

ANALYTICAL CHEMISTRY OF PRODUCTS FROM PROCESS STRATEGIES DESIGNED TO  
REDUCE THE BIOLOGICAL ACTIVITY OF DIRECT COAL LIQUEFACTION MATERIALS

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INTRODUCTION

The current status of understanding the chemical basis for the generally increased genetic activity of direct coal liquefaction materials, as compared to petroleum-derived products, has led to the investigation of a number of potential process strategies for reducing the biological activities of coal-derived liquids. Approaches that have been investigated include optimized fractional distillation, catalytic hydrotreatment, recycling of heavy-end and bottoms materials, and two stage liquefaction coupled with reduced liquefaction severity and improved quality hydrogen donor solvents.

Bidirected chemical analyses of coal liquefaction materials over the last several years have led to the identification of at least two important classes of compounds which are largely responsible for the biological response observed in laboratory systems upon exposure to these materials. The classical carcinogens in coal liquids are the polycyclic aromatic hydrocarbons (PAH), primarily those having from 4 to 6 aromatic rings. Kennaway, Cook and others in the early part of this century showed that certain coal-derived PAH could cause skin tumors in mice and rabbits (1,2,3). It has been found, in general, that genetic activity, particularly initiation of tumorigenesis, resides in high boiling heavy-end materials and correlates with overall PAH content better than with any other chemical class (4-6). More recently nitrogen-containing polycyclic aromatic compounds (N-PAC), specifically the amino-PAH, have been recognized as genotoxic constituents in several coal-derived materials. In quantitative terms, the amino-PAH occur at relatively lower concentrations as compared to the PAH. However, due to the increased sensitivity of the *Salmonella typhimurium* microbial mutagenicity test to amino-PAH, they are readily detected in the complex coal liquid mixtures by this biological assay (7-11). The possible contribution of amino-PAH to the etiology of any cancers induced in coal product workers is only now beginning to be understood. Amino-PAH such as 2-aminonaphthalene and 4-aminobiphenyl are recognized as human carcinogens (12). Furthermore, recent studies have demonstrated that the amino-PAH as a chemical class do contribute to the overall initiation of skin tumors in laboratory mice (13).

A common goal of the direct liquefaction process strategies considered in this study is the reduction of biological activity via reducing the concentration levels of the amino-PAH and the 4-, 5- and 6-ring PAH. In this report, coal liquefaction strategies such as distillation, bottoms recycle, hydrogenation, and two stage liquefaction will be discussed in terms of their effect on the chemical composition of process materials.

ANALYTICAL METHODS

The evolution and development of analytical methods at PNL (Pacific Northwest Laboratories) has been primarily directed by the requirement of determining the biologically adverse chemical classes and compounds in coal liquefaction materials. Accordingly, methods have been designed for the identification and quantification of not only homogeneous chemical classes, but also individual components. Figure 1 outlines the overall analytical approach currently used. An

initial separation of crude materials by adsorption column chromatography (14) enables the determination of gross chemical composition in terms of PAH and N-PAC content. Secondary chromatographic separations are achieved by HPLC methods (15) for the PAH, and a combination of adsorption and gel permeation chromatography (14,16) for the N-PAC. Finally, instrumental methods such as capillary column gas chromatography and mass spectrometry are used to provide detailed qualitative and quantitative chemical analysis of individual components in the separated materials.

During the last several years, the SRC (solvent refined coal) processes have received prime attention and consideration as potential direct coal liquefaction technologies. An illustration of the detailed data obtained from the previously described analytical procedures for the PAH fraction of a full boiling range SRC II end-product is provided in Figure 2 and Table 1. It should be noted at this point that all process materials investigated during this study and discussed in this paper were from process development units or pilot plants and may not necessarily be representative of products which will eventually be produced on a commercial scale.

## RESULTS AND DISCUSSION

### DISTILLATION

An effective process technique that has been used in the petroleum industry for the gross separation of end-products of refining according to volatility is distillation. Optimized fractional distillation has recently been applied to the products of direct coal liquefaction in an effort to effect a molecular weight separation and isolate the biologically active components in the higher boiling fractions (6). Bioassays of crude distillates and chemical class fractions from several direct liquefaction processes have shown that the majority (>99%) of genetic activity is contained in the distillate fractions boiling above 700°F (4-5). Figures 3 and 4 aid in understanding the chemical basis for this observation.

