II coal-derived materials. Mortality (non tumor related deaths) and dermatitis (clinically observed inflammation in the region of skin painting) data are included with that for tumor incidence to further the comparison.

The heteroatom content of the starting blends and the hydrogen consumption at each level of hydrotreatment severity differ for the H-Coal and SRC-II studies making direct quantitative comparisons impossible. The trends observed, however, are in excellent agreement. The starting blends (931 and 916) are similarly tumorigenic and low severity hydrotreatment greatly diminishes tumorigenicity. Further hydrotreatment appears to further reduce tumorigenicity of the SRC-II series very slightly. It is likely that this conclusion would change if the SRC-II experiment had proceeded an additional six or twelve months.

The similarities in mortality and dermatitis observed suggest that results of the two experiments can be confidently compared and combined in studies to identify relationships among processing, chemical properties, and tumorigenicity.

Table 3.6

## COMPARATIVE SKIN TUMORIGENICITY OF HYDROTREATED H-COAL AND SRC-II OILS

H-Coal Materials	Sample Number	Dose	Cumulative Percentage Animals at 12 Months								Dose	Sample Number	SRC-II Materials
			Skin Tumors		Dermatitis	Mortality	Mortality	Dermatitis	Skin Tumors				
			F	M	F+M	F+M	F+M	F+M	F	M			
Light Oil/Heavy Oil Blend, 5700 ppm N, Water Washed	931	100	80	64	14	0	0	22	84	88	100	916	Middle Distillate/ Heavy Distillate Blend, 9800 ppm N, Water Washed
		50	72	52	8	4	0	0	28	28	50		
		25	28	20	0	2	4	0	24	16	25		
Low Severity HDT of 931, 2700 ppm N, 900 SCF H <sub>2</sub> /BBL	934	100	0	0	-	0	6	0	0	8	100	917	Low Severity HDT of 916, 5300 ppm N, 975 SCF H <sub>2</sub> /BBL
		50	0	0	-	4	6	0	8	0	50		
		25	4	0	-	2	0	0	4	0	25		
High Severity HDT of 931, 0.2 ppm N, 3000 SCF H <sub>2</sub> /BBL	935	100	0	4	0	0	2	2	0	0	100	918	Medium Severity HDT 916, 1710 ppm N, 1450 SCF H <sub>2</sub> /BBL
		50	4	0	2	6	8	0	0	0	50		
		25	0	0	0	0	0	0	0	4	25		
Catalytic Reformate of 935, 0.1 ppm N	936	100	0	0	-	0	2	0	0	0	100	919	High Severity HDT of 916, 505 ppm N, 1850 SCF H <sub>2</sub> /BBL
		50	0	0	-	0	2	0	0	0	50		
		25	0	0	-	2	2	0	0	0	25		

Bacterial mutagenicity testing and ten-animal dermal testing were carried out in other parts of this program as indicators of potential tumorigenicity. Results from these tests are compared to those from longer term (or larger animal population) testing in Table 3.7 for materials examined both ways. Bacterial mutagenicity was carried out on DMSO/oil slurries using Salmonella strain TA98 with Arochlor 1254 induced S9 activation. The ten-animal studies were carried out using five female and five male C3H mice dosed twice per week (compared to three times per week for the fifty animal per group study) with the neat (100%) oil or a 50% dilution in acetone.

In testing whole oils, mutagenicity is clearly observed only for those materials which contain heavy oil (high boiling point) components. Low severity hydrotreatment reduces mutagenicity to an undetectable level. More sophisticated approaches such as chemical class fractionation and testing of the individual fractions are required to detect residual mutagenicity. The ten-animal dermal screening method is no more sensitive, however, than is mutagenicity testing. The dermal screening method also responds only to those materials containing heavy oil components. As is shown in Section 5 of this report, the utility of the dermal screening is not its sensitivity but rather that it responds to tumorigens rather than mutagens. The data (Table 3.7) suggest that both bacterial mutagenicity and ten-animal dermal screening are able to distinguish between heavy oils, the vacuum gas oil component of heavy oils, and diluted (e.g., blends with lower boiling distillates) heavy oils. Longer term skin applications for tumorigenicity screening or more sophisticated sample preparation for mutagenicity testing is required to detect lower levels of bioactivity. As used in the work reported here, the methods at best can detect a reduction in mutagenicity or tumorigenicity relative to that of a starting material containing a heavy oil component.

Table 3.7  
 UTILITY OF BACTERIAL MUTAGENICITY AND TEN-ANIMAL DERMAL SCREENING  
 AS INDICATORS OF DERMAL TUMORIGENICITY

Approximate Time Dose (% Material)	Sample Number	Cumulative Percentage Mice with Skin Tumors										Salmonella Mutagenicity TA98 + S9  rev/ug
		Fifty Animal Tumorigenicity Assay <sup>a</sup>						Ten Animal Screen <sup>b</sup>				
		12 Months		16 Months		20 Months		40 Weeks		11 Months		
Material		50	100	50	100	50	100	50	100	50	100	
H-Coal Pilot Plant -												
Heavy Oil	591	84	100	- <sup>c</sup>	-	-	-	-	-	-	-	5.4
Heavy Oil	888	96	92	-	-	-	-	-	60	-	-	9.8
Heavy Oil	1334	-	-	-	-	-	-	50	100	50	100	22
Light Oil	589	0	0	-	-	-	-	-	-	-	-	0
Light Oil	887	0	0	-	-	-	-	-	-	-	-	0
Naphtha	587	0	0	-	-	-	-	-	-	-	-	0
Naphtha	886	0	0	-	-	-	-	-	-	-	-	0
H-Coal Upgrading -												
Middle Distillate of Heavy Oil 888		-	-	-	-	-	-	-	0	-	-	0.3
Vacuum Gas Oil (>650°F) of 888		-	-	-	-	-	-	100	-	-	-	30
Vacuum Gas Oil (>650°F) of 1344		-	-	-	-	-	-	100	-	-	-	67
Light Oil/Heavy Oil Blend	931	62	72	90	82 <sup>d</sup>	e	e	-	30	-	-	4.9
Low Severity HDT of 931	934	0	0	6	2	10	10	-	0	-	-	<0.1
High Severity HDT of 931	935	2	2	6	2	20	14	-	-	-	-	<0.1
Naphtha Reformate of 935	936	0	0	0	0	0	0	-	-	-	-	<0.1
Heating Oil from 935	978	2	8	4	16	24	28	-	-	-	-	<0.1
SRCII Upgrading -												
Middle/Heavy Distillate Blend	916	28	86	-	-	-	-	-	-	-	-	1.7
Low Severity HDT of 916	917	4	4	-	-	-	-	-	-	-	-	<0.1
Medium Severity HDT of 916	918	0	0	-	-	-	-	-	-	-	-	<0.1
High Severity HDT of 916	919	0	0	-	-	-	-	-	-	-	-	<0.1
Miscellaneous -												
Petroleum Recluse Crude Oil	CRM5	-	-	15	-	-	-	-	-	-	-	<0.1
Petroleum Naphtha Reformate	976	0	0	0	0	6	4	-	-	-	-	<0.1
Petroleum No. 2 Fuel Oil	975	0	0	0	0	10	8	-	-	-	-	<0.1
Paraho Shale Crude Oil	4601	93	-	-	-	-	-	-	-	-	-	0.6

<sup>a</sup>25 male plus 25 female C3H mice, three applications per week. <sup>b</sup>5 male plus 5 female C3H mice, two applications per week.  
<sup>c</sup>Dash (-) indicates experiment not carried out. <sup>d</sup>At 14 months. <sup>e</sup>No surviving animals or insufficient number to  
 meaningfully affect results.

#### 4.0 INFLUENCE OF HYDROGENATION AND REFINING

Hydrogenation is found to be a very effective means of reducing the tumorigenicity of crude coal liquids. A complex series of chemical changes occurs in the composition of the coal liquid as hydrogenation severity increases and as tumorigenicity and complete tumorigens are reduced. However, the nature of the bulk sample matrix also apparently influences tumorigenicity, suggesting that besides complete tumorigens, other factors are important in the expression of tumorigenicity. Further research into optimum catalysts and conditions for elimination of tumorigenicity is suggested.

##### 4.1 Influence of Hydrogenation

The total nitrogen content of the coal liquids was used as the main engineering parameter to specify the level of hydrotreatment severity (e.g., for the low severity hydrotreatment, a ca. 50% reduction in the total nitrogen content of the crude coal liquid was specified). Because one major objective of this study is to evaluate the effectiveness of hydrotreatment for reducing the tumorigenicity of crude coal liquids, the relationship of the total nitrogen content to tumorigenicity is of considerable interest. The relationship, if any, of this useful engineering parameter to tumorigenicity can be determined by comparing mouse skin painting data from several studies with the total nitrogen content of the samples tested. Data from three different skin-painting studies are listed in Table 4.1. Intercomparison of the data from all three sets is prevented by the somewhat different experimental protocols used, which required different methods of expressing tumorigenicity: tumor incidence - the cumulative percentage of animals developing tumors in a specified period of treatment (a larger % of animals means greater tumorigenicity), and tumor latency ("median time-to-tumor") - the period of time between the start of the study and the point at which 50% of the final number of tumors has appeared (a shorter period of time suggests greater tumorigenicity).

TABLE 4.1  
COMPARISON OF HETEROATOM CONTENT AND TWO MEASURES OF TUMORIGENICITY FOR CRUDE AND UPGRADED  
H-COAL AND SRC-II SAMPLES

Sample No.	Sample <sup>a</sup>	Heteroatom Content			Animals with Skin Tumors, <sup>b</sup> %	
		N, ppm	S, ppm	O, %	100%	50%
916	SRC-II Blend-AWW	8,800	2,600	4.76	86	28
931	H-Coal Blend-AWW	5,200	1,100	0.58	72	62
917	SRC-II Blend-HDT/L	4,900	83	2.86	4	4
934	H-Coal Blend-HDT/L	2,600	<10	0.39	0	0
918	SRC-II Blend-HDT/M	1,400	26	1.21	0	0
919	SRC-II Blend-HDT/H	500	<10	0.24	0	0
935	H-Coal Blend-HDT/H	<100	<10	<0.01	2	2

Sample No.	Sample <sup>a</sup>	N, ppm	S, ppm	O, %	Median Time-to-Tumor, <sup>c</sup> days	
					Male	Female
1314	H-Coal VSOH-FO	5,000	---	---	129	123
1310	H-Coal VSOH-SC	4,200	---	---	135	106
1313	H-Coal ASB-FO	4,000	---	---	382	350
1601	H-Coal Distillate-Raw	3,700	990	0.94	301	342
1309	H-Coal ASB-SC	3,700	---	---	199	185
1312	H-Coal ASOH-FO	3,000	---	---	>420 <sup>d</sup>	>420 <sup>d</sup>
1602	H-Coal Distillate-HDT/L	2,600	770	0.47	450	>476 <sup>d</sup>
1308	H-Coal ASOH-SC	1,700	---	---	>112 <sup>d</sup>	>112 <sup>d</sup>
1603	H-Coal Distillate-HDT/M	1,800	440	0.16	>476 <sup>d</sup>	>476 <sup>d</sup>
1604	H-Coal Distillate-HDT/H	600	400	0.33	462	>476 <sup>d</sup>

<sup>a</sup>Abbreviations: VSOH = Vacuum still overheads; ASB = Atmospheric still bottoms; ASOH = Atmospheric still overheads; SC = Syncrude mode; FO = Fuel Oil mode

<sup>b</sup>Data for 52 weeks of three-times weekly treatment of 25 male plus 25 female C3H mice per dose group/substance. Male and female mice data combined.

<sup>c</sup>Median time-to-tumor for male and female C3H mice with three-times weekly dose at 50% concentration.

<sup>d</sup>Tumor not detected in treatment period. Latency listed as greater than end of treatment period.

The main observation from these data is that tumorigenicity is highest for the samples with the highest total nitrogen content, and tumorigenicity generally drops off rapidly with decreasing nitrogen content. The SRC-II Blend-AWW (No. 916), the H-Coal Blend-AWW (No. 931), and the H-Coal Vacuum Still Overhead-Fuel Oil Mode (No. 1314) exhibit the highest total nitrogen contents and the greatest tumorigenicity. However, there is no consistent relationship for the samples with lower total nitrogen content, and often two samples with similar total nitrogen levels are quite different in tumorigenicity. In some cases, higher tumorigenicity is observed for a sample with lower nitrogen content. Notable comparisons are the H-Coal Blend-AWW (No. 931) (5,200 ppm N and 78% neoplasm incidence at a 100% dose) versus the SRC-II Blend-HDT/L (No. 917) (4,900 ppm N and 4% neoplasm incidence at a 100% dose), and the H-Coal Atmospheric Still Bottoms, (No. 1309) (pilot demonstration unit-synchrude mode; 3,700 ppm N, 123-129 days tumor latency) versus the H-Coal Distillate - Raw (No. 1601, also 3,700 ppm N but 301 - 343 days tumor latency). The explanation for the generally poor correlation between the total nitrogen content and tumorigenicity probably lies in the fact that the tumorigenicity of coal-derived liquids is mainly contributed by PAH, not by N-containing species.

Similarly, there do not appear to be any consistent relationships between either total sulfur or total oxygen content and tumorigenicity, except that the two samples with the highest levels of these heteroatoms also are the most tumorigenic. As for the total nitrogen content, tumorigenicity drops rapidly as total sulfur and total oxygen decrease.

Hydrogenation creates a complex series of changes in the chemical composition of a crude coal liquid. The bulk compositional decreases in heteroatom content and increases in hydrogen content (Tables 2.6 and 4.1) result in a more saturated, less aromatic, and less heteroatomic liquid than the starting crude oil. These changes in the bulk character of the oil are attributable to changes at the level of chemical classes and specific chemical compounds. Table 4.2 includes data for the distribution of major

Table 4.2

## INFLUENCE OF HYDROTREATMENT ON CHEMICAL PARAMETERS, MUTAGENICITY, AND TUMORIGENICITY OF COAL LIQUIDS

Sample Number	Description	Chemical Class Fraction <sup>a</sup> , wt. %					Quinoline, ug/g	Phenol, mg/g	Benzo(a)pyrene, ug/g	Mutagenicity <sup>b</sup> rev/ug	Animals w/Skin Tumors <sup>c</sup> , %	
		ESB	ESA	Sat.	Aro.	Polyaro.					Dose (wt./vol.%)	
											100	50
931	H-Coal Blend - AWW	3.3	1.5	30.8	56.7	5.8	164	0.15	50	4.9	72	62
934	H-Coal Blend - HDT/L	2.4	0.8	38.3	46.5	1.3	6	0.13	0.6	<0.1	0	0
933	H-Coal Blend - HDT/M	0.6	0.6	35.9	46.7	0.8	<1	0.13	<1	<0.1	-	-
935	H-Coal Blend - HDT/H	0.7	0.5	58.9	8.3	0.5	<1	<0.1	<1	<0.1	2	2
936	H-Coal Blend - HDT/2X + Cat. Ref.	0.1	0.6	0.4	13.1	0.1	<1	<0.1	1.4	<0.1	0	0
916	SRC-II Blend - AWW	5.0	2.0	26.7	47.7	6.2	1,300	17	60	1.7	86	28
917	SRC-II Blend - HDT/L	2.0	0.2	32.5	40.2	2.1	200	6.0	1.2	<0.1	4	4
918	SRC-II Blend - HDT/M	0.7	0.2	39.2	27.9	0.6	<1	2.0	0.9	<0.1	0	0
919	SRC-II Blend - HDT/H	0.3	<0.1	44.6	21.2	0.3	<1	0.5	0.1	<0.1	0	0
1601	H-Coal Distillate Raw	1.5	1.4	12.7	48.9	6.3	-	8.2	57	1.2	-	(45) <sup>d</sup>
1602	H-Coal Distillate - HDT/L	1.2	0.2	13.9	47.6	3.0	-	2.9	9	0.3	-	(0.5) <sup>d</sup>
1603	H-Coal Distillate - HDT/M	0.8	<0.1	15.8	47.9	1.9	-	0.7	3	0.1	-	(0) <sup>d</sup>
1604	H-Coal Distillate - HDT/H	0.3	<0.1	18.5	42.3	1.4	-	<0.4	2	<0.1	-	(0.5) <sup>d</sup>

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

<sup>b</sup>TA-98 + S-9 activation.

<sup>c</sup>Data for 52 weeks of three-times weekly treatment of 25 male plus 25 female C3H mice per dose group/substance. Male and female mice data combined. Acetone solvent.

<sup>d</sup>Data for study similar to (c) above, except 68 weeks duration with 10 male plus 10 female mice per dose group/substance, and solvent was acetone/cyclohexane.

chemical classes (minor insoluble precipitates, water-soluble acids and bases, and the neutral polar residue are not listed) and selected chemical compounds in crude and hydrotreated coal liquids. Concomitant with decreases in the total nitrogen content, the percentage of ether-soluble base (ESB in Table 4.2) fraction also decreases. Although this fraction is the main repository of nitrogen compounds and mutagenicity (Guerin et al., 1980, Wilson, Pelroy, and Cresto, 1980) in coal liquids, the percentage decreases in the fraction follow, but do not exactly parallel, the decreases in total nitrogen or in mutagenicity of the whole oil. For example, 50% of the total nitrogen in the H-Coal Blend-AWW (No. 931) is reduced in producing the H-Coal Blend-HDT/L (No. 934), but only 27% of the ether-soluble base fraction is removed. Quinoline, a typical nitrogen-containing heterocyclic compound is reduced by 96%, and detectable bacterial mutagenicity is eliminated.

Similar comments apply to the relationship between the ether-soluble acid fraction (ESA in Table 4.2) and the total oxygen content. However, a potentially significant observation is that both the total oxygen content and phenol (as a representative acidic oxygenated compounds) are reduced less readily than the other heteroatom counterparts. The importance of this observation lies in the fact that phenols are known (Sax, 1981) to act as tumor promoters, and the removal (by alkaline extraction) of acidic compounds from a high-boiling crude coal liquid decreased its tumorigenicity (see Section V). The implication is that a class of tumor promoters may resist hydrogenation, relative to other heteroatom-containing compound classes. Evidence of residual tumorigenicity in refined products, to be presented later in this section, also suggests that promoters may survive the refining of finished products.

