

CHARACTERIZATION OF ARTIFACTS PRODUCED
FROM TETRALIN DONOR VEHICLE UNDER
COAL LIQUEFACTION CONDITIONS

Muthu S. Sundaram* and Peter H. Given
Coal Research Section
College of Earth and Mineral Sciences
The Pennsylvania State University
University Park, Pa. 16802

ABSTRACT

The hexane-soluble oil fraction of the heavy liquids produced from the liquefaction of coal using tetralin donor vehicle was fractionated by high pressure liquid chromatography. Three fractions were obtained: saturates, aromatics and polars. Each fraction was individually characterized via capillary column gas chromatography/mass spectrometry. Several binaphthyls and binaphthyl derivatives, produced from the donor solvent tetralin under coal liquefaction conditions, were identified in the aromatic fraction. These artifacts make up an important fraction of the whole aromatic fraction. There is a fairly clear tendency for the concentration of binaphthyls and derivatives to decrease with increasing rank of coal. A stepwise multiple regression analysis shows that the clay minerals and pyrite present in coal independently catalyze one or more of the types of artifact formation.

INTRODUCTION

Partially hydrogenated aromatic solvents such as tetralin, hydrophenanthrenes and hydroxyrenes are used as process solvents in several coal liquefaction processes. An important function of these solvents is to donate hydrogen necessary for capping the thermally produced free radicals from coal thereby preventing char formation. The effect of hydrogen donor concentration on the conversion of coal to THF or pyridine-soluble products has been thoroughly investigated (1,2) and several modern analytical techniques have been applied to characterize the ensuing products of liquefaction. Combined gas chromatography-mass spectrometry (GC/MS) has been extensively used in the characterization of liquefaction products from coal conversion processes (3-6). However, only a limited amount of work has been done on the identification of artifacts produced from the donor solvent itself under the coal liquefaction conditions (7-9). A knowledge of the artifacts generated from the process solvent will be very helpful in developing methods for down-stream processing of the coal-derived liquids. In this paper, we describe the identification of the artifacts produced from a process using tetralin as the hydrogen-donor solvent for liquefaction of coal and the influence of coal characteristics on the concentration of the artifacts is also discussed.

*Current Address: Process Sciences Division, Brookhaven National
Laboratory, Upton, NY 11973.

EXPERIMENTAL

Coal Samples:

Selected characteristics of the coals used in the liquefaction studies are shown in Table 1. The set of coals covers a wide range of rank and geologic province; the mineral matter content varies from a low of 6% to a high of 34% and a wide variation in the sulfur content can also be noted. Other characteristics of the coals, such as macerals content, calorific value, composition of the mineral matter are available from the Penn State/DoE coal data base. The aromaticities were determined by Gerstein, et al. using CP-MAS ^{13}C nmr (10).

Liquefaction:

The liquefaction runs were performed in duplicate in tubing bombs under the following conditions: 2.5 gm coal + 7 ml tetralin, 425°C, H_2 pressure (at temperature) 1400 psi, 30 min reaction period and agitation at 400 min^{-1} . After the gases had been vented, the products were rinsed out of the reactor into a Soxhlet thimble with ethyl acetate. Extraction was continued in the Soxhlet apparatus for 24 hours. After evaporation of the ethyl acetate, the residue was weighed to determine the total conversion and then mixed with 500 ml hexane and left to stand overnight, after which it was filtered. After removal of the hexane, the soluble portion was distilled at about 70°C and 5 mm Hg pressure to remove naphthalene and excess tetralin and the monomeric by-products formed from them during the process. The undistilled material was weighed and is reported as "oil".

Analytical Procedures:

i) HPLC Separation:

Prior to GC/MS analysis, group type separation of the hexane-soluble oil was performed using a Waters Model ALC/GPC-201 HPLC (Waters Associates, Milford, Mass.). The instrument contained of the following accessory hardware: Model 6000A solvent delivery system, a Model 660 solvent programmer, a Model U6K septumless injection system, a Rheodyne Model 7010 backflush valve and a Model 440 absorbance detector with inter-changeable UV filters.