Figure 3A and 3B present chemical class weight distribution information for the 50°F distillate cuts of typical end-products from the SRC II and EDS (Exxon Donor Solvent) coal liquefaction processes, respectively. For each process, greater than approximately 80% of the material is distilled below 700°F. In terms of chemical class composition, there is a decrease in aliphatic hydrocarbon content and increasing levels of N-PAC and polar hydroxylated polycyclic aromatic hydrocarbons (HO-PAH) with increasing boiling point temperature. The neutral PAH portion of each distillate cut generally remains constant.

The effect of distillation temperature on molecular weight is shown in Figure 4 for the PAH fraction of the SRC II boiling point cuts. As a general trend, compounds of increasing molecular weight can be correlated with increasing distillation temperature. For example, pyrene, which is noncarcinogenic, is at a maximum concentration in the 700-750°F cut, while the potent carcinogenic compounds such as benzo(a)pyrene are distilled in the greater than 800°F cuts. This trend is also observed for the mutagenic N-PAC and amino-PAH components of the distillate fractions.

In summary, optimized fractional distillation in effect eliminates the bulk of components from the full boiling range material (Figure 1) which have a molecular weight greater than approximately 200 daltons and minimizes the levels of compounds that contain polar nitrogen and oxygen functional groups. Additionally, materials resulting from this process strategy would have a higher aliphatic hydrocarbon content and would be nominally biologically inactive.

## BOTTOMS RECYCLE

Information from the distillation studies led to the suggestion that the greater than 700°F material, or bottoms, might simply be recycled continuously to extinction within the process to yield a non-biologically active end-product. Recently, experiments have been conducted with the SRC II process by the Merriam Coal Liquefaction Laboratory to determine the feasibility and applicability of this process strategy. Crude materials sampled from the SRC II process while operating in the bottoms recycle mode, with a recycle cut point temperature of 290°C (554°F) and assayed for microbial mutagenicity (*S. Typhimurium*, TA98) showed no detectable activity although these net products contained 5-10% (by weight) material boiling above the recycle cut point temperature. This work also demonstrated that an increased recycle of heavier-ends reduced the net yield of heavy distillate.

## CATALYTIC HYDROGENATION

Catalytic hydrogenation has been considered both as an off-line post-production upgrading step, as well as an integral process in direct coal liquefaction technologies. Early results with catalytic hydrotreatment of an SRC II fuel oil blend material showed that mutagenic activity was substantially reduced by hydrogenation (17). This was explained by the reduced levels of amino-PAH due to deamination of the nitrogen functionality which occurs readily under the reducing conditions of hydrogenation processes. Furthermore, hydrogenation of the PAH components can lead to reduced aromaticity and/or carbon-carbon bond scission of higher molecular weight PAH. This again leads to a reduction in the biological potency of the end-products.

Several direct liquefaction technologies including EDS and TSL (two stage liquefaction) incorporate some form of catalytic hydrogenation step within the process. Table 2 lists the quantitative results for the major components detected in the PAH fraction of the 700-750°F distillate cut of end-products from the SRC II (no hydrogenation) and EDS (process solvent hydrogenation) processes. An obvious effect of the hydrogenation process is a general reduction in the EDS material of the concentration levels of parent PAH, for example pyrene and benzofluorene, as compared to other constituents of the fraction such as the hydroaromatics and alkylated species. In general, the EDS distillate cut is composed of several compounds within a fairly narrow concentration range, while the SRC II material has a few major components with other constituents at much lower concentration levels. Table 3 gives an estimate of the magnitude of the chemical differences that result from the hydrogenation process. The increased proportions of alkylated and hydroaromatic PAH in hydrotreated materials has the net effect of increasing the hydrogen to carbon ratio and enhancing the quality of both process products and recycle solvents.