The changes in the polycyclic aromatic hydrocarbon (PAH) composition upon hydrogenation of a crude coal liquid are of particular importance because of the known (Holland et al., 1984, Mahlum et al., 1984) association of this class of compounds (and particularly those PAH in coal liquids fractions boiling above 343 to 371°C [650-700°F] [Mahlum et al., 1984, Wilson et al., 1982, Ho et al., 1985]) with tumorigenicity. As the hydrogen content of the sample increases (Table 2.6), both the polycyclic aromatic compound fraction (which contains PAH and neutral nitrogen heterocyclics)

and the benzo[a]pyrene decrease (Table 4.2). Tumorigenicity also drops rapidly. As for the other bioactive chemical class fractions, there is not a consistent correlation between the percentage of the polycyclic aromatic compound fraction and benzo[a]pyrene concentration, or between either of these and the tumorigenicity. The only major trend is that the samples highest in the polycyclic aromatic compound fraction and benzo[a]pyrene are the most tumorigenic. These are the crude samples, which contain 50 to 60 ug/g of benzo[a]pyrene and 5 to 6 wt.% of the polycyclic aromatic compound class. Reduction of the benzo[a]pyrene content to a level below ca. 10 ug/g and the polycyclic aromatic compound class to 2 or 3% drastically reduces tumorigenicity, but the data do not correlate well among individual samples. Part of the lack of correlation between the polycyclic aromatic compound fraction and benzo[a]pyrene is attributable to the differences in the ease of reduction of the various polycyclic aromatic hydrocarbons.

The data suggest that the polycyclic aromatic compounds are reduced more readily than the mono/diaromatic compounds. However, this apparent trend may not reflect the true susceptibilities to reduction of polycyclic aromatic versus mono/diaromatic compounds, because alkylated mono/diaromatic compounds can be formed from the cracking of one or more rings in a larger polycyclic aromatic compound. For example, alkyl benzenes are formed (Brammer and Weller, 1979) from the cracking and reduction of one of the rings in 1-methyl naphthalene. As the aromatic compounds are reduced, the percentage of saturated compounds increases. Contributions from the reduction products of ether-soluble acid and base fractions also may be present in the saturates, but to a lesser extent because of the relatively lower percentage of these fractions in the starting crude oil. The overall result of hydrogenation is a more saturated, less aromatic, and less heteroatomic oil which is more like petroleum crude oils in nature and tumorigenicity (see previous section).

#### 4.2 Influence of Refining

Two finished products were refined from the H-Coal Blend: a Home Heating Oil (No. 978), which was prepared by devolatilizing the H-Coal Blend HDT/H (No. 935) to meet the ASTM flash point specification for Fuel Oils,

and the H-Coal Reformed Naphtha (No. 936) which was prepared similarly to but separately from the H-Coal Blend-HDT/H (No. 935) and then hydrotreated once again before catalytic reforming. Some of the more important toxicological parameters of these three samples are compared in Table 4.3. The second hydrotreating and catalytic reforming conducted upon the H-Coal Reformed Naphtha (No. 936) have further reduced the content of the ether-soluble base and polycyclic aromatic compound fractions, and especially the saturates fraction. The reduction in the latter may be attributed mainly to the catalytic reforming operation. Interestingly, the percentage of the mono/diaromatic compound fraction increased by ca. 50% and the benzo[a]pyrene content increased approximately two-fold. The increase in benzo[a]pyrene was surprising, and the analytical result obtained from the sequential HPLC-HPLC procedure was verified by an independent procedure using capillary column GC. This increase in benzo[a]pyrene content also is attributed to the catalytic reforming operation. The increased aromaticity suggested by the higher benzo[a]pyrene level (but not by the polycyclic aromatic compound class fraction results) is consistent with the decrease in total hydrogen content of the sample (Table 2.6). The tumor incidence of the H-Coal Home Heating Oil (No. 978) appears slightly elevated over that of its immediate precursor, the H-Coal Blend-HDT/H (No. 935), but the tumor latency is the same. In contrast, tumorigenicity is eliminated in the H-Coal Reformed Naphtha (No. 936).

Data for equivalent (at least in intended usage) petroleum products are included in Table 4.3. It is seen that some variability in composition exists for products of a given type. For example, the benzo[a]pyrene content of naphthas varies from undetectable ( $<0.002$  ug/g) in the API Light Catalytically Cracked Naphtha (No. 976) to ca. 1 ug/g in the UOP Reformed Light Arabian Naphtha (No. 973) and in a locally purchased unleaded gasoline (No. 977). However, the benzo[a]pyrene content of the two home heating oils, the API No. 2 Fuel Oil (No. 976) and the UOP Hydrocracked Light Arabian VGO (No. 974), both are very low.

Differences in the tumorigenicity and PAH content of the four primary products are presented in more detail in Table 4.4. Several important differences are evident:

Table 4.3  
 INFLUENCE OF UPGRADING ON CHEMISTRY AND TUMORIGENICITY OF H-COAL LIQUIDS AND COMPARISON WITH EQUIVALENT PETROLEUM PRODUCTS

Sample No.	Description	Chemical Class Fraction <sup>a</sup> , wt%						Benzo(a)pyrene, ug/g	Sum of 5-Ring PAH <sup>b</sup> , ug/g	Animals with Skin Tumors <sup>c</sup> , %	Median Time-To-Tumor <sup>d</sup> , Weeks
		ESB	ESA	Sat.	Aro.	Polyaro.	Vol.				
935	H-Coal Blend - HDT/H	0.7	0.5	58.9	8.3	0.5	-	<1	-	20	96-116
978	H-Coal Home Heating Oil	-	-	-	-	-	-	0.8	24	28	91-111
936	H-Coal Reformed Naphtha	0.3	0.6	0.4	13.1	0.1	66.6	1.4	22	0	156-ND
975	API No. 2 Fuel Oil	0.1	0.3	69.8	12.5	1.2	-	0.04	0.07	12	104-ND
976	API Light Cat. Cr. Naphtha	<0.1	<0.1	1.0	12.1	<0.1	62.9	<0.002	<0.06	6	116-ND
973	UCP Ref. Lt. Arabian Naphtha	<0.1	0.2	2.3	7.2	0.3	47.5	0.9	-	-	-
974	UCP Hdck. Lt. Arabian VGO	<0.1	<0.1	80.8	3.9	1.7	0.1	0.04	-	-	-
977	Commercial Unleaded Gasoline	-	-	-	-	-	-	ca.1	4	-	-

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<sup>a</sup>See abbreviations in Table 4.2.

<sup>b</sup>Benzo(b/j)fluoranthenes + benzo(k)fluoranthene + benzo(e)pyrene + benzo(a)pyrene + dibenz(a,j)anthracene + Indeno(1,2,3-cd)pyrene + dibenz(a,c/a,h)anthracenes + benzo(ghi)perylene.

<sup>c</sup>Data for lifetime of three-times weekly application to 25 male and 25 female C3H mice per dose group/substance. Data for male and female mice combined. 100% dose (neat sample).

<sup>d</sup>Range including all dose groups and both sexes. ND = not detected (for zero tumor incidence).

Table 4.4

COMPARISON OF POLYCYCLIC AROMATIC HYDROCARBON CONTENT AND TUMORIGENICITY  
OF FINAL PRODUCTS REFINED FROM COAL LIQUIDS AND PETROLEUM

Parameter	No. 936 H-Coal Ref. Nap.		No. 976 API Lt. Cat. Cr. Nap.		No. 978 H-Coal Home Heating Oil		No. 975 API No. 2 Fuel Oil	
	F	M	F	M	F	M	F	M
Cumulative Tumor Incidence <sup>a</sup> , % Animals								
at 25% Dose	4	4	16	16	16	16	4	4
at 50% Dose	0	0	4	12	20	28	12	16
at 100% Dose	0	0	12	0	20	36	4	20
Median Time-to-Tumor <sup>b</sup> , Weeks	156-ND		116-ND		91-111		104-ND	
Benzo(a)pyrene, ug/q	1.4		<0.002		0.8		0.04	
Sum of 5 and 6-Ring PAH <sup>c</sup> , ug/q	22		<0.06		24		0.07	

<sup>a</sup>Lifetime data for three-times weekly application to 25 male and 25 female C3H mice per dose group/substance. Acetone solvent for 50% and 25% doses. F = female and M = male.

<sup>b</sup>Range including all dose groups and both sexes. ND = none detected (for zero tumor incidence).

<sup>c</sup>Sum of benzo(b/j)fluoranthenes + benzo(k)fluoranthene + benzo(e)pyrene + benzo(a)pyrene + dibenz(a,i)anthracene + indeno[1,2,3-cd]pyrene + dibenz(a,c/a,h)anthracenes + benzo(ghi)perylene.

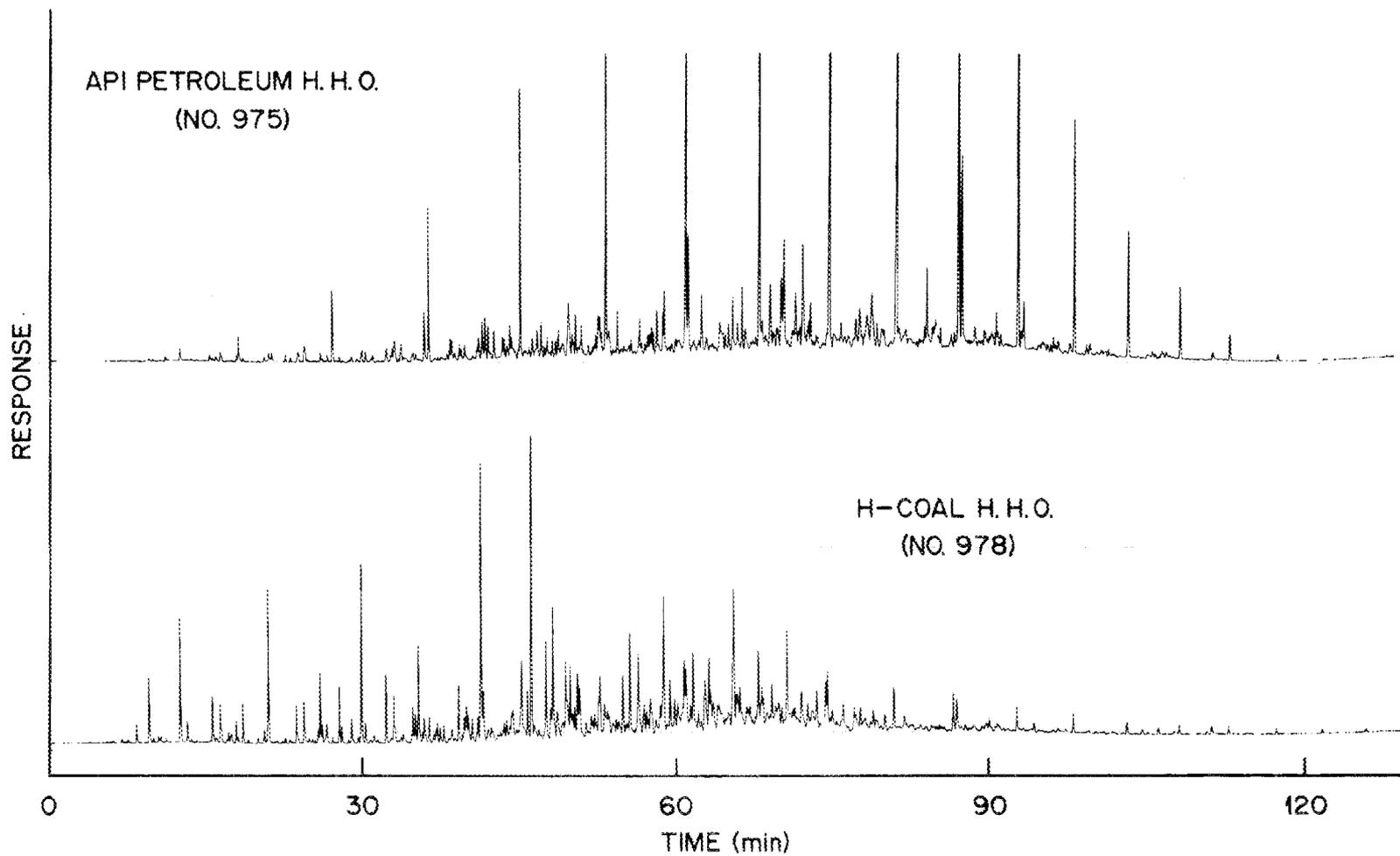
- a) the H-Coal Home Heating Oil (No. 978) produces a significantly higher tumor incidence and shorter latency period than does the H-Coal Reformed Naphtha (No. 936), even though the latter contains similar concentrations of tumorigenic PAH,
- b) the API Light Catalytically Cracked Naphtha (No. 976) yields a shorter latency period and slightly elevated tumor incidence than does the H-Coal Reformed Naphtha (No. 936), although the latter contains higher levels of tumorigenic PAH, and
- c) the H-Coal Home Heating Oil (No. 978) causes a somewhat greater tumor incidence and a slightly shorter latency period than does the API No. 2 Fuel Oil (No. 975).

These findings demonstrate that a small residual level of tumorigenic activity is carried over into (or created in) final products refined from coal liquids, and that in the case of home heating oils, this coal-derived product is slightly more tumorigenic than an equivalent petroleum product. In contrast, the coal-derived naphtha is benign. The disparity between relative PAH content and tumorigenicity may be the result of at least three factors operating singly or in concert.

An hypothesis for which some further evidence exists, is that these differences in tumorigenicity (especially between the H-Coal Home Heating Oil [No. 978] and the H-Coal Reformed Naphtha [No. 936]) arise because of differences in promoting agents and tumor promoting activity. As noted in Section 4.1, the phenols and other oxygenated species appear to resist reduction relative to other heteroatomic species, and evidence for the importance to tumorigenicity of acidic compounds in high-boiling crude coal liquids has been obtained (see Section V).

Another hypothesis is that the apparent differences between the tumorigenicities of the two naphtha products and possibly between the two home heating oil products, (but not between the home heating oil and naphtha products) is a result of the experimental uncertainties associated with measurements in the low slope portion of a classical dose-response curve. This hypothesis probably is most appropriate for the naphtha samples.

An important hypothesis which can be tested is that differences in the bulk sample matrices affect the uptake and distribution of tumorigenic compounds from the samples. As shown in the comparative capillary column GC profiles of the neat liquids in Figure 4.1, the major organic compounds are quite different for the sample matrices of the two home heating oils. As summarized in Table 4.5 (see Appendix Figure A.2 and Tables A.7 and A.12 for



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Figure 4.1. Comparison of Major Organic Compound Composition of No. 975 API No. 2 Fuel Oil and No. 978 H-Coal Home Heating Oil.

Table 4.5

COMPARISON OF MAJOR ORGANIC COMPOUNDS IN H-COAL HOME HEATING OIL  
(NO. 978) AND API NO. 2 FUEL OIL (NO. 975)

Major Organic Compounds (In Decreasing Order of Concentration)	
<u>H-Coal Home Heating Oil (No. 978)</u>	<u>API No. 2 Fuel Oil (No. 975)</u>
Decahydronaphthalene	C <sub>7</sub> -C <sub>24</sub> n-Paraffins
C <sub>1</sub> -C <sub>4</sub> -Decahydronaphthalenes	C <sub>0</sub> -C <sub>5</sub> -Naphthalenes
C <sub>0</sub> -C <sub>4</sub> -Cyclohexanes	C <sub>0</sub> -C <sub>4</sub> -Benzenes
C <sub>0</sub> -C <sub>4</sub> -Tetrahydronaphthalenes	C <sub>1</sub> -C <sub>4</sub> -Indanes
C <sub>1</sub> -C <sub>4</sub> -Indanes	C <sub>0</sub> -C <sub>1</sub> -Phenanthrenes
C <sub>7</sub> -C <sub>25</sub> n-Paraffins	
C <sub>0</sub> -C <sub>4</sub> -Benzenes	

a more detailed comparison), the API No. 2 Fuel Oil (No. 975) consists largely of straight-chain paraffins and alkylated mono- and diaromatic hydrocarbons. In contrast, the H-Coal Home Heating Oil (No. 978) is made up of alkylated one and two-ring cycloparaffins. It may be significant to note that a recent API skin-painting study of petroleum distillates (Lewis et al., 1984) suggested that mono and dicycloparaffins might accelerate tumor development and progression. The results observed here might indicate that cycloparaffins are more effective than straight-chain paraffins (some of which, like dodecane, are considered [Sax, 1981] as promoters in their own right) in enhancing uptake of tumorigens through the skin, and otherwise acting as important cofactors in tumorigenicity.

The content of benzene, C<sub>1</sub> and C<sub>2</sub>-benzenes, and some C<sub>3</sub>-benzenes is greater for the H-Coal Home Heating Oil (No. 978) than for either the API No. 2 Fuel Oil (No. 975) or a locally-purchased home heating oil (No. 984), as illustrated in Table 4.6. This trend is expected from the more aromatic nature of the parent H-Coal Blend versus typical petroleum crude oils. However, the difference is reversed (at least for the API No. 2 Fuel Oil [No. 975]) for most of the C<sub>4</sub>-benzenes (see Figure A.2 and Tables A.7 and A.12 in the Appendix). These differences in the bulk composition are reflected in the inhaleable volatile organic compounds found in the headspace vapors of the liquids.

It should be noted that, consistent with the matrix-effects hypothesis, the H-Coal and petroleum-derived naphthas, which are more similar in their weak tumorigenicity than are the home heating oils, also are more similar in their major organic compound composition. Figure 4.2 shows that the H-Coal Reformed Naphtha (No. 936) and the API Light Catalytically Cracked Naphtha (No. 976) share most of their major compounds, such as benzene, C<sub>1</sub>-C<sub>4</sub>-benzenes and C<sub>4</sub>-C<sub>7</sub> saturated hydrocarbons. The main differences are quantitative, not qualitative. The benzene, toluene, and xylenes composition of the H-Coal Reformed Naphtha (No. 936) is greater (Table 4.6 than that of the API Light Catalytically Cracked Naphtha (No. 976) and the UOP Reformed Light Arabian Naphtha (No. 973). The API petroleum naphtha appears more enriched in C<sub>5</sub>-C<sub>8</sub> saturated hydrocarbons and their unsaturated analogs (see Figure A.1 and Tables A.6 and A.10 in the Appendix). These differences are expected from the nature of their parent crude oils.