Typically, 20 microliter of the oil was injected on to a semi-preparative (8mm ID X 30 cm length) micro-Bondapak-NH₂ column (Waters Associates, Milford, MA.). The mobile phase was spectral quality n-hexane distilled in glass (Burdick and Jackson, Muskegon, MI) and a flow rate of 6.0 ml min^{-1} was used. Saturates are not retained in the column and are eluted first followed by aromatic hydrocarbons. Polars have greater affinity towards the stationary phase which makes the analysis time longer. Hence after the elution of the aromatic hydrocarbons, solvent flow through the column was reversed using the backflush valve and the eluting material was collected as the polar fraction. UV detector response at 254 nm was recorded for the aromatic and polar fractions.

The three fractions--saturate, aromatic and polar--were collected in separate flasks and excess hexane from the fractions was distilled off in a rotary evaporator. Further concentration was effected by blowing a gentle stream of nitrogen using a Sillivap concentrator.

ii) GC/MS Characterization:

Identifications of individual components in each fraction were performed on an integrated GC/MS/Computer system. The instrument used was a Finnigan Model 4000 automated EI/CI mass spectrometer equipped with a quadrupole ion detector and interfaced with a Finnigan Model 9610 gas chromatograph and a dedicated LSI computer with 16K memory.

Several stationary phases coated on glass capillary columns were tested for their application which included SP-2100, SP-2250 (both from Supelco Inc., Bellefonte, Pa.), SE-30, SE-52, SE-54 and Dexsil 300 (all from Applied Science Lab., State College, Pa.). A 30 meter SE-54 (methylphenylsilicone) stationary phase coated-glass capillary column (film thickness, 0.25 micrometer) was found satisfactory for the analyses of both aromatic and polar fractions.

The operating conditions used for the GC were: injector temperature 250°C; carrier gas, helium; flow-rate, 1 ml/min. The sample was quantitatively introduced into the capillary column by purged splitless injection technique (11). The oven temperature was initially programmed to increase from 50° to 100°C at 20°C min⁻¹ and then to 300°C at 5°C min⁻¹.

The mass spectrometer was operated in the electron-impact mode (70eV electron energy). Chemical ionization mass spectra (methane reagent gas) of the eluting components were obtained when necessary. Spectral data acquisition was performed at appropriate scanning intervals and the mass spectra were recorded on magnetic tapes for later retrieval. Specific compound identification was made from the characteristic mass spectral splitting patterns. Retention time data and response factors were obtained for representative compounds. By monitoring the specific ion current (single ion monitoring), detection of compounds present at trace levels was considerably improved.

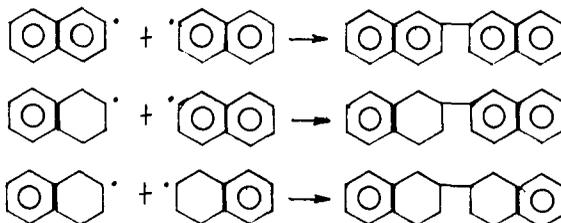
RESULTS AND DISCUSSION

Tetralin has been widely used as a hydrogen donor solvent in many coal liquefaction studies. In addition to the transfer of hydrogen from the hydroaromatic ring to coal free radicals, tetralin undergoes the following changes under coal liquefaction conditions:

1. Isomerization: Tetralin rearranges (isomerizes) to produce methylindans. This reaction is temperature dependent (12) and is catalyzed by pyrite (13).

2. Fragmentation: In this case, tetralin decomposes to produce a mix of smaller molecules which is mainly made up of alkylbenzenes. Curran et al. reported that the decomposition of tetralin to C₄ benzenes was enhanced in the presence of coal extracts (14).

3. Adduction/Polymerization: From deuterium labelling studies, Franz et al. showed that both 2-tetralyl and 1-tetralyl radicals are produced in competitive amounts when a low-rank coal is heated in tetralin (15). The tetralyl or naphthyl radical intermediates can react with free radicals generated from coal or they can recombine among themselves leading to polymerized products such as binaphthyls and their derivatives.