## TWO STAGE LIQUEFACTION

Two stage liquefaction processes such as the second generation integrated two stage liquefaction (ITSLS) incorporate several process features which lead to both process streams and potential product materials which show reduced genotoxicity (18,19). It appears that the two most important features are reduced liquefaction severity in the first stage and catalytic hydrotreatment in the second stage. Low severity extraction depends upon the availability of high quality hydrogen-rich solvent which results from hydrotreatment. Severity in the initial liquefaction step is reduced primarily by lowering the residence time of the coal slurry in the first stage reactor. The improved solvation and hydrogenation properties of the higher quality solvent allows the coal to be solvated quickly and efficiently, thus minimizing the possibility of retrograde reaction which leads to the formation of polar materials and may cause polymerization or coking.

Reduction in nitrogen content of the distillates is the main reason for the lower genotoxicity of the ITSL materials as compared to the single stage processes. Figure 6 compares gas chromatograms of the nitrogen-containing PAH fractions after the first and second stages of the ITSL process. Deamination that is only partial in the low severity reactor is relatively complete in the hydrotreater product. This reduces the overall concentration of genotoxic amino-PAH in the process material and end-products. Similarly, hydrogenation and cracking occurs for the other PAH components in the process material resulting in the superior recycle solvent properties required for low severity liquefaction in the first stage and high quality end-products that are suitable for upgrading and refining.

## CONCLUSION

The ability to perform detailed chemical analysis provides insights and understanding into both the areas of biological effects and process strategies. There are a number of chemical differences which have been discussed for the different products from direct liquefaction strategies, including hydrogenation, de-nitrogenation, and alkylation. The higher molecular weight genotoxic PAH and N-PAC which are minor constituents in most full range distillate coal liquids can be effectively reduced in concentration by optimized fractional distillation, bottoms recycle, or hydrogenation. Furthermore, two stage liquefaction with enhanced recycle solvents under low severity conditions coupled with hydrogenation reduces the aromatic and polar PAH content while increasing the hydrogen to carbon ratio of the process material. In general, the strategies investigated in this work result in higher quality process materials and end-products which are suitable either for refining or upgrading into usable products.

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## REFERENCES

1. Cook, J. W., Proc. Royal Soc. B., 1932, 111, 455-484.
2. Kennaway, N. M.; Kennaway, E. L., J. Hyg., 1936, 36, 236-267.
3. Cook, J. W.; Hewett, C. J.; Heiger, I., J. Chem. Soc., 1933, 395-405.
4. Mahlum, D. D., J. Appl. Toxicol., 1983, (in press).
5. Later, D. W.; Pelroy, R. A.; Mahlum, D. D.; Wright, C. W.; Lee, M. L.; Weimer, W. C.; Wilson, B. W., In: "Proceedings of the 9th International Symposium on Polynuclear Aromatic Hydrocarbons," Battelle Press, Columbus, OH, 1982.
6. Wilson, B. W.; Willey, C.; Later, D. W.; Lee, M. L., Fuel, 1982, 61, 473-477.
7. Later, D. W.; Pelroy, R. A.; Lee, M. L.; Wilson, B. W., Mutat. Res., 1983, (submitted).
8. Wilson, B. W.; Pelroy, R. A.; Cresto, J. T., Mutat. Res., 1980, 79, 193-202.
9. Later, D. W.; McFall, T.; Booth, G. M.; Lee, M. L.; Tedjamulia, M.; Castle, R. N., Environ. Mut., 1983, (submitted).
10. Geurin, M. R.; Ho, C.-h.; Rao, T. K.; Clark, B. R.; Epler, J. L., Environ. Res., 1980, 23, 42-53.
11. Haugen, D. A.; Peak, M. J.; Suhrbler, K. M.; Stamoudis, V. C., Anal. Chem., 1982, 54, 32-37.
12. Radomski, J. L., Ann. Rev. Pharmacol. Toxicol., 1979, 19, 129-157.
13. Pelroy, R. A.; Later, D. W.; Mahlum, D. D., Environ. Mut., 1983, (submitted).
14. Later, D. W.; Lee, M. L.; Bartle, K. D.; Kong, R. C.; Vassilaros, D. L., Anal. Chem., 1981, 53, 1612-1620.