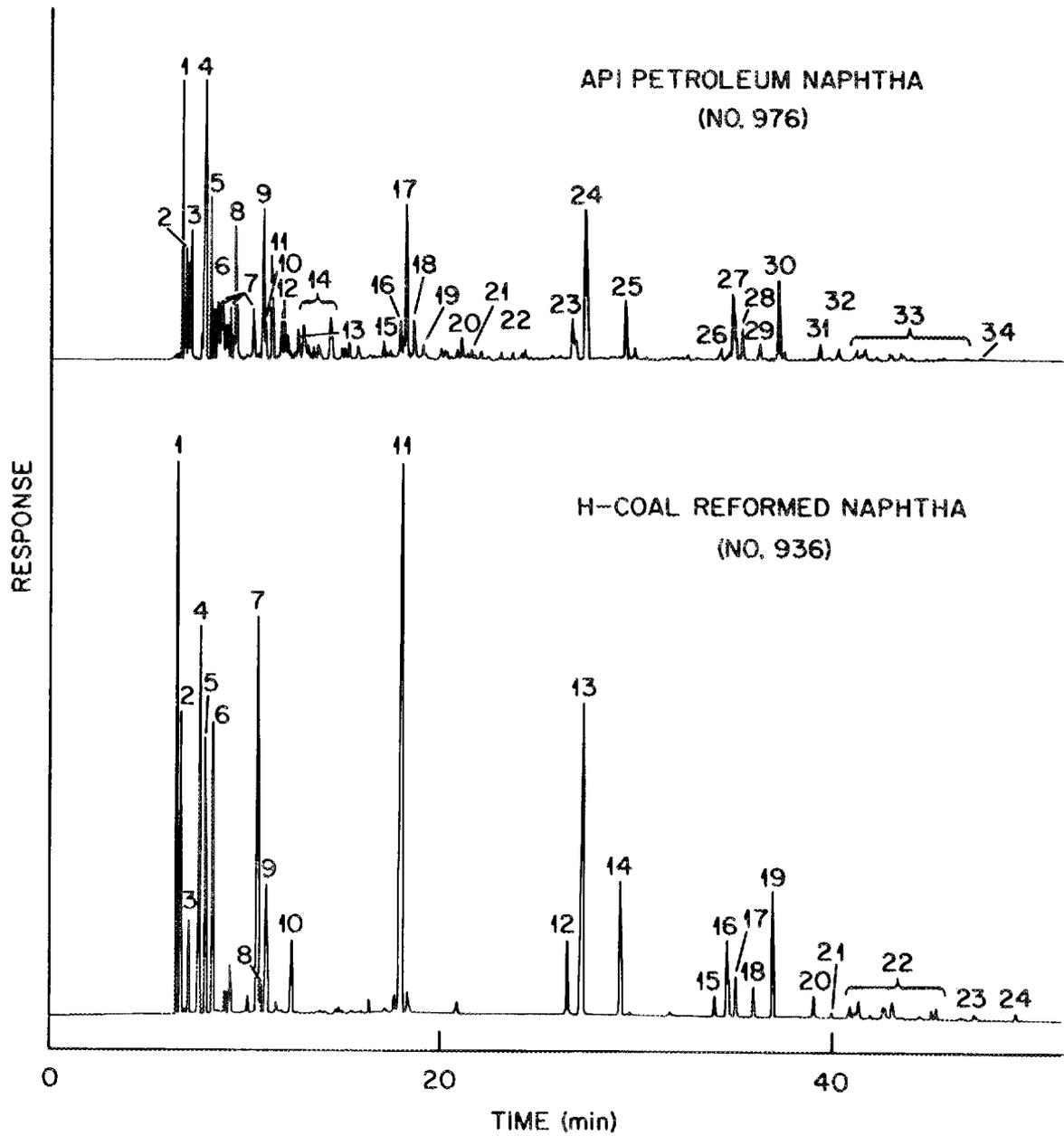


Figure 4.2. Comparison of Major Organic Compound Composition of No. 976 API Light Catalytically Cracked Naphtha and No. 936 H-Coal Reformed Naphtha.

Table 4.6

COMPARISON OF BENZENE AND ALKYL BENZENE CONTENT OF NAPHTHAS AND HOME HEATING OILS REFINED FROM COAL LIQUIDS AND PETROLEUM

Compound	Concentration, mg/g					
	No. 936 H-Coal Reformed Nap.	No. 976 API Lt. Cat. Cr. Nap.	No. 973 UOP Ref. Lt. Ar. Nap.	No. 978 H-Coal Home Heating Oil	No. 975 API No. 2 Fuel Oil	No. 984 Commercial Home Heating Oil
Benzene	49.7	7.4	19.1	2.9	<0.02	0.05
Toluene	180	43.1	106	3.3	0.3	0.5
Ethyl Benzene	23.6	14.1	32.2	2.6	0.2	0.5
m-Xylene	89.0	} 58.6	} 104	} 3.5	1.3	1.7
p-Xylene	37.7				0.8	0.8
o-Xylene	47.4	20.2	46.3	1.5	0.6	0.8
i-Propyl Benzene	1.4	-	11.3	1.3	<0.3	<0.5
n-Propyl Benzene	7.5	3.6	11.3	2.4	0.2	0.5
1,3,5-Trimethyl Benzene	15.6	12.3	15.6	<0.5	<2	<2
n-Butyl Benzene	0.5	-	4.2	<1	<0.7	<1

An important finding relevant to potential differences in the inhalation toxicity of coal- and petroleum-derived finished products is depicted in Figures 4.3 and 4.4, and quantified in Table 4.7. The composition of the inhaleable compounds in the headspace vapors reflects the composition of the bulk liquids. Consistent with the bulk composition similarities and differences discussed above, the headspace vapors of the coal-derived products contain higher concentrations of benzene and toluene than do the petroleum-derived products. The vapors of the more volatile naphthas, of course, yield headspace vapors more concentrated by factors of 10 to 100 or more than do the home heating oils. These results suggest that coal-derived reformed naphthas such as the H-Coal Reformed Naphtha (No. 936) may present a more toxic inhalation hazard to refinery personnel and users than do the petroleum-derived naphthas.

#### 4.3 Chemistry of Tumorigen Hydrogenation

Differences between the reduction of benzo[a]pyrene and the polycyclic aromatic compound fraction may reflect, among other things, the differences in the ease of reduction of benzo[a]pyrene and other tumorigenic PAH. This point can be examined by analyzing coal liquids for selected dermal tumorigen PAH before and after hydrogenation. Table 4.8 presents data calculated from analyses of four pairs of samples. It must be noted that only in the case of the H-Coal Blend-AWW (No. 931) and H-Coal Blend-HDT/L (No. 934) was the hydrogenation conducted outside of the liquefaction process specifically for beneficiation of tumorigenic activity. In the other three sample sets, the hydrogenation is conducted as integral part of the overall liquefaction process. In spite of the different process designs, purposes of hydrogenation, and (probably) hydrogenation conditions, some consistent trends are observed for the reduction behavior of PAH in complex coal liquids.

Ease of hydrogenation varies with the number of rings in the PAH ring system, with the larger PAH generally being reduced less readily than smaller PAH. Benzo[ghi]perylene, a six-ring PAH, is more resistant to reduction than is benz[a]anthracene, a four-ring PAH, and benzo[a]pyrene, a five-ring PAH. The susceptibility to reduction also depends upon the

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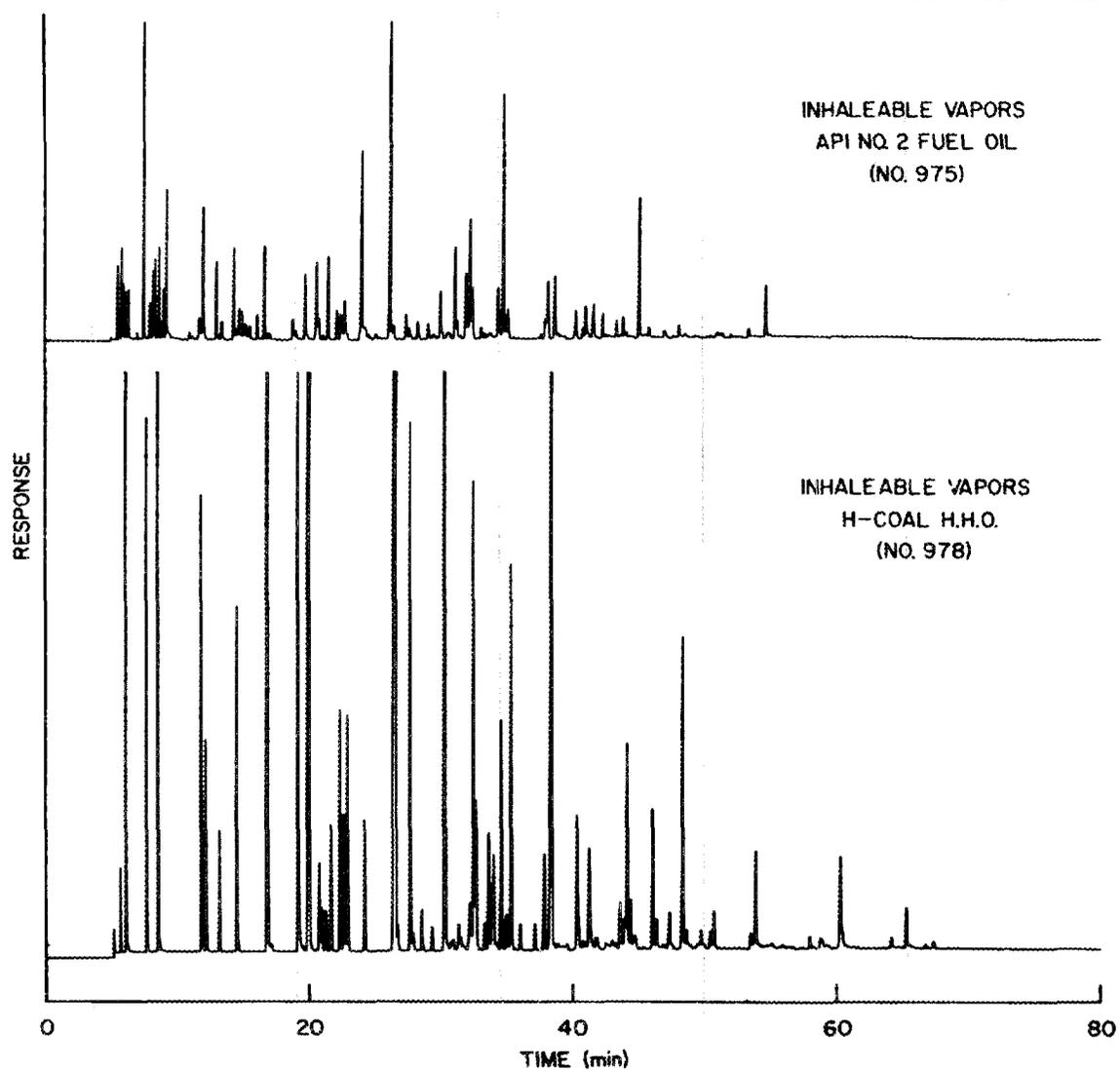


Figure 4.3. Capillary Column Gas Chromatograms of Inhalable Vapors in the Headspace Vapors over API No. 2 Fuel Oil (No. 975) and H-Coal Home Heating Oil (No. 978) at 25°C.

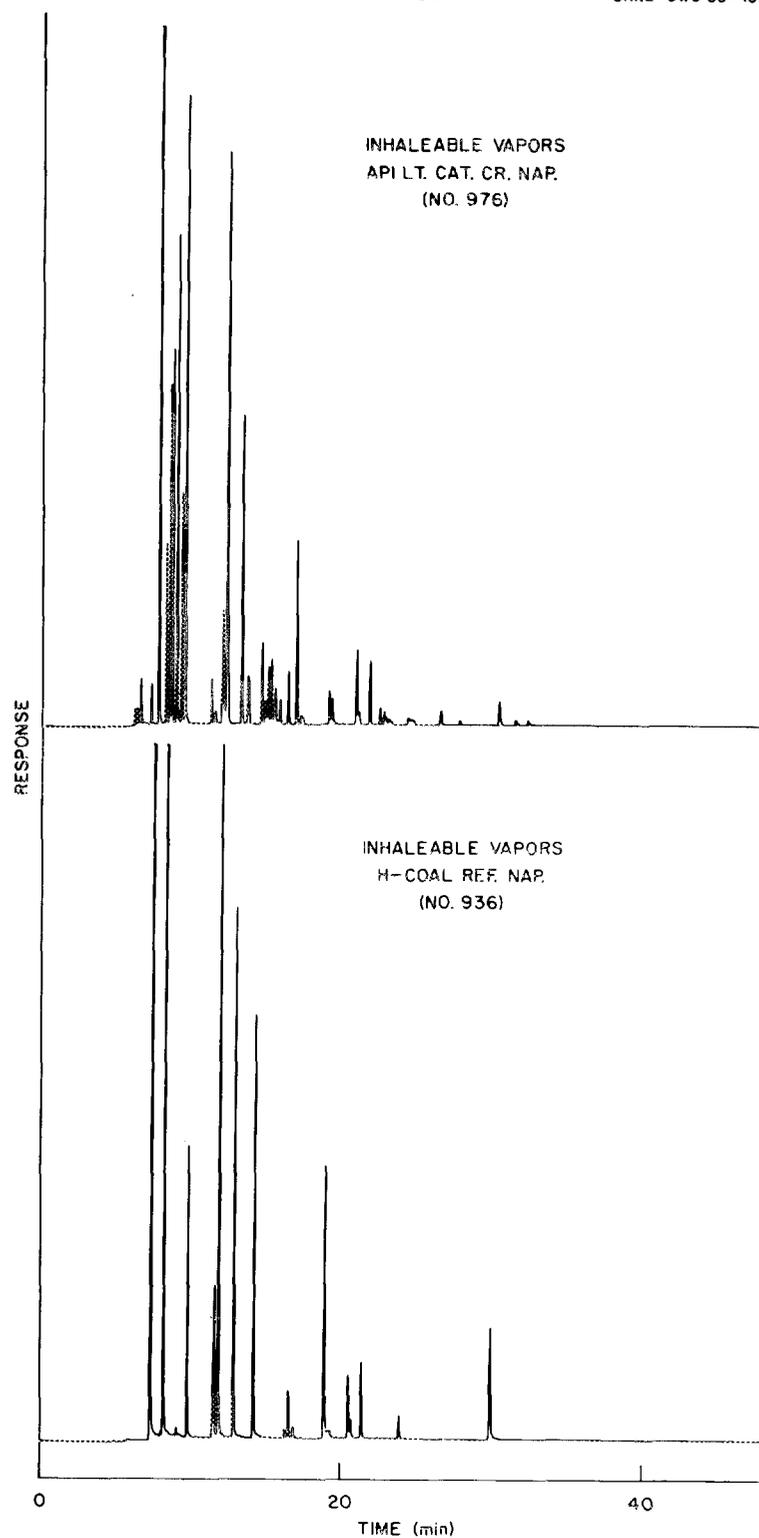


Figure 4.4. Capillary Column Gas Chromatograms of Inhalable Volatiles in the Headspace Vapors over API Light Catalytically Cracked Naphtha (No. 976) and H-Coal Reformed Naphtha (No. 936) at 25°C.

Table 4.7

COMPARISON OF INHALABLE VOLATILE ORGANIC COMPOUNDS IN THE HEADSPACE VAPORS OF NAPHTHAS AND HOME HEATING OILS REFINED FROM COAL LIQUIDS AND PETROLEUM

Component	Concentration <sup>a</sup> , mg/L						
	No. 936 H-Coal Reformed Nap.	No. 976 API Lt. Cat. Cr. Nap.	No. 973 UOP Ref. Lt. Ar. Nap.	No. 977 Com. Unleaded Gas.	No. 978 H-Coal Home Heating Oil	No. 975 API No. 2 Fuel Oil	No. 984 Commercial Home Heating Oil
I-Pentane	186	85	94	80	0.27	0.16	0.60
n-Pentane	72	17	49	23	0.42	0.04	0.27
2,2-Dimethyl Butane	15	0.7	8.8	1.0	-	-	0.01
3-Methyl Pentane	28	20	16	3.9	0.08	0.06	0.09
n-Hexane	26	7.6	16	2.5	0.24	0.07	0.15
Benzene	18	3.6	8.7	1.0	0.41	0.01	0.34
3-Methyl Hexane	5.6	6.4	13	0.9	0.10	0.07	0.76
n-Heptane	2.3	1.8	6.3	-	0.10	0.15	0.12
Toluene	12	4.9	11	0.6	0.58	0.04	0.08
n-Octane	0.1	0.4	0.8	-	0.03	0.18	0.11
m-Xylene	2.0	2.0	2.6	-	0.08	0.05	0.06
n-Nonane	-	0.1	0.1	-	-	0.12	0.08
1,3,5-Trimethyl Benzene	0.1	0.1	0.1	-	-	-	0.02
n-Decane	-	-	-	-	<0.01	0.05	0.05

61

<sup>a</sup>Concentration in mg of compound per L of headspace air at 25°C.

Table 4.8

COMPARISON OF PERCENTAGE REDUCTION OF SELECTED FOUR-TO-SIX RING PAH DERMAL TUMORIGENS  
IN CRUDE COAL LIQUIDS BY CATALYTIC HYDROGENATION

PAH	Relative Tumorigenicity <sup>a</sup>	Percentage Removed Upon Hydrogenation			
		H-Coal No. 934/931	EDS No. 1657/1658	ITSL (N-1) <sup>b</sup>	ITSL (O-2) <sup>b</sup>
Benz(a)anthracene	+	>99	99	97	88
Chrysene/Triphenylene	<u>+</u>	99	90	98	71
2-Methyl Chrysene <sup>c</sup>	+	97	87	96	68
Benzo(b/j)fluoranthenes	++ to +++	95	75	91	65
Benzo(k)fluoranthene	++ to +++	>99	>98	92	75
Benzo(e)pyrene	<u>+</u>	92	81	88	46
Benzo(a)pyrene	++++	99	98	90	82
Dibenz(a/j)anthracene	++	>79	82	-	-
Indeno(1,2,3-cd)pyrene	+	-	71	71	49
Dibenz(a,h/a,c)anthracenes	+++/ <u>+</u> <sup>d</sup>	>89	76	76	56
Benzo(ghi)perylene	<u>+</u>	76	74	35	6

<sup>a</sup>Compiled from Committee on Pyrene and Selected Analogs (1983) and Lee et al. (1981).

<sup>b</sup>Calculated from Wilson et al. (1984). ITSL = integrated two-stage liquefaction in normal (N-1) and off-normal (O-2) operation.

<sup>c</sup>May include isomeric methyl benzanthracenes.