15. Lucke, R. B.; Later, D. W., Wright, C. W.; Weimer, W. C., Anal. Chem., 1983, (submitted).
16. Later, D. W.; Lee, M. L.; Pelroy, R. A.; Wilson, B. W., In: "Polynuclear Aromatic Hydrocarbons: Physical and Biological Chemistry," Cooke, M., Dennis, A. J.; Fisher, G. L., eds., Battelle Press, Columbus, OH. 1982, pp. 427-438.
17. Wilson, B. W.; Petersen, M. R.; Pelroy, R. A.; Cresto, J. T., Fuel, 1981, 60, 289-294.
18. Wilson, B. W.; Pelroy, R. A.; Mahlum, D. D.; Frazier, M. E., In: "Proceedings ITSL Program Contractors Project Review Conference," Albuquerque, NM, October 6-7, 1982.
19. Wilson, B. W.; Pelroy, R. A.; Mahlum, D. D.; Frazier, M. E.; Later, D. W.; Wright, C. W., Fuel, 1983, (submitted).

TABLE 1. Quantitative and Qualitative Analysis of the PAH in the SRC II Full Range Distillate(a)

Peak No.	Mol. Wt.(b)	Compound Identification	PAH Fraction (PPM (ug/g))(c)
	128	Naphthalene	730 ± 50 <sup>(d)</sup>
1	142	2-Methylnaphthalene	15,040 ± 680
2	142	1-Methylnaphthalene	2,840 ± 130
3	156	2-Ethyl-naphthalene	11,400 ± 540
4	156	2,6- and/or 2,7-Dimethylnaphthalene	12,500 ± 1000
5	156	1,7- and 1,6- or 1,3-Dimethylnaphthalene	8,260 ± 440
6	156	C <sub>2</sub> -Naphthalene	
	152	Acenaphthylene	340 ± 20
7	154	Acenaphthene	7,990 ± 450
8	170	C <sub>2</sub> -Naphthalene	
9	170	C <sub>2</sub> -Naphthalene	
10	168	Dibenzofuran	13,360 ± 740
11	166	Fluorene	13,960 ± 1180
12	168	C <sub>1</sub> -Acenaphthene and/or Dihydrofluorene	39,960 ± 4140
13	184	C <sub>2</sub> -Naphthalene	
14	180	9-Methylfluorene	16,650 ± 3040
15	182	C <sub>1</sub> -Dibenzofuran and/or C <sub>2</sub> -Acenaphthene and/or C <sub>1</sub> -Dihydrofluorene	
16	180	2-Methylfluorene	11,750 ± 680
17	180	1-Methylfluorene	9,830 ± 480
18	180,182,198	C <sub>1</sub> -Fluorene and/or C <sub>2</sub> -Acenaphthene and/or C <sub>1</sub> -Dihydrofluorene, and/or C <sub>1</sub> -Dibenzofuran	
19	184	Dibenzothiophene	12,290 ± 750
20	196	C <sub>2</sub> -Acenaphthene and/or C <sub>2</sub> -Dihydrofluorene	
21	178	Phenanthrene	44,640 ± 2840
22	194,196	C <sub>2</sub> -Fluorene and/or C <sub>2</sub> -Dihydrofluorene	
23	196	C <sub>2</sub> -Dihydrofluorene	
24	192	3-Methylphenanthrene	9,300 ± 840
25	192	2-Methylphenanthrene	11,950 ± 800
26	192	1-Methylphenanthrene	3,680 ± 490
27	212	2-Chloroanthracene Internal Standard	
28	204	Dihydrofluoranthene	8,780 ± 100
29	202	Fluoranthene	3,820 ± 30
30	202	Pyrene	19,520 ± 470
31	204	Dihydropyrene	
32	218	C <sub>1</sub> -Dihydrofluoranthene and/or Benzo(a)naphthofuran	
33	216	Benzo(a)fluorene	2,840 ± 230
34	216	Benzo(b)fluorene and/or 2- or 4-methylpyrene	10,360 ± 1110
35	218	Dihydrobenzo(b)fluorene and/or Benzo(b)naphthofuran	
36	216	1-Methylpyrene	2,650 ± 470
37	230	C <sub>1</sub> -Benzofluorene and/or C <sub>2</sub> -pyrene/fluoranthene	
38	228	Benzo(a)anthracene	660 ± 60
39	228	Chrysene	1,110 ± 120
40	242	6- or 4-Methylchrysene	2,110 ± 210
41	252	Benzo(j or b)fluoranthene	250 ± 50
42	252	Benzo(e)pyrene	200 ± 60

(a) SRC II Full Range Distillate obtained from Gulf Research and Development Co., Merrian Coal Liquefaction Laboratory, Shawnee Mission, KS. An Amax Belle Ayr Mine subbituminous coal was used during run DOE 454RA which was made in the convention recycle mode.

(b) As determined by capillary column gas chromatographic-mass spectrometry.

(c) Determined from response factors of standard compounds.

(d) Based on three determinations; 10 mg/ml, 5 mg/ml, and 2.5 mg/ml dilutions.

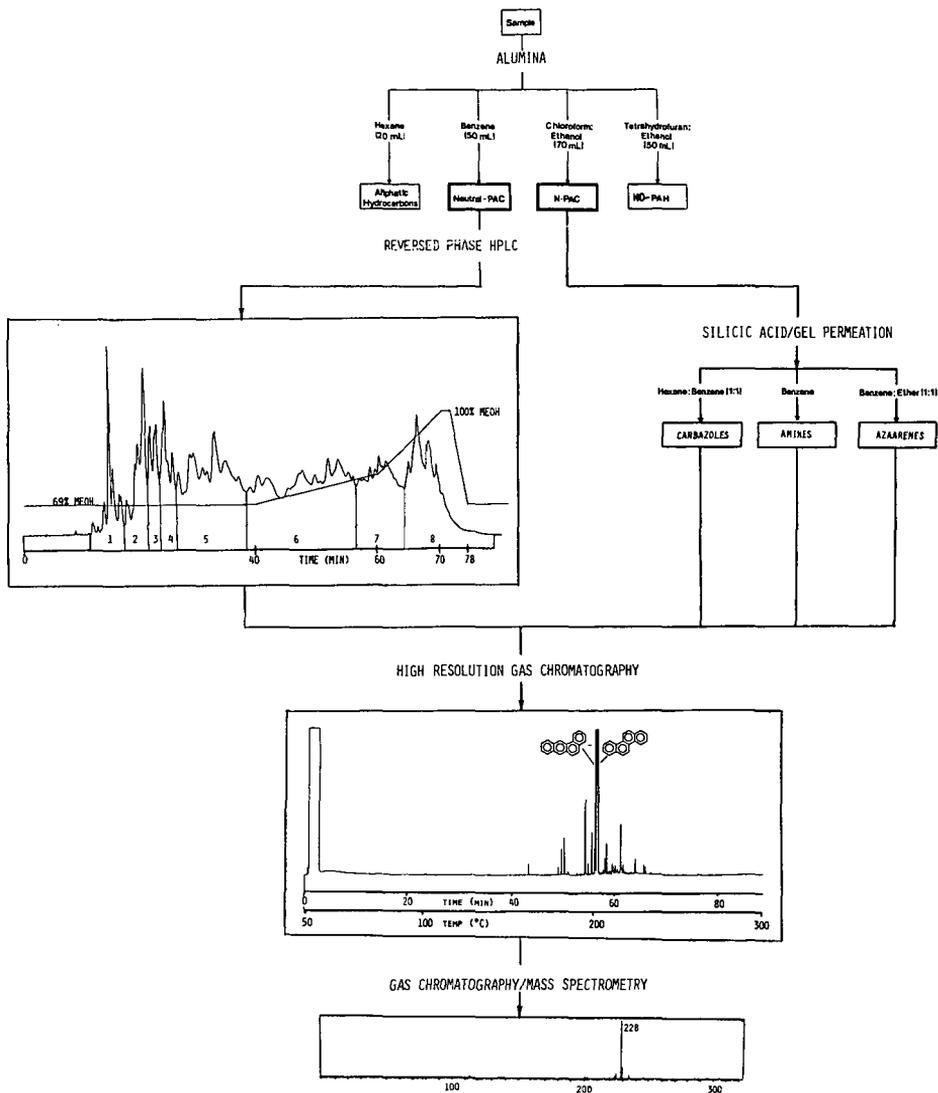
TABLE 2. Concentrations of the Major Components of the 700-750°F Distillate Fractions of SRC II and EDS End-Products.