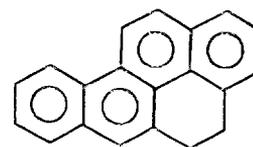
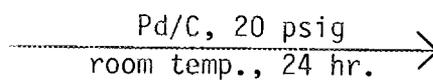
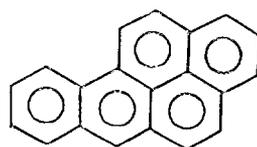
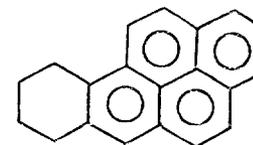
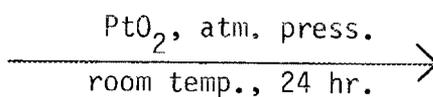
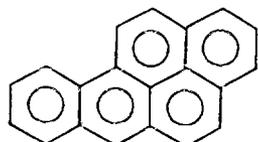
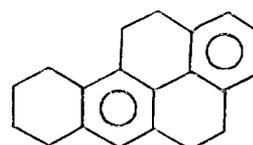
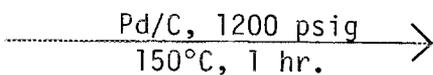
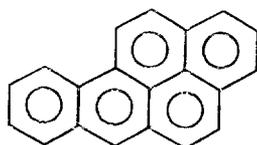
<sup>d</sup>Activities listed for a,h and a,c isomers, respectively.

specific structure of the PAH, with different isomeric structures having different susceptibilities to reduction. For example, of the  $C_{20}H_{12}$  (molecular weight 252) isomers, the ease of reduction ranks approximately benzo[a]pyrene > benzo[k]fluoranthene > benzo[b/j]fluoranthenes > benzo[e]-pyrene. There does not appear to be any consistent relationship between the tumorigenicity of a PAH and the percentage reduced upon hydrogenation.

Of the PAH analyzed, benzo[a]pyrene is one of the more readily reduced tumorigenic PAH. This observation indicates that benzo[a]pyrene is a conservative "indicator" of the reduction of dermal tumorigen PAH. That is, if benzo[a]pyrene is not reduced in a hydrogenation experiment, then these other PAH probably are not significantly affected, either. However, complete removal of benzo[a]pyrene by hydrogenation does not necessarily indicate that all other tumorigenic PAH are equally reduced. These differences in susceptibility of the various PAH to reduction, plus the fact that partially hydrogenated PAH (such as dihydrobenzo[a]pyrene) are recovered in the polycyclic aromatic compound fraction, explains why the reduction of benzo[a]pyrene concentration in coal liquids does not closely correlate with the reduction of the percentage of polycyclic aromatic compound fraction.

Both the conditions chosen for conducting the hydrogenation and the nature of the sample matrix can affect the products obtained from PAH reduction. Figure 4.5 illustrates the differences in degree of PAH reduction which can be achieved under different catalysts and conditions. Using a 300 ml volume, no. 4561 Parr Mini-Reactor (Parr Instrument Company, Moline, IL) ca. 75 mg quantities of benzo[a]pyrene or dibenz[a,h]anthracene in 100 ml of heptane were reduced with 10-15 mg of catalyst under the conditions listed. The products were analyzed quantitatively using capillary column GC with flame ionization detection, and were identified by GC-MS and NMR spectroscopy. A nearly quantitative (98%) yield of 4,5,7,8,9,10,11,12-octahydrobenzo[a]pyrene was obtained using a 10% palladium on charcoal catalyst at 1,200 psig of hydrogen pressure and 150°C for one hr, while under lower pressure and temperature conditions, a 60% yield of 4,5-dihydrobenzo[a]pyrene was achieved. A run similar to the latter, but using a platinum oxide catalyst produced instead a 71% yield of 7,8,9,10-tetrahydrobenzo[a]pyrene.

Benzo(a)pyrene

4,5-dihydrobenzo[a]pyrene  
(60%)7,8,9,10-tetrahydro-  
benzo[a]pyrene (71%)4,5,7,8,9,10,11,12-octa-  
hydrobenzo[a]pyrene (98%)

Dibenz(a,h)anthracene

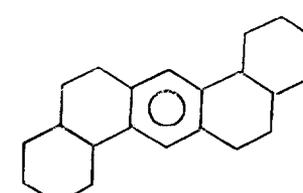
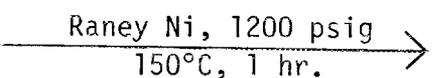
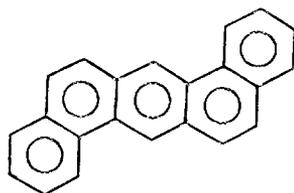
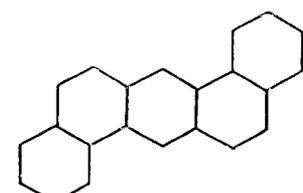
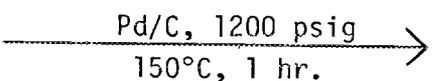
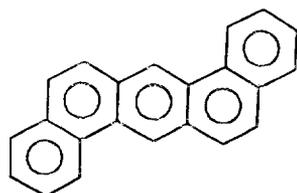
hexadecahydro-dibenz[a,h]-  
anthracene (100%)perihydro-dibenz[a,h]-  
anthracene (100%)

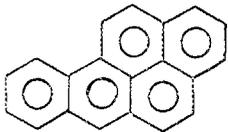
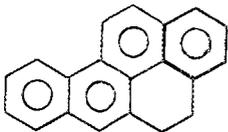
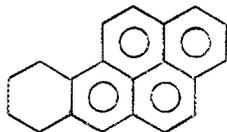
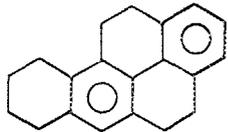
Figure 4.5. Hydrogenation of Benzo(a)pyrene and Dibenz(a,h)anthracene Under Different Catalytic Conditions.

Although reactions with pure compounds are useful for identifying reduction products, the presence of a complex mixture such as a coal liquid for the sample matrix can drastically alter the product distribution from hydrogenation. Table 4.9 compares the yield of three hydrogenated products for reductions conducted with and without H-Coal Vacuum Gas Oil (No. 1334) present. Whereas the octahydrobenzo[a]pyrene is the major product in the reduction of benzo[a]pyrene in a pure solvent, the addition of a vacuum gas oil considerably alters the reduction, and the main product identified is the dihydroderivative. These results appear to be independent of the amount of benzo[a]pyrene spike used, and indicates that components of the vacuum gas oil complicate the reaction by successfully competing with benzo[a]pyrene for taking up hydrogen and/or poisoning the catalyst so that it cannot as effectively reduce benzo[a]pyrene. The effect this can have on the tumorigenicity of the product is suggested by the mutagenic activities measured for the different reduction products of benzo[a]pyrene, using strain TA-98 with S-9 activation: benzo[a]pyrene, 58 rev./ug; 4,5-dihydrobenzo[a]pyrene, 22 rev./ug; 7,8,9,10-tetrahydrobenzo[a]pyrene, 3.8 rev./ug; and 4,5,7,8,9,10,11,12-octahydrobenzo[a]pyrene, 0.2 rev./ug. A greater degree of hydrogenation results in a less mutagenic product, with mutagenicity being almost completely eliminated at the octahydro level of reduction.

Identification of optimum hydrogenation conditions for reducing tumorigens at the laboratory scale can provide information useful for designing larger-scale, more industrially relevant hydrogenation experiments. Laboratory scale hydrogenations were carried out in a batch-reactor mode using a Parr Instrument Company (Moline, IL) no. 4561 Mini-Reactor, which is rated at a maximum of 2,000 psig and 350°C (662°F). The general procedure used was to react ca. three g of H-Coal Vacuum Gas Oil (No. 1334: > 343°C/> 650°F) dissolved in 150 ml of heptane with hydrogen gas at elevated temperatures and pressures in the presence of ca. 300 mg of catalyst. After the hydrogenation reaction, the reactor was allowed to cool and was depressurized. The product suspension was filtered and aliquots were removed for analysis of benzo[a]pyrene as an indicator of tumorigenic PAH and of potential tumorigenicity. The various catalysts tested in this

Table 4.9

IMPACT OF H-COAL VACUUM GAS OIL NO. 1334 (>343°C/>650°F) AS THE MATRIX MATERIAL ON THE HYDROGENATION OF BENZO(a)PYRENE<sup>a</sup>

Starting Material	Products (%)				
	 (BaP)	 (4,5-Dihydro-BaP)	 (7,8,9,10-Tetrahydro-BaP)	 (4,5,6,7,8,9,10,11,12-Octahydro-BaP)	(Other) <sup>b</sup>
100% BaP (without a Matrix Material)	0	<1	<1	98	<1
BaP (6%) Spiked In H-Coal No. 1334 VGO	37	16	3	1	43
BaP (0.6%) Spiked In H-Coal No. 1334 VGO	25	15	5	1	54

<sup>a</sup>A general experimental procedure for this matrix impact study is as follows: One gram of H-Coal vacuum gas oil spiked with BaP was dissolved in 150 mL of heptane. The solution was then hydrogenated over Pd/C under 1200 psig (H<sub>2</sub> and solvent) at 150°C. The resultant reaction mixture was fractionated on a reversed-phase HPLC column to obtain a fraction containing hydrogenated products of BaP and unreacted BaP. Their identities and quantities were established by GC and GC/MS.

<sup>b</sup>Including other hydrogenated BaP products which were not identified because of lack of standard compounds.

study are described in Table A.17 in the Appendix. Sulfiding of the catalysts was kindly conducted by Mr. Gary Stiegel of the Pittsburgh Energy Technology Center, Pittsburgh, Pennsylvania.

The effectiveness of several different laboratory and industrial catalysts were compared (Table 4.10). The laboratory catalysts are found to be much more effective than the industrial catalysts for reducing benzo[a]pyrene under equivalent conditions. Raney Nickel is by far the most efficient catalyst, reducing more than 99% of the benzo[a]pyrene in one hr. at only 150°C. Poisoning may have limited the effectiveness of palladium on charcoal; two hydrogenations with fresh catalyst each time were required to reduce 99% of the benzo[a]pyrene.

None of the industrial catalysts were able to significantly reduce benzo[a]pyrene at 150°C, even after three sequential hydrogenations using fresh catalyst each time or after sulfiding the Shell 324M catalyst. This result would seem to rule out catalyst poisoning as the cause of poor reduction efficiency at this temperature. The industrial catalysts are designed for high temperature operation, and increasing the temperature to 320°C improved the reduction of benzo[a]pyrene significantly. In addition, catalyst sulfiding vastly increased the activity of the catalyst, with the most efficient reduction (82% of the benzo[a]pyrene reduced in a single one hr. hydrogenation) occurring with the sulfided version of the Shell 324M catalyst at 320°C. This result compares with a 27% reduction of benzo[a]pyrene at 320°C using the Shell 324M catalyst in its oxide form, and only an 11% reduction using the sulfided Shell 324M catalyst at 150°C. However, even with this most efficient combination of industrial catalyst/conditions, three sequential hydrogenations with fresh catalyst each time were required to reach a level of reduction (97%) comparable to that achieved (>99%) in a single hydrogenation at 150°C using Raney Nickel.

Comparison of the result (97% reduction) for three separate hydrogenations using fresh catalyst each time versus a single three-hour hydrogenation without catalyst replacement (87% reduction) plus the incremental improvements in the percent of benzo[a]pyrene reduced when fresh batches of any industrial catalyst are used sequentially suggests that catalyst poisoning is a major factor limiting catalyst efficiency for reducing PAH tumorigens at elevated temperatures. The Parr Mini-Reactor is

Table 4.10

EFFECTIVENESS OF DIFFERENT LABORATORY AND INDUSTRIAL CATALYSTS  
IN REDUCING BaP IN H-COAL VACUUM GAS OIL NO. 1334 (<343°C/650°F)

Catalyst	Temperature, °C	%Benzo[a]pyrene Remaining in H-Coal No. 1334 VGO After Sequential Hydrotreatment		
		Number of Hydrotreatments <sup>a</sup>		
Laboratory Catalyst		One	Two	Three
Pd/C (1/10)	150	63	1	1
Raney Nickel	150	<1	<1	<1
<u>Commercial Catalysts</u>				
Shell 324 M (3% NiO; 20% MoO <sub>3</sub> )	150	99	95	97
Amocat 1C (3% NiO; 14% MoO <sub>3</sub> )	150	94	97	100
HDS-1442A (2% CoO; 16% MoO <sub>3</sub> )	150	97	94	93
Sulfided Shell 324 M (S = 10.9%)	150	89	98	99
Shell 324 M (3% NiO; 20% MoO <sub>3</sub> )	320	73	-	-
Sulfided Shell 324 M	320	18	10	3(13) <sup>b</sup>
Strem Chemical Co., Sulfided (6% NiO; 19% WO <sub>3</sub> )	320	37	21	13

<sup>a</sup>Fresh catalyst used in each step.

<sup>b</sup>Single three hour hydrotreatment without replacement of catalyst.

limited to a maximum temperature of 350°C. The efficiency of sulfided catalysts at higher temperatures and pressures will be explored using a downflow tubular reactor which is being set up.

Other studies of fresh and used catalyst provide additional evidence for the catalyst poisoning hypothesis. Figure 4.6 shows the reduction of benzo[a]pyrene in H-Coal Vacuum Gas Oil No. 1334 (> 343°C/> 650°F) over a period of six hours using sulfided Shell 324 M catalyst at 320°C and 1,200 psig of hydrogen in the Parr Mini Reactor. The hydrogenation was interrupted to take samples for benzo[a]pyrene analysis. The decrease in benzo[a]pyrene concentration is roughly exponential, with a rapid decrease in the first hour of hydrogenation and a slow leveling off to 10% of the benzo[a]pyrene. A second hydrogenation was conducted with fresh H-Coal Vacuum Gas Oil No. 1334 under the same conditions, but with the used catalyst from the first hydrogenation. The used catalyst left 65% of the benzo[a]pyrene after two hrs and was unable to reduce any more of the benzo[a]pyrene after four hours of hydrogenation. This study strongly indicates catalyst deactivation as the major problem hindering more efficient reduction of PAH tumorigens.

Examination of the temperature-dependence of the reduction of benzo[a]pyrene can provide useful thermodynamic information and may allow estimation of the minimum temperature required to reduce 99% or more of the benzo[a]pyrene under the conditions of the batchwise hydrogenation in the Parr Mini Reactor. Table 4.11 presents the results of studies using both laboratory and industrial catalysts. Both the palladium on charcoal and the Shell 324M catalysts require at least 320°C before appreciable percentages of benzo[a]pyrene are reduced. A least-squares fit to an Arrhenius-type plot of the percentage of benzo[a]pyrene reduced in one hour at the indicated temperature versus the reciprocal of the hydrogenation temperature in °K allows an estimation of the apparent activation energy for the reduction of benzo[a]pyrene in this complex mixture. The activation energy for the reduction with palladium on charcoal is ca. 2 kcal/mole, and ca. 6 kcal/mole for the sulfided Shell 324M catalyst. These differences reflect the lesser efficiency of the industrial catalyst under these conditions. However, more data points are needed to construct a better plot and calculate more precise activation energies. Extrapolating the curves to a

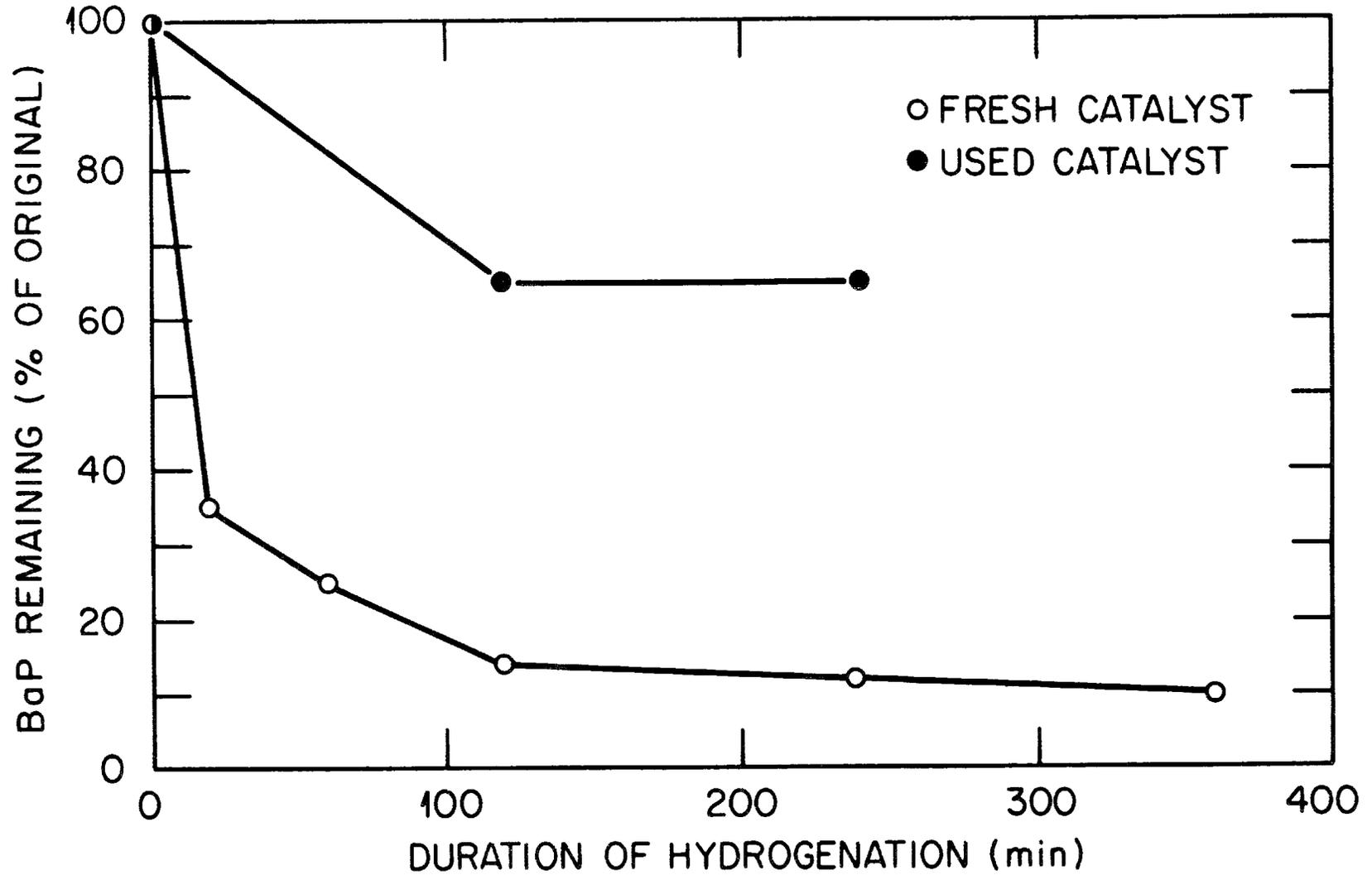


Figure 4.6. Comparison of Effectiveness of New and Used Shell 324M Sulfided Catalyst for the Reduction of BaP in H-Coal No. 1334 Vacuum Gas Oil (>343°C/>650°F).

Table 4.11

THE EFFECTS OF HYDROTREATMENT TEMPERATURE ON THE REDUCTION OF BaP IN  
H-COAL VACUUM GAS OIL NO. 1334 (>343°C/>650°F) BY VARIOUS CATALYSTS

Catalyst	% Benzo[a]pyrene Remaining in H-Coal No. 1334 VGO After Hydrotreatment				
	<u>20°C</u>	<u>100°C</u>	<u>150°C</u>	<u>240°C</u>	<u>320°C</u>
Pd/C (1/10)	83	70	63	-	7
Shell 324 M (3% NiO; 20% MoO <sub>3</sub> )	-	-	99	-	73
Sulfided Shell 324 M (S = 10.9%)	-	-	89	85	18

99% reduction of benzo[a]pyrene suggests that temperatures of ca. 350°C (662°F) would be required for batchwise reductions such as are conducted using the Parr Mini Reactor. Certainly much research remains for the optimization of tumorigen PAH reduction conditions and catalyst.

## 5.0 ALTERNATIVE AND SUPPLEMENTAL TREATMENTS

The studies reported in the previous section clearly demonstrate that hydrotreatment is very effective for virtually eliminating the tumorigenicity of crude coal liquids. However, hydrotreatment is relatively expensive (Wu et al. 1968, Maruhnich et al. 1982) and the main issue now is one of economics. The central question is whether other treatments may be effective and economical in replacing or supplementing hydrotreatment in the toxicity beneficiation of crude coal liquids. This section discusses and evaluates several alternative and supplemental treatments tested in this laboratory for coal liquids in terms of their tumorigenicity reduction. Bacterial mutagenicity, ten-animal dermal screening, and benzo(a)pyrene are used as tumorigenicity measures.

### 5.1 Alternate Upgrading Treatments

The two general approaches to reduce the toxicity of complex organic mixtures are to either remove or chemically change the offending chemical constituents. Thermal separation, acid/base washing, precipitation, solvent extraction, and adsorption are common petroleum upgrading methods for removing non-desirable materials. Chemical reactions involving hydrotreatment, oxidation, and catalytic conversion are general petroleum refinery processes for effecting chemical change.

Although well developed, petroleum refinery processes (Gruse et al. 1960, Chem Tech 1972) are not specifically designed for eliminating the toxicity of crude petroleum. It is logical to evaluate such available petroleum refinery processes for dealing with the toxicity problems caused by crude coal liquids because they are likely to be used to prepare final products. Seven alternative treatments related in some way to processes commonly carried out in a petroleum refinery were chosen and evaluated for their effectiveness in reducing the tumorigenicity of coal liquids. These seven treatments (Ho et al. 1984, 1985) were:

1. Distillation (thermal separation)
2. Acid Treatment (washing)
3. Alkaline Treatment (washing)
4. Pentane Deasphalting (precipitation)

5. Pentane/Furfural Partition (solvent extraction)
6. Clay Percolation (adsorption), and
7. Air/H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>-Catalyst Oxidation (oxidation)

The degree of effectiveness of those treatments was determined based on product yield, mutagenicity, and tumorigenicity. Product yield was measured by weighing the product after the treatment. Mutagenicity was determined by the Ames bacterial assay and tumorigenicity was measured by a 40-week C3H mouse skin painting assay.

Distillation is the most common refinery process. It separates products or process stream materials on the basis of boiling range. This process was investigated using a laboratory large scale still (four-liter charge capacity). About four liters of each oil sample was first mixed with anhydrous calcium chloride to remove suspended water. (It is very important to remove water in order to prevent water-bumping during a vacuum distillation.) After the filtration, the dried oil sample was placed in a 5 L capacity distillation flask. The oil sample was then distilled in a Kontes-Martin MKIV-B Fractionator system. This system consists of a 1 M long, 25 mm Oldershaw column and a temperature controller/monitor. The column has 30 physical plates efficiency. Vacuum was generated either by aspirator or oil pump. During the distillation, the highest pot temperature did not exceed 265°C (530°F) at 1 mm of pressure. The boiling ranges of fractions collected are specified in the accompanying tables as the atmospheric equivalent temperature. Four oil samples (H-Coal Heavy Oil No. 695, 888, and 1334, and H-Coal Blend No. 931) were subjected to distillation. H-Coal Heavy Oil No. 695 was distilled into six fractions while the other three oil samples were distilled into two fractions.

The results of mutagenicity and tumorigenicity testing of each distillate fraction are summarized in Table 5.1. The data clearly shows that both mutagenicity and tumorigenicity are localized in distillate fractions boiling above ca. 343°C (650°F). This finding is expected from the boiling points of known mutagens and tumorigens, such as benzo[a]pyrene (b.p. 495°C). Distillation is again confirmed as an effective means (Wilson et al. 1982a, 1982b; Ho et al. 1984, 1985) of segregating mutagens and tumorigens from crude coal liquids. From each of the four H-Coal oil samples fractionated in this study, 70% to 80% of the original mass had a boiling range of less than 343°C (650°F) and was virtually non-tumorigenic



and non-mutagenic. Thus, simple distillation allows recovery of more than 70% of the mass of each Heavy Oil or of the H-Coal Blend studied in a form that is toxicologically acceptable for direct use or only requiring a mild upgrading. Distillation may be a generally desirable first step in the tumorigenicity beneficiation of crude coal liquids.

Segregating tumorigens by boiling range is helpful but not sufficient. Up to 30% of the heavy oil product is lost to the usable product slate if its toxicological properties preclude further use. Vacuum Gas Oil (>343°C/650°F) fractions of several H-Coal Heavy Oil products were prepared to evaluate hydrogenative and other treatments which promise to reduce their tumorigenicity. Non-hydrogenative procedures tested are summarized as follows:

- a. Concentrated Sulfuric Acid Treatment. One hundred grams of each vacuum gas oil and 450 mL of benzene were stirred and heated to ca. 70°C in a bottle. A total of 8.2 g of concentrated H<sub>2</sub>SO<sub>4</sub> (98%) was added dropwise, and the mixture was stirred overnight. The reaction mixture was filtered to separate the phases and the acid residue was washed with benzene. The benzene in the combined filtrate and solvent wash was removed by rotary evaporation, and the remaining oil was weighed.
- b. Sodium Hydroxide Treatment. One hundred grams of coal-derived liquid (vacuum gas oil and heavy oil samples) were placed in a 500 mL flask. One hundred mL heptane and 100 mL of 10 N NaOH were added and the mixture was refluxed (98°C) and stirred overnight. The reaction mixture was filtered through a coarse filter paper, and the residue was washed with 500 mL of benzene. The filtrate was transferred to a separatory funnel and the NaOH layer was drained off. The benzene layer was washed with 100 mL of 2 N NaOH, and then three times with 50 mL portions of water. The benzene layer was dried over calcium chloride, filtered, rotary evaporated, and weighed.
- c. Pentane Deasphalting. A 100 gram aliquot of vacuum gas oil was mixed with 60 mL of benzene in a 4 L bottle using a teflon-coated stirring bar at room temperature. Three liters of pentane was added and the mixture was allowed to stand overnight. After filtration through pre-pleated 0.195 mm thick filter paper, the solvent was removed by rotary evaporation and the residue was weighed.

- d. Pentane/Furfural Partitioning. A 100 gram quantity of vacuum gas oil was stirred vigorously at room temperature in an extraction bottle along with 100 mL of furfural. A 100 mL volume of furfural-saturated pentane was added dropwise below the oil-solvent interface. The pentane phase was collected by decantation. The combined pentane phases from eight serial extractions were filtered through filter paper and evaporated to obtain the pentane-soluble material. The furfural phase was evaporated to collect the furfural-soluble product.
- e. Clay Percolation. Twenty-five grams of Attapulgis clay (50-80 mesh) was packed in a glass column of 1.0 cm ID using benzene. Two grams of vacuum gas oil dissolved in five mL of benzene was placed on the column, and was eluted with 200 mL of benzene. The column eluate was collected, evaporated using rotary evaporation, and weighed.
- f. Air/H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>-Ascorbic Acid (Three-Step Oxidation). A 5.42 gram aliquot of sample (VGO-2 of H-Coal No. 888) was extracted thoroughly with boiling heptane. The extract was evaporated to obtain a viscous oil which dissolved completely in 163 mL of heptane. This solution was purged with heptane-saturated air at room temperature for two weeks, and then was filtered to remove the black precipitate. The filtrate was stirred with five mL of 10% H<sub>2</sub>O<sub>2</sub> for one week at room temperature, and then was filtered. The heptane layer was reacted with 10 mL of 5% H<sub>2</sub>O<sub>2</sub> for one week at room temperature. Small amounts of ascorbic acid catalyst (Warren 1943, Kauffmann 1951) were added daily (a total of 1.1 g). The dark precipitate was filtered and the straw-colored heptane layer was evaporated to obtain 2.69 g (72.1% yield) of viscous oil.

Results of mutagenicity testing are summarized in Table 5.2. The data clearly indicate that concentrated H<sub>2</sub>SO<sub>4</sub> treatment, pentane deasphalting, pentane/furfural partition, and clay percolation all are capable of reducing the mutagenicity of high mutagenicity vacuum gas oil samples. Acid treatment is particularly effective. These findings are consistent with what is known of the origin of mutagenicity in coal liquids. Aromatic amines have been identified as the determinant mutagens (Guerin et al. 1980, Wilson et al. 1980) in crude coal liquids, and their basicity would cause them to be extracted by acidic medias (e.g., H<sub>2</sub>SO<sub>4</sub>). Because they also are aromatic, they will preferentially distribute into furfural rather than pentane phase. The polar and aromatic character of aromatic amines also aids in their adsorption on clay. The decrease in mutagenicity upon deasphalting suggests that the aromatic amines are partially precipitated

TABLE 5.2

EFFECT OF ALTERNATE UPGRADING TREATMENTS ON MUTAGENICITY OF H-COAL VACUUM GAS OILS

Treatment	VGO-1 (>343°C/650°F) of H-Coal HO No. 888		VGO-2 (>399°C/750°F) of H-Coal HO No. 888		VGO (>371°C/700°F) of H-Coal HO No. 695		VGO of (>343°C/650°F) of H-Coal HO No. 1334	
	% Yield	Mutag. <sup>a</sup> (rev/ug)	% Yield	Mutag. <sup>a</sup> (rev/ug)	% Yield	Mutag. <sup>a</sup> (rev/ug)	% Yield	Mutag. <sup>a</sup> (rev/ug)
Non-treated VGO	100	30	100	75	100	78	100	67
Conc. H <sub>2</sub> SO <sub>4</sub> Treatment	82	0	57	0	54	0	---	--
10 N NaOH Treatment	---	--	---	--	---	--	73	54
Pentane Deasphalting	80	20	72	6	75	5	---	--
Pentane/Furfural Partition								
Pentane Phase	51	2	21 <sup>b</sup>	1	29 <sup>b</sup>	1	---	--
Furfural Phase	52	44	---	--	82 <sup>b</sup>	22	---	--
Clay Percolation	---	--	81	14	---	--	---	--

<sup>a</sup>Salmonella strain TA98 with Arochlor 1254 induced S9 activation.

<sup>b</sup>A single pentane/furfural (1/1) partition.

out or occluded with the asphaltenes. Aromatic amines are not extractable by alkaline media; thus, NaOH-treated vacuum gas oil still exhibits a very high mutagenicity.

It is worth noting that although pentane/furfural partition was by far one of the most efficient procedures for removing mutagenic activity, it was also the least efficient in recovering upgraded product (20-50% in the pentane phase) which definitely reduces its practical applicability.

Table 5.3 summarizes the skin tumorigenicity data for vacuum gas oils after alternate upgrading treatments. The results show that acid or alkaline treatment, deasphalting, and pentane/furfural partition do not significantly diminish the overall tumorigenicity even though they do eliminate or reduce mutagenicity (above). This finding is not surprising since the tumorigenicity of crude coal liquids is mainly due to polycyclic aromatic hydrocarbons (including heterocyclics) (Holland et al. 1984) which are not affected by alkaline, or acid, or deasphalting treatments. Although polycyclic aromatic hydrocarbons preferentially distribute into the furfural phase in the pentane/furfural partitioning treatment, the extraction into the furfural phase is not complete (See Table 5.4), and concentrations of dermal tumorigen polycyclic aromatic hydrocarbons left behind in the pentane phase are sufficient to induce tumors.

The data (Table 5.3) also show that clay percolation and three-step oxidation treatments are not effective for reducing benzo[a]pyrene concentrations. It is predicted that no tumorigenicity reduction will be achieved by these treatments (no skin tumorigenicity assay has been carried out for the samples treated by these two methods).

Besides total apparent tumor numbers, it is also very important to compare tumor latencies of treated materials before drawing conclusions about the effectiveness of alternate upgrading treatments (Table 5.3). Table 5.5 summarizes the tumor latencies of treated H-Coal vacuum gas oils. In the case of the VGO-1 of H-Coal HO No. 888, none of the treatments delay the tumor-development. In the case of NaOH treated VGO of H-Coal HO No. 1334 the percentage of tumor-development early in the test is less than that of the non-treated counterpart. This finding may indicate that the compounds (acidic) removed by NaOH may exhibit a tumor promoting effect. This is further suggested by the finding (Table 5.6) that NaOH-treated Heavy Oil 1334 is less tumorigenic than its untreated parent.

Table 5.3

EFFECT OF ALTERNATE UPGRADING TREATMENTS ON TUMORIGENICITY<sup>a</sup>  
AND BENZO[a]PYRENE CONTENT OF H-COAL VACUUM GAS OILS

Treatment	VGO-1 (>343°C/650°F) of H-Coal HO No. 888			VGO of (>343°C/650°F) of H-Coal HO No. 1334			VGO-2 (>399°C/750°F) of H-Coal HO No. 888	
	% Animals with Neoplasms		Mutag. <sup>b</sup> (rev/ug)	% Animals with Neoplasms		Mutag. <sup>b</sup> (rev/ug)	BaP (ug/g)	Mutag. <sup>b</sup> (rev/ug)
	Female	Male		Female	Male			
Non-treated VGO	100	100	30	100	100	67	1150	75
Conc. H <sub>2</sub> SO <sub>4</sub> Treatment	100	100	0	---	---	--	1110	0
10 N NaOH Treatment	---	---	--	100	100	54	----	--
Pentane Deasphalting	100	100	20	---	---	--	1060	6
Pentane/Furfural Partition								
Pentane Phase	100	100	2	---	---	--	149	1
Furfural Phase	100	100	44	---	---	--	----	--
Clay Percolation	---	---	--	---	---	--	1230	14
Three-Step Oxidation	---	---	--	---	---	--	912	--

<sup>a</sup>5 male plus 5 female C<sub>3</sub>H mice per group, 2 X per week, 40 weeks of topical application, 50% dose group.

<sup>b</sup>Mutagenicity is included for comparison purposes. Salmonella strain TA98 with Arochlor 1254 induced S9 activation.

Table 5.4

DERMAL TUMORIGEN DISTRIBUTION BETWEEN THE PENTANE AND FURFURAL PHASES OF VGO-1 (>343°C/650°F) OF H-COAL HO, NO. 888

Compound	Pentane Phase (ug/g)	Furfural Phase <sup>a</sup> (ug/g)
Benz(a)anthracene	30	1000
Chrysene	30	670
Benzo(a)pyrene	40	160
Benzo(b)fluoranthene	40	40
Benzo(k)fluoranthene	43	131
Indeno(1,2,3-cd)pyrene	57	275
Benzo(ghi)perylene	60	235
Dibenz(a,h)anthracene	ND <sup>b</sup>	63

<sup>a</sup>It was estimated that 25% of this fraction was not soluble in a 1:1 mixture of hexane and methylene chloride. This may have caused the analytical results to be biased low.

<sup>b</sup>ND = not detected.

Table 5.5

## TUMORIGENIC LATENCIES OF H-COAL VACUUM GAS OILS TREATED BY ALTERNATE UPGRADING METHODS

Cumulative Percentage of Mice with Skin Neoplasms <sup>a</sup>								
Month	VGO-1 (>343°C/650°F) of H-Coal HO, No. 888					VGO (>343°C) of H-Coal HO, No. 1334		
	Non-treated	Conc. H <sub>2</sub> SO <sub>4</sub> Treatment	Pentane Deasphalting	Pentane Phase (Pentane/Furfural Part.)	Furfural Phase (Pentane/Furfural Part.)	Non-treated	10N NaOH Treatment	
1	0	0	0	0	0	0	0	
2	0	0	0	0	0	0	0	
3	0	0	0	10	0	20	10	
4	0	20	0	40	0	30	10	
5	20	30	20	60	30	60	30	
6	30	60	20	90	60	80	70	
7	60	60	60	90	80	100	90	
8	100	100	100	100	100		90	

<sup>a</sup>Five male plus five female C3H mice per group, 2X per week, 50% dose.

Table 5.6

## TUMORIGENICITY OF ACID-DEPLETED H-COAL HEAVY OIL NO. 1334 AND ITS VACUUM GAS OIL FRACTION

Month	Cumulative Percentage of Mice with Skin Tumor <sup>a</sup>					
	H-Coal HO No. 1334				VGO (>343°C/650°F) of H-Coal HO, No. 1334	
	Non-treated HO		Acid Depleted HO <sup>b</sup>		Non-treated VGO	Acid Depleted VGO <sup>b</sup>
	50% <sup>c</sup>	100% <sup>c</sup>	50% <sup>c</sup>	100% <sup>c</sup>	50% <sup>c</sup>	50% <sup>c</sup>
1	0	0	0	0	0	0
2	0	0	0	0	0	0
3	0	0	0	0	20	10
4	0	20	0	0	30	10
5	0	30	0	10	60	30
6	0	30	10	20	80	70
7	20	30	10	40	100 <sup>d</sup>	90
8	20	70	10	50		90
9	50	100 <sup>d</sup>	10	60		90
10	50		10	90		90
11	50		10	90		90

<sup>a</sup>Five male plus five female C3H mice per group, 2X per week.

<sup>b</sup>Treated with 10 N NaOH.

<sup>c</sup>Dose (w/v) in percentage.

<sup>d</sup>100% tumor incidence, no animals remaining for test.

## 5.2 Supplemental Treatments

From the above, it is clearly shown that alternate upgrading processes tested here are not able to eliminate or significantly reduce the tumorigenicity or tumorigens in coal-derived vacuum gas oils. However, these processes used as pretreatments to hydrogenation may improve the efficiency of detoxification by removing compounds which poison the catalyst and which act as a "hydrogen sink".

Since benzo[a]pyrene (BaP) is useful as a qualitative indicator for skin tumorigenicity, the effectiveness of the supplemental (prior to hydrogenation) treatments investigated is based on their ability to reduce BaP. Hydrogenation was carried out in a stainless steel, 300 mL Parr "Mini" Reactor. The hydrogenation procedure is described in Section 4 of this report. The applied temperature and pressure are relatively low (compared to petroleum hydrotreatment conditions) since this study is only designed for comparison purposes and not for optimal condition development.