Compound	PAH FRACTION PPM ( $\mu\text{g/g}$ ) <sup>(a)</sup>	
	E.D.S. <sup>(b)</sup>	SRC II <sup>(c)</sup>
Dihydrofluoranthene	2,098 $\pm$ 36	21,822 $\pm$ 6,335
Fluoranthene	1,089 $\pm$ 16	30,210 $\pm$ 1,819
Pyrene	29,838 $\pm$ 976	275,991 $\pm$ 32,372
Dihdropyrene	6,391 $\pm$ 157	27,733 $\pm$ 8,413
Benzo(b)fluorene and/or 2- or 4-Methylpyrene	47,042 $\pm$ 11,610	257,629 $\pm$ 70,359
1-Methylpyrene	26,567 $\pm$ 6,371	34,335 $\pm$ 4,405
Benz(a)anthracene	308 $\pm$ 23	4,098 $\pm$ 942
Chrysene	1,554 $\pm$ 335	2,086 $\pm$ 561

- (a) Concentration of components in the PAH fraction as determined from response factors of standards. Based on three determinations at 10 mg/mL, 5mg/mL, 2.5 mg/mL dilutions.
- (b) EDS 50° distillate from a feed blend of naphtha and process solvent of Illinois No. 6 coal; ECLP operations, Exxon Research and Engineering Co., Baytown, TX.
- (c) SRC II 50° distillates from a feed blend of naphtha and process solvent of Powhatan No. 5 mine coal; PDU P-99 operated by Gulf Science and Technology Co., Harmarville, PA.

TABLE 3. Concentration Ratios of Selected 4-Ring PAH in the 700-750°F Distillate Fractions of SRC II and EDS

Compound Ratio	EDS	SRC II
<u>pyrene</u> 1-methylpyrene	1.1	8.0
<u>pyrene</u> dihdropyrene	4.7	10.0
<u>fluoranthene</u> dihydrofluoranthene	0.5	0.7



**FIGURE 1.** Overview of the analytical methodology used for the detailed chemical characterization of coal liquefaction materials.