The acidic treatment is very efficient in removing basic nitrogen compounds (mutagens) and alkaline treatment is very effective in removing acidic oxygen compounds (tumorigenic promoters). Since nitrogen and oxygen compounds also easily poison hydrogenation catalysts, acidic and alkaline treatments were chosen as supplemental treatments for initial study.

The procedures for both 10 N alkaline and 10 N acid pretreatments is similar to that shown in the alternate upgrading treatment section (10 N NaOH treatment). An aliquot of three grams of pretreated or non-treated vacuum gas oil was reacted for one hour in a Parr "Mini" Reactor with 1,200 psig of hydrogen in 150 mL of heptane or dodecane at 150°C (or 320°C) over 300 mg of catalyst. A sample was taken for benzo[a]pyrene analysis.

Table 5.7 summarizes the percentage of BaP reduced by Pd/C or sulfided Shell 324 M catalytic hydrotreatment with and without acid/alkaline pretreatment. Pd/C catalytic hydrotreatment was carried out at mild temperature (150°C) but sulfided Shell 324 M catalytic hydrotreatment was carried out under more severe conditions (320°C). In Section 4, it was shown that commercial catalysts should be tested under severe conditions in order to determine their effects on the reduction of BaP. The data (Table 5.7) clearly indicate that the percentage of BaP reduced by the industrial catalyst (sulfided Shell 324 M) was unaffected by the acidic pretreatment of

Table 5.7

THE INFLUENCE OF ACIDIC AND ALKALINE SAMPLE PRETREATMENTS ON THE  
REDUCTION OF BaP IN VGO (>343°/650°F) OF H-COAL HO NO. 1334

<u>Catalyst</u>	<u>% BaP Remaining After Hydrogenation</u>	
	<u>Pd/C</u> <u>(1/10)<sup>a</sup></u>	<u>Sulfided</u> <u>Shell 324 M<sup>b</sup></u>
<u>Sample Pretreatment</u>		
None-Pretreatment	63	18
10 N H <sub>2</sub> SO <sub>4</sub> Pretreatment at 91°C and 14.7 psig (1 atm.)	5	16
10 N NaOH Pretreatment at 91°C and 14.7 psig (1 atm.)	34	65
2 N NaOH Pretreatment <sup>c</sup> at 23°C and 14.7 psig (1 atm.)	49	-
2 N NaOH Pretreatment <sup>d</sup> at 343°C and 2,400 psig	82	-

<sup>a</sup>Hydrogenation for one hour at 150°C and 1200/psig.

<sup>b</sup>Hydrogenation for one hour at 320°C and 1200/psig.

<sup>c</sup>Pretreatment carried out at room temperature (without solvent refluxing).

<sup>d</sup>The high temperature and pressure pretreatment carried out in a Parr  
"Mini" Reactor.

the sample, but this pretreatment dramatically improved the reduction of BaP by Pd/C under milder conditions. The alkaline treatments have no significant positive effects and, under some conditions, appear to produce compounds which interfere in the hydrogenation of BaP with both commercial and laboratory catalysts.

## 6.0 Conclusions

Hydrotreatment is confirmed to be a very effective means for reducing the tumorigenicity of coal liquids. Tumorigenicity is not totally eliminated by hydrotreatment but it can be reduced to levels comparable to those exhibited by petroleum equivalents. Removing residual tumorigenicity completely may require treatments which totally eliminate complete tumorigens, or alter tumor promoters in addition to reducing tumor initiators. Variations in catalyst, hydrotreatment conditions, or combining pretreatments with hydrogenation may allow a practical further reduction in tumorigenicity.

Physical specifications are inadequate to predict the tumorigenicity of refined products. Measures of benzo(a)pyrene or bacterial mutagenicity and ten-animal dermal tumorigenicity screening are useful at high levels of tumorigenicity found in refined products. The relationship between these measures remains inadequately defined. Lifetime skin painting bioassays are currently required to quantitate tumorigenicity of refined products.

Distillation is effective for reducing the mutagenicity and tumorigenicity of oils by segregating the bioactive constituents into the vacuum gas oil boiling range material. The concentrated bioactive materials must subsequently be treated, however. Other treatments such as acid or alkaline washing, furfural partition, and clay adsorption exhibit varying degrees of success for segregating tumorigens. None are as effective as is hydrotreatment.



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## APPENDIX A

## Chemical and Physical Properties of Oils

The physical and chemical properties of samples considered in this report are summarized here for future reference and to allow the readers assessment of the relevance of the samples to petroleum equivalents. Details of major organic composition are included for further documentation.



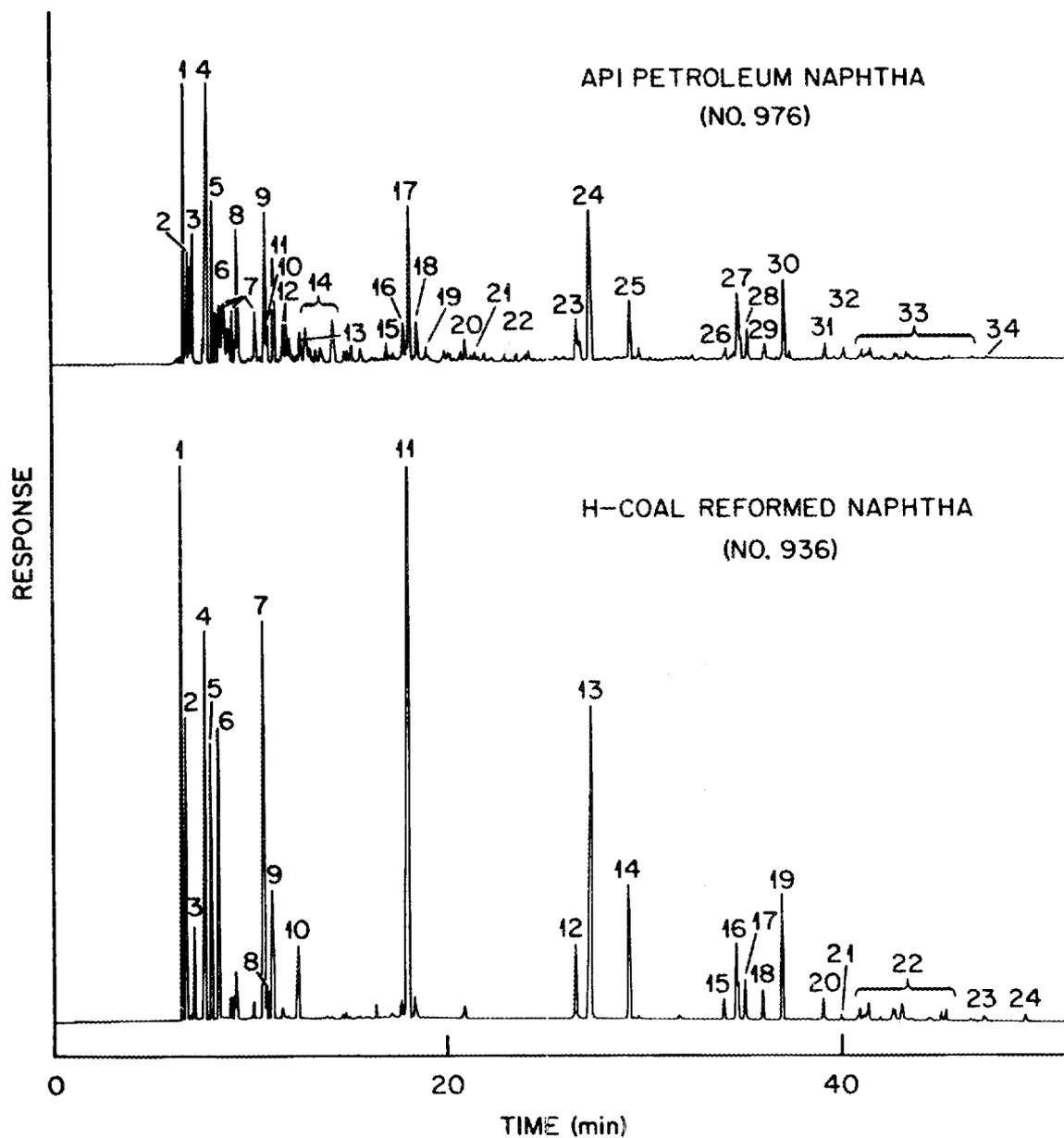


Figure A.1. Capillary Column Gas Chromatography Major Composition Profiles of a) No. 976 API Light Catalytically Cracked Naphtha and b) No. 936 H-Coal Reformed Naphtha. (Peak identifications are listed in Tables A.6 and A.10.)

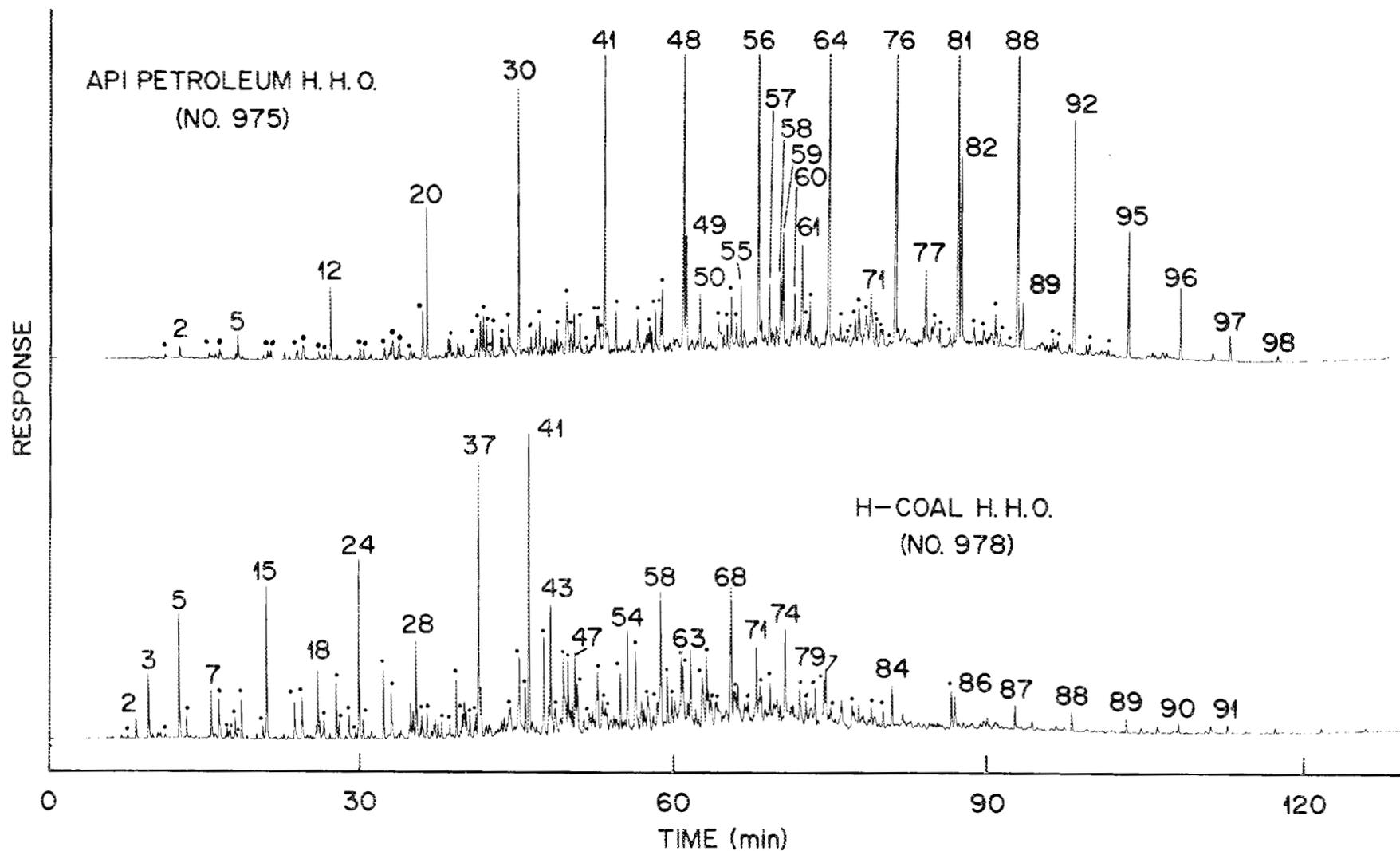


Figure A.2. Capillary Column Gas Chromatography Major Composition Profiles of a) No. 975 API No. 2 Fuel Oil and b) No. 978 H-Coal Home Heating Oil. (Peak identifications in Tables A.7 and A.12.)

TABLE A.1

ORIGIN, PROPERTIES, AND COMPOSITIONAL DATA FOR H-COAL BLEND AFTER WATER WASHING  
(No. 931)

Origin: 40/60 (wt./wt.) blend of Light and Heavy Oils collected at the H-Coal Pilot Plant (Catlettsburg, KY) on September 25, 1981, during run no. 8 on Ill. No. 6 Coal in the Synfuel mode.

Upgrading: Blended and water-washed by the Chevron Research Company (Richmond, CA).

Ultimate Analysis

C, wt. %	88.67
H, wt. %	10.12
N, ppm	5,200
S, ppm	1,100
O, wt. %	0.58

Chemical Class Fractions

Ether-Soluble Bases, wt. %	3.3
Ether-Soluble Acids, wt. %	1.5
Saturates, wt. %	30.8
Mono/Diaromatics, wt. %	56.7
Polyaromatics, wt. %	5.8

Physical Parameters

Simulated Distillation	
IBP, °C (°F)	193 (379)
ABP, °C (°F)	260 (500)
FBP, °C (°F)	396 (745)
Density, g/cm <sup>3</sup> @ 25°C	0.968
Viscosity, cSt @ 25°C	7.05
Pour Point, °C (°F)	-25 (-13)
Flash Point, °C (°F)	96 (205)

Selected Compounds

Benzo(a)pyrene, ug/g	50
Phenol, mg/g	0.15
o-Cresol, mg/g	0.55
Quinoline, ug/g	164

TABLE A.2

ORIGIN, PROPERTIES, AND COMPOSITIONAL DATA FOR H-COAL  
BLEND-HYDROTREATED AT LOW SEVERITY (No. 934)

Origin: 40/60 (wt./wt.) blend of Light and Heavy Oils collected at the H-Coal Pilot Plant (Catlettsburg, KY) on Sept. 25, 1981, during run no. 8 on Ill. No. 6 Coal in the Symfuel mode.

Upgrading: Blended, water-washed, and hydrotreated at low severity (900 SCF H<sub>2</sub>/BBL) by the Chevron Research Company (Richmond, CA).

Ultimate Analysis

C, wt. %	88.16
H, wt. %	11.19
N, ppm	2,600
S, ppm	<10
O, wt. %	0.39

Chemical Class Fractions

Ether-Soluble Bases, wt. %	2.4
Ether-Soluble Acids, wt. %	0.8
Saturates, wt. %	38.3
Mono/Diaromatics, wt. %	46.5
Polyaromatics, wt. %	1.3

Physical Parameters

Simulated Distillation	
IBP, °C (°F)	125 (257)
ABP, °C (°F)	256 (493)
FBP, °C (°F)	388 (730)
Density, g/cm <sup>3</sup> @ 25°C	0.934
Viscosity, cSt @ 25°C	4.82
Pour Point, °C (°F)	-18 (0.4)
Flash Point, °C (°F)	66 (151)

Selected Compounds

Benzo(a)pyrene, ug/g	<0.6
Phenol, mg/g	0.13
o-Cresol, mg/g	0.36
Quinoline, ug/g	6

TABLE A.3

ORIGIN, PROPERTIES, AND COMPOSITIONAL DATA FOR H-COAL BLEND-HYDROTREATED AT  
MEDIUM SEVERITY (No. 933)

Origin: 40/60 (wt./wt.) blend of Light and Heavy Oils collected at the H-Coal Pilot Plant (Catlettsburg, KY) on September 25, 1981, during run no. 8 on Ill. No. 6 Coal in the Synfuel mode.

Upgrading: Blended and hydrotreated at medium severity (1,400 SCF H<sub>2</sub>/BBL) by the Chevron Research Company (Richmond, CA)

<u>Ultimate Analysis</u>		<u>Chemical Class Fractions</u>	
C, wt. %	88.81	Ether-Soluble Bases, wt. %	0.6
H, wt. %	11.64	Ether-Soluble Acids, wt. %	0.6
N, ppm	500	Saturates, wt. %	35.9
S, ppm	<10	Mono/Diaromatics, wt. %	46.7
O, wt. %	<0.01	Polyaromatics, wt. %	0.8
<u>Physical Parameters</u>		<u>Selected Compounds</u>	
Simulated Distillation		Benzo(a)pyrene, ug/g	<1
IBP, °C (°F)	107 (225)	Phenol, mg/g	0.13
ABP, °C (°F)	249 (480)	o-Cresol, mg/g	0.41
FBP, °C (°F)	387 (729)	Quinoline, ug/g	<1
Density, g/cm <sup>3</sup> @ 25°C	0.916		
Viscosity, cSt @ 25°C	3.74		
Pour Point, °C (°F)	-25 (-13)		
Flash Point, °C (°F)	48 (118)		

TABLE A.4

ORIGIN, PROPERTIES, AND COMPOSITIONAL DATA FOR H-COAL BLEND-HYDROTREATED  
AT HIGH SEVERITY (No. 935)

Origin: 40/60 (wt./wt.) blend of Light and Heavy Oils collected at the H-Coal Pilot Plant (Catlettsburg, KY) on Sept. 25, 1981, during run no. 8 on Ill. No. 6 Coal in the Synfuel mode.

Upgrading: Blended, water-washed, and hydrotreated at high severity (3,000 SCF H<sub>2</sub>/BBL) by the Chevron Research Company (Richmond, CA).

<u>Ultimate Analysis</u>		<u>Chemical Class Fractions</u>	
C, wt. %	87.77	Ether-Soluble Bases, wt. %	0.7
H, wt. %	13.53	Ether-Soluble Acids, wt. %	0.5
N, ppm	<100	Saturates, wt. %	58.9
S, ppm	<10	Mono/Diaromatics, wt. %	8.3
O, wt. %	<0.01	Polyaromatics, wt. %	0.5
 <u>Physical Parameters</u>		 <u>Selected Compounds</u>	
Simulated Distillation		Benzo(a)pyrene, ug/g	<1
IBP, °C (°F)	84 (183)	Phenol, mg/g	<0.1
ABP, °C (°F)	241 (466)	o-Cresol, mg/g	<0.1
FBP, °C (°F)	363 (685)	Quinoline, ug/g	<1
Density, g/cm <sup>3</sup> @ 25°C	0.867		
Viscosity, cSt @ 25°C	2.68		
Pour Point, °C (°F)	-28 (-18)		
Flash Point, °C (°F)	-40 (-40)		

TABLE A.5

## ORIGIN, PROPERTIES, AND COMPOSITIONAL DATA FOR H-COAL REFORMED NAPHTHA (No. 936)

Origin: 40/60 (wt./wt.) blend of Light and Heavy Oils collected at the H-Coal Pilot Plant (Catlettsburg, KY) on Sept. 25, 1981, during run no. 8 on Ill. No. 6 Coal in the Synfuel mode.

Upgrading: Blended, water-washed, hydrotreated at high severity, and hydrocracked by the Chevron Research Company (Richmond, CA). Catalytically reformed by Universal Oil Products Inc. (Now the Signal Research Center, Inc., Des Plaines, IL).

<u>Ultimate Analysis</u>		<u>Chemical Class Fractions</u>	
C, wt. %	87.5	Volatiles, wt. %	66.6
H, wt. %	12.2	Ether-Soluble Bases, wt. %	0.1
N, ppm	<100	Ether-Soluble Acids, wt. %	0.6
S, ppm	<1	Saturates, wt. %	0.4
O, wt. %	0.3	Mono/Diaromatics, wt. %	13.1
		Polyaromatics, wt. %	0.1
<u>Physical Parameters</u>		<u>Selected Compounds</u>	
Simulated Distillation		Benzo(a)pyrene, ug/g	1.4
IBP, °C (°F)	78 (172)	Benzene, mg/g	49.7
ABP, °C (°F)	102 (216)	Toluene, mg/g	180
FBP, °C (°F)	198 (389) <sup>a</sup>	Ethyl Benzene, mg/g	23.6
Density, g/cm <sup>3</sup> @ 25°C	0.781	m-Xylene, mg/g	89.0
Viscosity, cSt @ 25°C	0.60	p-Xylene, mg/g	37.7
Pour Point, °C (°F)	<-30 (<-22)	o-Xylene, mg/g	47.4
Flash Point, °C (°F)	<-10 (<14)	i-Propyl Benzene, mg/g	1.4
		n-Propyl Benzene, mg/g	7.5
		1,3,5-Trimethyl Benzene, mg/g	15.6
		n-Butyl Benzene, mg/g	0.5

<sup>a</sup>UOP data.

Table A.6

IDENTIFICATION OF MAJOR ORGANIC COMPOUNDS IN H-COAL  
REFORMED NAPHTHA (NO. 936) BY GC RETENTION AND/OR GC-MS

Peak No. <sup>a</sup>	Identification <sup>b</sup>
1	i-C <sub>5</sub> H <sub>12</sub>
2	n-C <sub>5</sub> H <sub>12</sub>
3	C <sub>5</sub> H <sub>12</sub>
4	C <sub>6</sub> H <sub>14</sub> , possibly 2,3-Dimethyl C <sub>4</sub> and/or 2-Methyl C <sub>5</sub>
5	C <sub>6</sub> H <sub>14</sub> , maybe 3-Methyl C <sub>5</sub>
6	n-C <sub>6</sub> H <sub>14</sub>
7	Benzene
8	C <sub>7</sub> H <sub>16</sub>
9	C <sub>7</sub> H <sub>16</sub> , maybe 3-Methyl C <sub>6</sub>
10	n-C <sub>7</sub> H <sub>16</sub>
11	Toluene
12	Ethyl Benzene
13	m- and/or p-Xylene
14	o-Xylene
15	n-Propyl Benzene
16	C <sub>3</sub> -Benzene
17	1,3,5-Trimethyl Benzene
18	C <sub>3</sub> -Benzene
19	C <sub>3</sub> -Benzene
20	C <sub>3</sub> -Benzene
21	Indane
22	C <sub>4</sub> -Benzene (6 isomers)
23	C <sub>1</sub> -Indane
24	Naphthalene

<sup>a</sup>See Figure A.1

<sup>b</sup>Specific isomer named if retention time and mass spectrum match authentic standard. Other assignments possible where only generic isomer listed.

TABLE A.7

## ORIGIN, PROPERTIES, AND COMPOSITIONAL DATA FOR H-COAL HOME HEATING OIL (No. 978)

Origin: 40/60 (wt./wt.) blend of Light and Heavy Oils collected at the H-Coal Pilot Plant (Catlettsburg, KY) on September 25, 1981, during run no. 8 on Ill. No. 6 Coal in the Synfuel mode.

Upgrading: Blended, water-washed, and hydrotreated at high severity (ca. 3,000 SCF H<sub>2</sub>/BBL) by Chevron Research Company (Richmond, CA). Devolatilized to meet ASTM flash point specification for No. 2 Fuel Oil by the Oak Ridge National Laboratory (Oak Ridge, TN).

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 Physical Parameters
 

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Simulated Distillation	
IBP, °C (°F)	156 (313)
ABP, °C (°F)	234 (453)
FBP, °C (°F)	333 (631)
Density, g/cm <sup>3</sup> @ 16°C (60°F)	0.8747
Viscosity, cSt @ 38°C (100°F)	2.19
Pour Point, °C (°F)	-33 (-27)
Flash Point, °C (°F)	40 (104)

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 Selected Compounds
 

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Benzo(a)pyrene, ug/g	0.08
Benzene, mg/g	2.9
Toluene, mg/g	3.3
Ethyl Benzene, mg/g	2.6
m+p-Xylenes, mg/g	3.5
o-Xylene, mg/g	1.5
i-Propyl Benzene, mg/g	1.3
n-Propyl Benzene, mg/g	2.4
1,3,5-Trimethyl Benzene, mg/g	<0.5
n-Butyl Benzene	<1

Table A.8

IDENTIFICATION OF MAJOR ORGANIC COMPOUNDS IN H-COAL HOME HEATING OIL  
(NO. 978) BY GC RETENTION AND/OR GC-MS

Peak No. <sup>a</sup>	Identification <sup>b</sup>
1	C <sub>1</sub> -Cyclopropane
2	Benzene + Cyclohexane
3	C <sub>1</sub> -Cyclohexane
4	n-C <sub>7</sub> H <sub>16</sub>
5	C <sub>1</sub> -Cyclohexane
6	C <sub>2</sub> -Cyclopropane
7	Toluene
8	C <sub>2</sub> -Cyclohexane
9	C <sub>3</sub> -Cyclopropane
10	C <sub>3</sub> -Cyclopropane
11	C <sub>2</sub> -Cyclohexane
12	n-C <sub>8</sub> H <sub>18</sub>
13	C <sub>2</sub> -Cyclohexane
14	C <sub>2</sub> -Cyclohexane
15	C <sub>2</sub> -Cyclohexane or C <sub>3</sub> -Cyclopropane
16	Ethyl Benzene
17	m- and/or p-Xylene
18	C <sub>3</sub> -Cyclohexane
19	o-Xylene
20	C <sub>3</sub> -Cyclohexane
21	C <sub>3</sub> -Cyclohexane
22	C <sub>3</sub> -Cyclohexane
23	C <sub>3</sub> -Benzene
24	C <sub>3</sub> -Cyclohexane
25	C <sub>4</sub> -Cyclopropane
26	C <sub>3</sub> -Benzene
27	C <sub>3</sub> -Benzene
28	m/z 124, possibly 1-H, octahydroindene
29	C <sub>3</sub> -Benzene + C <sub>4</sub> -Cyclohexane
30	C <sub>4</sub> -Cyclohexane
31	Unsaturated Hydrocarbon, maybe C <sub>10</sub> H <sub>18</sub>
32	C <sub>4</sub> -Benzene
33	C <sub>4</sub> -Cyclohexane
34	Indane
35	C <sub>4</sub> -Benzene

Table A.8 (Cont'd)

IDENTIFICATION OF MAJOR ORGANIC COMPOUNDS IN H-COAL HOME HEATING OIL  
(NO. 978) BY GC RETENTION AND/OR GC-MS

Peak No. <sup>a</sup>	Identification <sup>b</sup>
36	C <sub>4</sub> -Benzene
37	trans-Decahydronaphthalene
38	C <sub>1</sub> -Indane
39	cis-Decahydronaphthalene
40	C <sub>1</sub> -Decahydronaphthalene
41	C <sub>1</sub> -Decahydronaphthalene
42	C <sub>1</sub> -Decahydronaphthalene
43	C <sub>1</sub> -Decahydronaphthalene
44	C <sub>1</sub> -Indane
45	C <sub>1</sub> -Decahydronaphthalene
46	C <sub>1</sub> -Indane
47	C <sub>4</sub> -Naphthalene
48	C <sub>2</sub> -Decahydronaphthalene
49	C <sub>2</sub> -Decahydronaphthalene
50	C <sub>2</sub> -Decahydronaphthalene
51	n-C <sub>12</sub> H <sub>26</sub>
52	C <sub>1</sub> -Indane
53	C <sub>1</sub> -Tetrahydronaphthalene, possibly 2-Methyl isomer
54	C <sub>2</sub> -Decahydronaphthalene
55	m/z 168
56	C <sub>1</sub> -Indane
57	C <sub>1</sub> -Indane
58	C <sub>1</sub> -Tetrahydronaphthalene
59	m/z 166
60	C <sub>1</sub> -Indane
61	C <sub>1</sub> -Tetrahydronaphthalene
62	n-C <sub>13</sub> H <sub>28</sub>
63	bicyclic hydrocarbon, possibly bicyclohexyl
64	C <sub>7</sub> -Benzene
65	C <sub>3</sub> -Decahydronaphthalene
66	C <sub>3</sub> -Indane
67	m/z 182
68	m/z 178, possibly Dodecahydrofluorene
69	C <sub>3</sub> -Indane
70	C <sub>4</sub> -Decahydronaphthalene
71	n-C <sub>14</sub> H <sub>30</sub>

Table A.8 (Cont'd)

IDENTIFICATION OF MAJOR ORGANIC COMPOUNDS IN H-COAL HOME HEATING OIL  
(NO. 978) BY GC RETENTION AND/OR GC-MS

Peak No. <sup>a</sup>	Identification <sup>b</sup>
72	m/z 192
73	Unknown
74	C <sub>4</sub> -Decahydronaphthalene
75	C <sub>4</sub> -Indane
76	m/z 192
77	m/z 192
78	m/z 192
79	n-C <sub>15</sub> H <sub>32</sub>
80	m/z 192
81	m/z 192
82	C <sub>4</sub> -Dihydronaphthalene
83	C <sub>4</sub> -Dihydronaphthalene
84	n-C <sub>16</sub> H <sub>34</sub>
85	m/z 218
86	n-C <sub>17</sub> H <sub>36</sub>
87	n-C <sub>18</sub> H <sub>38</sub>
88	n-C <sub>19</sub> H <sub>40</sub>
89	n-C <sub>20</sub> H <sub>42</sub>
90	n-C <sub>21</sub> H <sub>44</sub>
91	n-C <sub>22</sub> H <sub>46</sub>

<sup>a</sup>See Figure A.2

<sup>b</sup>Specific isomer named if retention time and mass spectrum match authentic standard. Other assignments possibly where only generic isomer listed.

TABLE A.9  
 ORIGIN, PROPERTIES, AND COMPOSITIONAL DATA FOR API  
 LIGHT CATALYTICALLY CRACKED NAPHTHA (No. 976)

Origin: Petroleum-derived product API number 81-04 supplied by the American Petroleum Institute (Washington, DC).

Upgrading: "Produced by distillation of products from a catalytic cracking process."<sup>a</sup>

<u>Ultimate Analysis</u>		<u>Chemical Class Fractions</u>	
C, wt. %	85.2	Volatiles, wt. %	62.9
H, wt. %	13.8	Ether-Soluble Bases, wt. %	<0.1
N, ppm	250	Ether-Soluble Acids, wt. %	<0.1
S, ppm	<10	Saturates, wt. %	1.0
O, wt. %	0.97	Mono/Diaromatics, wt. %	12.1
		Polyaromatics, wt. %	<0.1
 <u>Physical Parameters</u>		 <u>Selected Compounds</u>	
Simulated Distillation		Benzo(a)pyrene, ug/g	<0.002
IBP, °C (°F)	148 (298)	Benzene, mg/g	7.4
ABP, °C (°F)	154 (309)	Toluene, mg/g	43.1
FBP, °C (°F)	197 (387)	Ethyl Benzene, mg/g	14.1
Density, g/cm <sup>3</sup> @ 25°C	0.730	m+p-Xylenes, mg/g	58.6
Viscosity, cSt @ 25°C	0.57	o-Xylene, mg/g	20.2
Pour Point, °C (°F)	<-40 (<-40)	n-Propyl Benzene, mg/g	3.6
Flash Point, °C (°F)	<-35 (<-31)	1,3,5-Trimethyl Benzene, mg/g	12.3

<sup>a</sup>Description supplied with the sample by the API.

Table A.10

IDENTIFICATION OF MAJOR ORGANIC COMPOUNDS IN API LIGHT  
CATALYTICALLY CRACKED NAPHTHA (NO. 976) BY GC RETENTION AND/OR GC-MS

Peak No. <sup>a</sup>	Identification <sup>b</sup>
1	i-C <sub>5</sub> H <sub>12</sub>
2	C <sub>6</sub> H <sub>14</sub>
3	C <sub>5</sub> H <sub>10</sub> (2 isomers)
4	C <sub>6</sub> H <sub>14</sub>
5	C <sub>6</sub> H <sub>14</sub>
6	n-C <sub>6</sub> H <sub>14</sub>
7	C <sub>6</sub> H <sub>12</sub> (4 isomers)
8	C <sub>1</sub> -Cyclopropane
9	Benzene
10	C <sub>7</sub> H <sub>16</sub>
11	C <sub>7</sub> H <sub>16</sub> , maybe 3-Methyl C <sub>6</sub>
12	C <sub>2</sub> -Cyclopropane (3 isomers)
13	C <sub>7</sub> H <sub>16</sub>
14	C <sub>7</sub> H <sub>14</sub> (4 isomers)
15	C <sub>7</sub> H <sub>12</sub> or C <sub>8</sub> H <sub>16</sub>
16	C <sub>8</sub> H <sub>18</sub>
17	Toluene
18	C <sub>8</sub> H <sub>18</sub>
19	C <sub>2</sub> -Cyclohexane
20	C <sub>8</sub> H <sub>18</sub>
21	C <sub>2</sub> -Cyclohexane
22	C <sub>2</sub> -Cyclohexane
23	Ethyl Benzene
24	m- and/or p-Xylene
25	o-Xylene
26	n-Propyl Benzene
27	C <sub>3</sub> -Benzene
28	1,3,5-Trimethyl Benzene
29	C <sub>3</sub> -Benzene
30	C <sub>3</sub> -Benzene
31	C <sub>3</sub> -Benzene
32	Indane
33	C <sub>4</sub> -Benzene (6 isomers)
34	C <sub>1</sub> -Indane

<sup>a</sup>See Figure A.1

<sup>b</sup>Specific isomer named if retention time and mass spectrum match authentic standard. Other assignments possible where only generic isomer listed.

TABLE A.11

## ORIGIN, PROPERTIES, AND COMPOSITIONAL DATA FOR API NO. 2 FUEL OIL (No. 975)

Origin: Petroleum-derived product supplied by the American Petroleum Institute (Washington, DC). API number 83-02

Upgrading: 70% Straight run middle distillate (straight run diesel [VPS #5 stripper, 82-3808] plus 30% light catalytically cracked distillate (FC light cycle gas oil, 82-3843).

<u>Ultimate Analysis</u>		<u>Chemical Class Fractions</u>	
C, wt. %	85.9	Ether-Soluble Bases, wt. %	0.1
H, wt. %	13.6	Ether-Soluble Acids, wt. %	0.3
N, ppm	200	Saturates, wt. %	69.8
S, ppm	280	Mono/Diaromatics, wt. %	12.5
O, wt. %	0.4	Polyaromatics, wt. %	1.2
 <u>Physical Parameters</u>		 <u>Selected Compounds</u>	
Simulated Distillation		Benzo(a)pyrene, ug/g	0.04
IBP, °C (°F)	180 (356)	Benzene, mg/g	<0.02
ABP, °C (°F)	261 (502)	Toluene, mg/g	0.3
FBP, °C (°F)	351 (664)	Ethyl Benzene, mg/g	0.2
Density, g/cm <sup>3</sup> @ 25°C	0.827	m-Xylene, mg/g	1.3
Viscosity, cSt @ 25°C	3.13	p-Xylene, mg/g	0.8
Pour Point, °C (°F)	-17 (1.4)	o-Xylene, mg/g	0.6
Flash Point, °C (°F)	65 (149)	i-Propyl Benzene, mg/g	<0.3
		n-Propyl Benzene, mg/g	0.2
		1,3,5-Trimethyl Benzene, mg/g	<2
		n-Butyl Benzene, mg/g	<0.7

Table A.12

IDENTIFICATION OF MAJOR ORGANIC COMPOUNDS IN API No. 2 FUEL OIL  
(NO. 975) BY GC RETENTION AND/OR GC-MS

Peak No. <sup>a</sup>	Identification <sup>b</sup>
1	n-C <sub>7</sub> H <sub>16</sub>
2	C <sub>1</sub> -Cyclohexane
3	Toluene
4	C <sub>2</sub> -Cyclohexane
5	n-C <sub>8</sub> H <sub>18</sub>
6	C <sub>2</sub> -Cyclohexane
7	C <sub>3</sub> -Cyclohexane
8	Ethyl Benzene
9	m- and/or p-Xylenes
10	C <sub>3</sub> -Cyclohexane
11	o-Xylene
12	n-C <sub>9</sub> H <sub>20</sub>
13	Saturated Hydrocarbon
14	Saturated Hydrocarbon
15	n-Propyl Benzene
16	C <sub>3</sub> -Benzene
17	1,3,5-Trimethyl Benzene + Saturated Hydrocarbon
18	C <sub>3</sub> -Benzene
19	C <sub>3</sub> -Benzene
20	n-C <sub>10</sub> H <sub>22</sub>
21	C <sub>4</sub> -Benzene
22	C <sub>4</sub> -Benzene
23	C <sub>4</sub> -Benzene
24	C <sub>4</sub> -Benzene
25	C <sub>4</sub> -Benzene
26	n-Butyl Benzene
27	C <sub>4</sub> -Benzene + Saturated Hydrocarbon
28	C <sub>4</sub> -Benzene
29	C <sub>4</sub> -Benzene
30	n-C <sub>11</sub> H <sub>24</sub>
31	C <sub>4</sub> -Benzene
32	C <sub>4</sub> -Benzene
33	C <sub>1</sub> -Indane
34	C <sub>4</sub> -Benzene + C <sub>1</sub> -Indane
35	Saturated Hydrocarbon

Table A.12 (Cont'd)