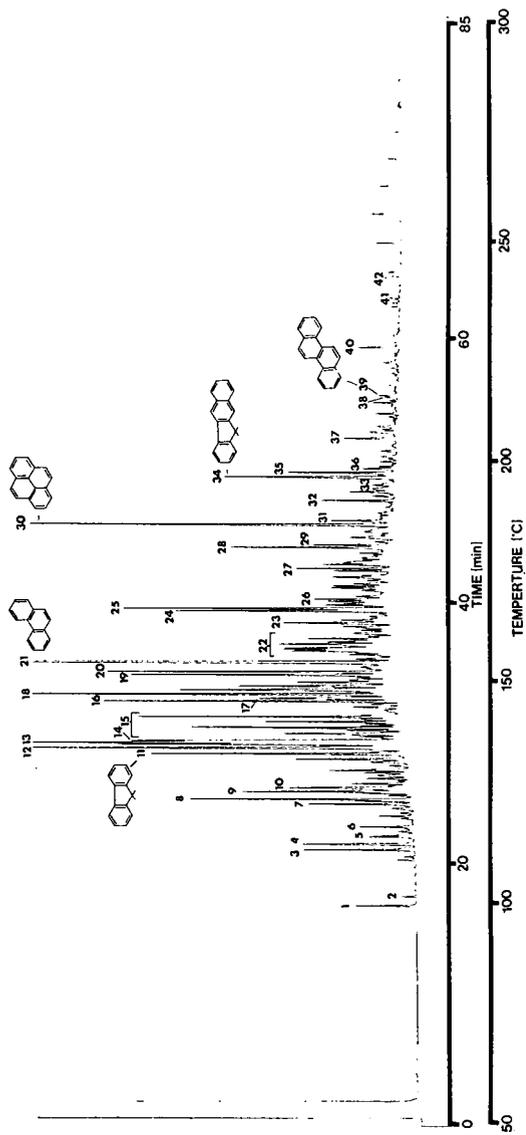
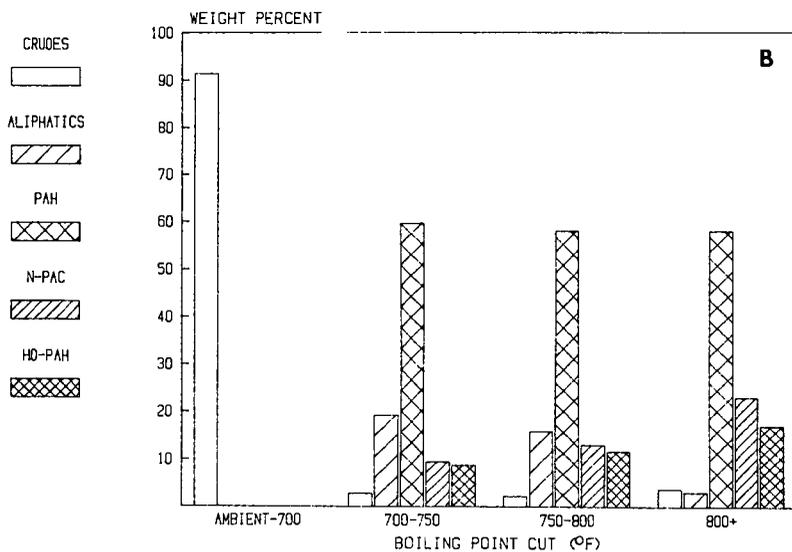
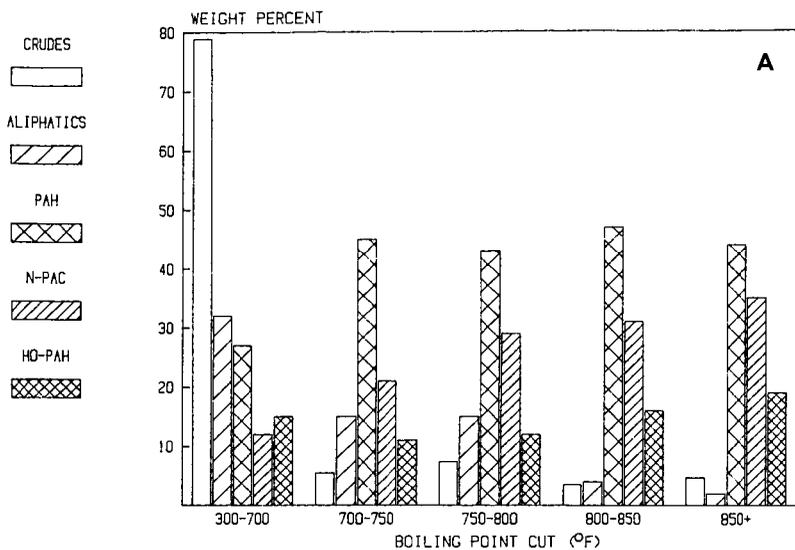
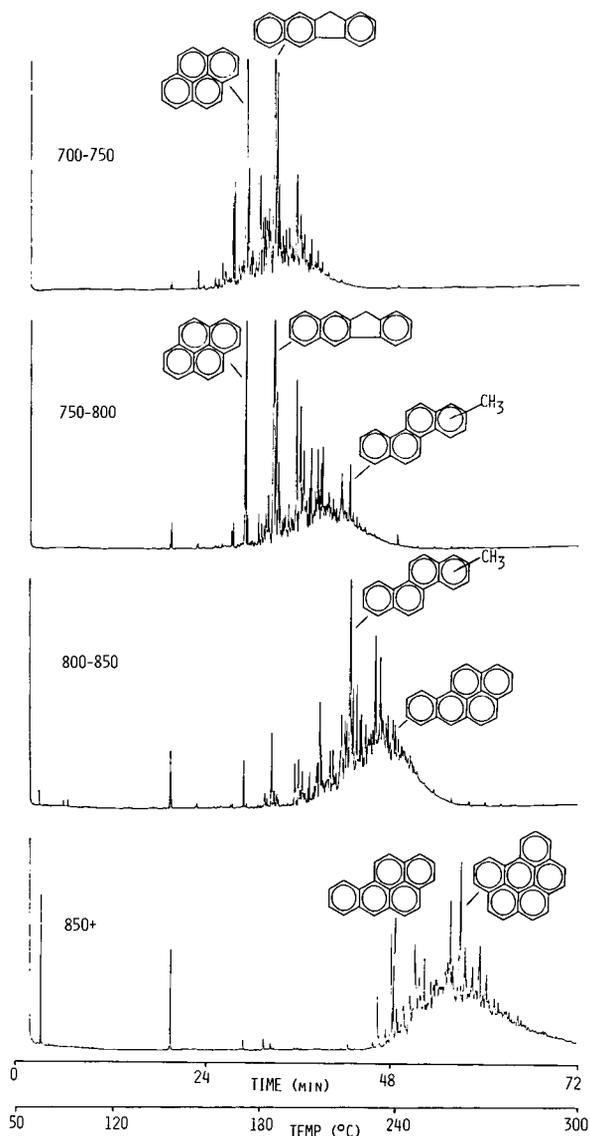