IDENTIFICATION OF MAJOR ORGANIC COMPOUNDS IN API NO. 2 FUEL OIL  
(NO. 975) BY GC RETENTION AND/OR GC-MS

Peak No. <sup>a</sup>	Identification <sup>b</sup>
36	Saturated Hydrocarbon, possibly 3-Me C <sub>11</sub>
37	C <sub>5</sub> -Benzene
38	Naphthalene
39	C <sub>2</sub> -Indane
40	C <sub>2</sub> -Indane
41	n-C <sub>12</sub> H <sub>26</sub>
42	Saturated Hydrocarbon
43	Saturated Hydrocarbon
44	C <sub>2</sub> -Indane
45	Saturated Hydrocarbon, possibly 2-Me C <sub>12</sub>
46	Saturated Hydrocarbon
47	Saturated Hydrocarbon
48	n-C <sub>13</sub> H <sub>28</sub>
49	2-Methyl Naphthalene
50	1-Methyl Naphthalene
51	C <sub>4</sub> -Indane
52	Saturated Hydrocarbon
53	Saturated Hydrocarbon
54	Saturated Hydrocarbon
55	Saturated Hydrocarbon
56	n-C <sub>14</sub> H <sub>30</sub>
57	2-Ethyl Naphthalene
58	1,3-Dimethyl Naphthalene
59	1,5-Dimethyl Naphthalene
60	1,4-Dimethyl Naphthalene
61	C <sub>2</sub> -Naphthalene
62	Saturated Hydrocarbon
63	Saturated Hydrocarbon
64	n-C <sub>15</sub> H <sub>32</sub>
65	C <sub>3</sub> -Naphthalene
66	C <sub>3</sub> -Naphthalene
67	C <sub>3</sub> -Naphthalene
68	C <sub>3</sub> -Naphthalene
69	C <sub>3</sub> -Naphthalene
70	Saturated Hydrocarbon
71	C <sub>3</sub> -Naphthalene
72	C <sub>3</sub> -Naphthalene

Table A.12 (Cont'd)

IDENTIFICATION OF MAJOR ORGANIC COMPOUNDS IN API NO. 2 FUEL OIL  
(NO. 975) BY GC RETENTION AND/OR GC-MS

Peak No. <sup>a</sup>	Identification <sup>b</sup>
73	Saturated Hydrocarbon
74	C <sub>3</sub> -Naphthalene
75	Fluorene + Unknown
76	n-C <sub>16</sub> H <sub>34</sub>
77	Saturated Hydrocarbon
78	Saturated Hydrocarbon
79	Saturated Hydrocarbon, possibly 3-Me C <sub>16</sub>
80	C <sub>5</sub> -Naphthalene
81	n-C <sub>17</sub> H <sub>36</sub>
82	Pristane
83	1-Methyl Fluorene + C <sub>2</sub> -Acenaphthene/Biphenyl
84	Saturated Hydrocarbon
85	Saturated Hydrocarbon
86	3-Methyl C <sub>17</sub>
87	Phenanthrene
88	n-C <sub>18</sub> H <sub>38</sub>
89	Phytane
90	Saturated Hydrocarbon
91	Saturated Hydrocarbon
92	n-C <sub>19</sub> H <sub>40</sub>
93	2-Methyl Phenanthrene
94	Phthalate
95	n-C <sub>20</sub> H <sub>42</sub>
96	n-C <sub>21</sub> H <sub>44</sub>
97	n-C <sub>22</sub> H <sub>46</sub>
98	n-C <sub>23</sub> H <sub>48</sub>

<sup>a</sup>See Figure A.2

<sup>b</sup>Specific isomer named if retention time and mass spectrum match authentic standard. Other assignments possible where only generic isomer structure is named.

TABLE A.13

ORIGIN, PROPERTIES, AND COMPOSITIONAL DATA FOR SRC-II BLEND - AFTER WATER WASHING  
(No. 916)

Origin: 1.7 to 1 (wt./wt.) blend of Middle and Heavy Distillates produced at the SRC-II pilot plant (Ft. Lewis, WA) on April 4-6, 1980, during SRC-II mode run with Powhatan No. 5 coal.

Upgrading: Blended and water-washed by the Chevron Research Company (Richmond, CA).

Ultimate Analysis

C, wt. %	85.36
H, wt. %	8.74
N, ppm	8,800
S, ppm	2,600
O, wt. %	4.76

Chemical Class Fractions

Ether-Soluble Bases, wt. %	5.0
Ether-Soluble Acids, wt. %	2.0
Saturates, wt. %	26.7
Mono/Diaromatics, wt. %	47.7
Polyaromatics, wt. %	6.2

Physical Parameters

<u>Simulated Distillation</u>	
IBP, °C (°F)	147 (297)
ABP, °C (°F)	243 (469)
FBP, °C (°F)	401 (754)
Density, g/cm <sup>3</sup> @ 25°C	0.989
Viscosity, cSt @ 25°C	9.39
Pour Point, °C (°F)	-39 (-38)
Flash Point, °C (°F)	88 (190)

Selected Compounds

Benzo(a)pyrene, ug/g	60
Phenol, mg/g	17
o-Cresol, mg/g	12
Quinoline, ug/g	1,300

TABLE A.14

ORIGIN, PROPERTIES, AND COMPOSITIONAL DATA FOR SRC-II BLEND-HYDROTREATED  
AT LOW SEVERITY (No. 917)

Origin: 1.7 to 1 blend of Middle and Heavy Distillates produced at the SRC-II pilot plant (Ft. Lewis, WA) on April 4-6, 1980 during SRC-II mode run with Powhatan No. 5 coal.

Upgrading: Blended, water-washed, and hydrotreated at low severity (975 SCF H<sub>2</sub>/BBL) by the Chevron Research Company (Richmond, CA)

Ultimate Analysis

C, wt. %	86.74
H, wt. %	9.90
N, ppm	4,900
S, ppm	83
O, wt. %	2.86

Chemical Class Fractions

Ether-Soluble Bases, wt. %	2.0
Ether-Soluble Acids, wt. %	0.2
Saturates, wt. %	32.5
Mono/Diaromatics, wt. %	40.2
Polyaromatics, wt. %	2.1

Physical Parameters

<u>Simulated Distillation</u>	
IBP, °C (°F)	76 (169)
ABP, °C (°F)	241 (466)
FBP, °C (°F)	385 (725)
Density, g/cm <sup>3</sup> @ 25°C	0.942
Viscosity, cSt @ 25°C	4.93
Pour Point, °C (°F)	-45 (-49)
Flash Point, °C (°F)	35 (95)

Selected Compounds

Benzo(a)pyrene, ug/g	1.2
Phenol, mg/g	6.0
o-Cresol, mg/g	7.6
Quinoline, ug/g	200

TABLE A.15

ORIGIN, PROPERTIES, AND COMPOSITIONAL DATA FOR SRC-II BLEND-HYDROTREATED  
AT MEDIUM SEVERITY (No. 918)

Origin: 1.7 to 1 blend of Middle and Heavy Distillates produced at the SRC-II pilot plant (Ft. Lewis, WA) on April 4-6, 1980, during SRC-II mode run with Powhatan No. 5 coal.

Upgrading: Blended, water-washed, and hydrotreated at medium severity (1,450 SCF H<sub>2</sub>/BBL) by the Chevron Research Company (Richmond, CA)

<u>Ultimate Analysis</u>		<u>Chemical Class Fractions</u>	
C, wt. %	87.87	Ether-Soluble Bases, wt. %	0.7
H, wt. %	10.78	Ether-Soluble Acids, wt. %	0.2
N, ppm	1,400	Saturates, wt. %	39.2
S, ppm	26	Mono/Diaromatics, wt. %	27.9
O, wt. %	1.21	Polyaromatics, wt. %	0.6
<u>Physical Parameters</u>		<u>Selected Compounds</u>	
Simulated Distillation		Benzo(a)pyrene, ug/g	0.9
IBP, °C (°F)	75 (167)	Phenol, mg/g	2.0
ABP, °C (°F)	228 (442)	o-Cresol, mg/g	4.2
FBP, °C (°F)	375 (707)	Quinoline, ug/g	<1
Density, g/cm <sup>3</sup> @ 25°C	0.913		
Viscosity, cSt @ 25°C	2.76		
Pour Point, °C (°F)	-40 (-40)		
Flash Point, °C (°F)	25 (77)		

TABLE A.16

ORIGIN, PROPERTIES, AND COMPOSITIONAL DATA FOR SRC-II BLEND-HYDROTREATED  
AT HIGH SEVERITY (No. 919)

Origin: 1.7 to 1 blend of Middle and Heavy Distillates produced at the SRC-II pilot plant (Ft. Lewis, WA) on April 4-6, 1980 during SRC-II mode run with Powhatan No. 5 coal.

Upgrading: Blended, water-washed, and hydrotreated at high severity (1,850 SCF H<sub>2</sub>/BBL) by the Chevron Research Company (Richmond, CA)

Ultimate Analysis

C, wt. %	88.25
H, wt. %	11.46
N, ppm	500
S, ppm	<10
O, wt. %	0.24

Chemical Class Fractions

Ether-Soluble Bases, wt. %	0.3
Ether-Soluble Acids, wt. %	<0.1
Saturates, wt. %	44.6
Mono/Diaromatics, wt. %	21.2
Polyaromatics, wt. %	0.3

Physical Parameters

<u>Simulated Distillation</u>	
IBP, °C (°F)	75 (167)
ABP, °C (°F)	225 (437)
FBP, °C (°F)	373 (703)
Density, g/cm <sup>3</sup> @ 25°C	0.901
Viscosity, cSt @ 25°C	2.54
Pour Point, °C (°F)	-27 (-17)
Flash Point, °C (°F)	24 (75)

Selected Compounds

Benzo(a)pyrene, ug/g	0.1
Phenol, mg/g	0.5
o-Cresol, mg/g	2.2
Quinoline, ug/g	<1

TABLE A.17  
PHYSICAL AND CHEMICAL PROPERTIES OF TEST CATALYSTS

	Shell 324M <sup>b</sup>	Amocat 1C	HDS-1442A	Strem Chem. <sup>c</sup> Co., Ni/W
Bulk Density, g/cm <sup>3</sup>	0.770	0.621	---	---
Pellet Density, g/cm <sup>3</sup>	1.400	1.084	1.020	---
Pore Volume, cm <sup>3</sup> /g	0.425	0.649	0.634	---
Pore Volume > 1000Å, %	---	14.2	23.5	---
Surface Area, m <sup>2</sup> /g	174	182	313	150
Average Pore Diameter, Å				
Mesopore	113	120	48	---
Macropore	---	2400	3500	---
Metals, wt. %				
NiO	3.18	2.92	---	6
MoO <sub>3</sub>	19.5	14.13	16.0	---
Co O	---	---	2.4	---
W O <sub>3</sub>	---	---	---	19
Al <sub>2</sub> O <sub>3</sub>	63.5	72.91	71.6	---
P <sub>2</sub> O <sub>5</sub>	6.42	---	---	---
Active Metals Loading g/cm <sub>3</sub> of Catalyst	0.175	0.106	---	---

<sup>a</sup>Data supplied by Pittsburg Energy Technology Center, except where noted.

<sup>b</sup>S-content of sulfided Shell 324M is 10.8%.

<sup>c</sup>Data obtained from Strem Chemical Company catalog.



Appendix B

Chemical and Physical Characterization Procedures



## Chemical and Physical Characterization Procedures

Physical Properties/Engineering Parameters. These properties were measured to define the samples and to allow comparison of the similarities of coal- and petroleum-derived products. Standard or published procedures were used whenever possible. Non-standard or unpublished procedures are briefly described.

Ultimate Analysis:	C,H by ASTM D 2178-73 N,S by combustion with oxygen in a Parr Bomb and ion chromatography of the oxides O was calculated by difference
Simulated Distillation	ASTM D 2887-73
Density:	A 10 ml volumetric flash is weighed before and after filling with the sample at the indicated temperature
Viscosity:	ASTM D 445-53T
Pour Point:	ASTM D 97-66
Flash Point:	ASTM D 56-70

Benzo[a]pyrene Determination. BaP was used as an indicator of dermal tumorigen PAH and of potential relative tumorigenicity. BaP was determined in the raw and upgraded coal liquids by a sequential HPLC-HPLC (high performance liquid chromatography) procedure (Tomkins et al. 1981). Briefly, the coal oil was diluted with methylene chloride and spiked with a known activity of carbon-14 labeled BaP. A BaP-enriched fraction was isolated using semipreparative scale, normal phase HPLC. The BaP was measured using analytical scale, reverse phase (Zorbax octadecylsilane) HPLC with fluorescence detection at 360 nm (excitation) and 425 nm (emission). The recovery of the BaP was determined by liquid scintillation spectroscopic measurement of the radiotracer. The radiotracer was omitted when analyzing highly refined products, and the recovery was assumed to be quantitative. Previous experience with highly upgraded samples indicated that such an assumption was reasonable.

Four to Six-Ring PAH Dermal Tumorigens Estimation. Selected four to six-ring dermal tumorigen PAH were determined for a more complete characterization of known tumorigenic agents. These PAH were analyzed in the crude and upgraded H-Coal samples using normal phase, semipreparative

scale HPLC to obtain a PAH-enriched fraction, followed by capillary column gas chromatography (GC) with flame ionization detection (samples nos. 931, 934, 1658 and 1659). The procedures are described in detail elsewhere (Tomkins et al. 1982). The home heating oil samples were analyzed similarly. The concentrations of selected PAH dermal tumorigens in the naphtha samples were estimated by GC-MS. Neat samples of the naphthas were spiked with deuterated PAH internal standards, and were analyzed by GC-MS using a splitless injector, a 30 m x 0.25 mm ID, 0.25  $\mu$ m film DB-5 bonded phase, fused silica capillary column. The column temperature was programmed from 150°C (hold 5 min.) to 280°C at 2°/min. Selected ion monitoring and the method of internal standards were used for quantitation. Electron impact ionization at 70 eV was employed.

Major Composition Profile. Comparative compositional profiles of the major components of the home heating oil and naphtha samples were made to characterize differences in the bulk matrix of the samples. These profiles were obtained by capillary column GC, using split injection (200:1 split) of the neat sample, a 60 m x 0.25 mm ID x 0.25  $\mu$ m film DB-5 bonded phase, fused silica capillary column, and flame ionization detection. The column was temperature programmed from 40°C (hold 10 min.) to 275°C at 2°/min. Components were tentatively identified by co-chromatography, and were confirmed by GC-mass spectroscopy under similar chromatographic conditions and electron impact ionization at 70 eV.

Inhaleable Volatile Organic Compounds. Comparative analyses were made of the composition of the headspace vapors from the finished coal and petroleum-derived products to determine if differences in the composition of the bulk liquid samples would be reflected in the composition of the vapors to which a refiner or user might be exposed. Two ml aliquots of each sample were equilibrated with 22 ml of headspace in a sealed vial at 25°C for one hr. A five  $\mu$ l (naphtha) or 0.5 ml (home heating oil) volume of the headspace was withdrawn by syringe and was injected and cryothermally collected in a loop at the head of a 60 m, one  $\mu$ m thickness DB-5 fused silica capillary column. The temperature of the column was programmed from 25°C to 200°C at 2°C/min., and the separated components were detected by flame ionization. Quantitation was accomplished by the method of external standards.

Benzene/Alkyl Benzene Analysis. The content of benzene and selected alkyl benzenes were measured by capillary column GC, using the method of internal standards. A 0.2 ml aliquot of sample was diluted with diethyl ether to 10.0 ml along with 1.6 mg of tetrachloroethylene internal standard. The sample was analyzed by splitless injection, capillary column GC using a 60 m x 0.25 mm ID x 0.25  $\mu$ m film DB-5 fused silica column, temperature programmed from 20°C (hold 15 min.) to 100°C at 2°/min. Flame ionization detection was employed.

Phenols. Phenol and o-cresol were determined by a procedure (Yeatts et al. 1983) involving extraction followed by HPLC. A 25 mg sample of coal liquid was dissolved in a 3 ml of methylene chloride and a known activity of <sup>14</sup>C-labeled phenol was added. The solution was extracted with 3 ml of 0.1 N NaOH, and the aqueous extract was neutralized with glacial acetic acid, diluted to a known volume, and sampled for liquid scintillation counting <sup>14</sup>C-phenol recovery measurement. An aliquot of the neutralized extract or of an aqueous sample (no treatment required) was injected onto a highly loaded, end capped C<sub>18</sub>-reversed phase HPLC column eluted with 40% acetonitrile in water (held at pH 4.6 with acetate buffer). Phenols were detected by fluorescence at 270 nm excitation and 300 nm emission. Quantitation was by external standardization. The procedure was evaluated with NBS.

Quinoline. The quinoline in the coal oils was tentatively identified and measured using a GC equipped with a nitrogen selective thermionic detector. A 200 mg aliquot of the sample was diluted in 10 ml of tetrahydrofuran, and a 2  $\mu$ l portion of the resulting solution was injected into the instrument without further treatment. The column used was a three meter x 3.3 mm OD glass column packed with 3% (w/w) Dexsil 400 on Supelcoport (100/120 mesh). The instrument used was a Perkin-Elmer Sigma I, which was operated under the following conditions: injector temperature 300°C; detector temperature 320°C; helium carrier gas flow rate 26 ml/min; chart speed 2 mm/min. The thermionic detector (nitrogen-selective mode) response was optimized with a hydrogen flow of 1.9 ml/min, air flow of 110 ml/min, and a bead voltage setting of 400. The oven was programmed from 90°C (hold for 8 min) to 275°C (hold for 15 min) at a rate of 2°C/min, for a

total analysis time of about 120 min. The data system of the Sigma I was used to identify and quantitate thirty-one aromatic nitrogen compounds using the method of external standards.

Chemical Class Distribution. The procedure of chemical class separation has been described in detail elsewhere (Guerin et al. 1981). In brief, each sample was stirred in diethyl ether and reacted overnight with 1 N HCl in a continuous extractor. Volatile material (VOL) was removed from some of the samples prior to this step by rotary evaporation. A five g aliquot of oil was typically processed using 250 ml of ether and 50 ml of aqueous phase. The aqueous extracts were adjusted to pH 11 and were extracted with 250 ml of diethyl ether. The basic constituents were thus back-extracted into ether to yield ether-soluble bases (ESB), and a basic precipitate. The acid constituents of the ether phase were similarly removed by extraction with 1 N NaOH, then back-extracted into ether to yield ether-soluble acids (ESA), and a acidic precipitate. The neutral constituents remaining in the ether phase were then separated using Sephadex LH-20 into aliphatic (SAT), mono/di aromatic (ARO), and polycyclic aromatic (> 3 fused aromatic rings, Poly) fractions by isopropanol and followed by acetone elution of a residue (N-Res) elution as has been described. Elution solvents were removed by rotary evaporation and the residue was weighed to allow calculation of each fraction as a weight percentage of the original sample.

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