FIGURE 2. Capillary column gas chromatogram of the PAH fraction from SRC II full boiling range material. Peak numbers refer to compounds listed in Table I. Conditions: 30 m x 0.25 mm Durabond 5 (J & W Scientific) fused silica column, temperature programmed from 50°C to 280°C at 4°C/min.



**FIGURE 3.** Weight distribution of chemical classes in the (A) SRC II and (B) EDS distillate fractions (see Table 2 footnotes for a detailed description of these process materials).



**FIGURE 4.** Capillary column gas chromatograms of the PAH fractions from the SRC II 50°F distillates fractions. (See Table 2 footnotes for a detailed description of this coal-derived material.) Conditions as in Figure 2.

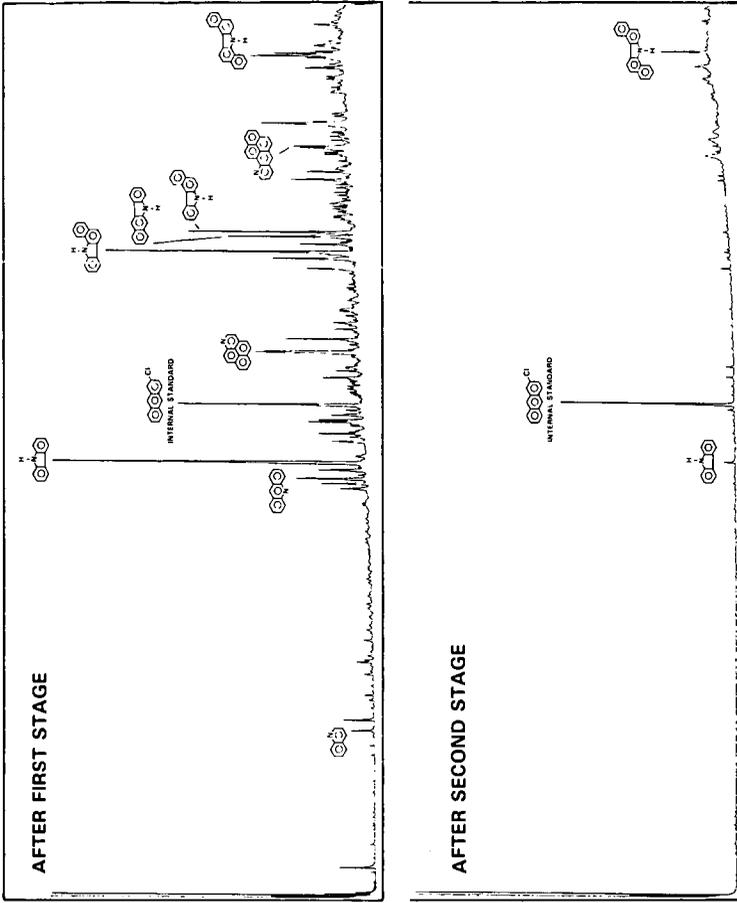


FIGURE 5. Process effects on the N-PAC content of two stage liquefaction products. Gas chromatographic condition as in Figure 2. Samples were from the ITSU process development unit operated by C. E. Lummus, New Brunswick, NJ.