Various other isomers of the above representative compounds are also possible.

On the basis of their results from the flash pyrolysis of 1- and 2-tetralyl radical precursors in vacuum, the above authors suggested that the hydroaromatic radical intermediates 'may prefer disproportionation over combination pathways as temperatures increase'. While this is true for pyrolysis experiments at high temperatures and short residence times, it can not be generalized for coal liquefaction experiments at intermediate temperatures (400-450°C) and considerably long residence times (ca. 30 min.). Our results indicate that the dimerization of solvent radical intermediates occurs to a significant extent in a coal-tetralin system and that the concentration of the resulting artifacts seems to be affected by the coal characteristics.

A representative HPLC separation of an oil product is shown in Figure 1. Figure 2 shows the reconstructed Total Ion Chromatogram (TIC) of the aromatic fraction of the oil from PSOC-739. The large peaks at scan numbers 370 to 410 in the TIC in figure 2 are due to binaphthyls and related compounds, which evidently make up an important fraction by weight of the whole aromatic fraction. Similar results were obtained with other coals. Figure 3 shows the Specific Ion Chromatograms (SIC) for m/e values of 254, 258 and 262 corresponding to the molecular ions of binaphthyl and its tetrahydro and octahydro derivatives. The peaks are numbered and identified by number in Table 2. It will be seen that, in peak height, 2,2'-binaphthyl and its derivatives predominate, indicating the higher reactivity of the 2-position compared to that of the 1-position.

When all the peaks are examined at the same attenuation, it is seen that binaphthyls and hydrogenated derivatives account for over 70% of the dimeric artifacts formed in the hydrogenation of all coals but that of highest rank, PSOC-801 (Stigler seam, Oklahoma). Having regard to the small size of other peaks in the TIC, it is unlikely that binaphthyls generated from the coals account for much of the peak heights observed. Philip et al. reported the presence of two isomers of octahydrobinaphthyls in a sample from the liquefaction of a Texas lignite using tetralin as the hydrogen-donor solvent (16). The actual amount of these and other products, however, was not specified. Schultz et al. identified 2,2'-binaphthyl (only) among the aromatic hydrocarbons in a SRC pilot plant product with a mixture of Kentucky Nos. 9 and 14 coals as feedstock, but only in trace amount (6). Thus the binaphthyls found in our work are indeed very largely artifacts of the solvent. In what follows, all of the compounds named are assumed to be derived entirely from the solvent.

In addition to the binaphthyls discussed, a number of phenyl naphthalene were identified: C₁-, C₂- and C₄-phenyl naphthalenes, and a phenyl tetralin. Only the sum of these compounds are shown in Table 3, under the heading $\Sigma\phi-v$. Furthermore, a number of alkyl naphthalenes and either alkyl indans or alkyl tetralins (or a mixture) were found (C₁-C₄). Again, only the sum of the concentrations of these compounds is shown in Table 3, under the heading ΣC_n-v . The part of the HPLC fraction 2 (aromatics) accounted for by solvent artifacts is shown as a percentage in the final column of Table 3.

There is a fairly clear tendency for the concentration of binaphthyls and derivatives to decrease with increasing rank. The concentration of phenyl naphthalenes, whose formation involves ring-splitting, tends to increase with rank, as does the concentration of alkyl naphthalene/indan derivatives, whose formation involves isomerization. As mentioned before, the isomerization of tetralin to methyl indans is catalyzed by pyrite (13); yet there is no correlation between the concentration of these derivatives and pyrite content. In fact, it is reasonable to suppose that many factors determine the yields of the various kinds of artifacts. This is substantiated by an equation developed by stepwise multiple regression:

$$\text{Concentration of artifacts (\%)} = 0.919 \text{ MM} + 14.5 S_{\text{pyr}} - 9.81 f_a + 38.2$$

The variables provided for the regression were: contents of C, O, S_p, S_{tot} and MM, and the aromaticity, f_a. The fraction of variance explained by this regression, R², is 0.851. The equation suggests that both clay minerals and pyrite independently catalyze one or more of the types of artifact formation. Abdel-Baset (13) found that clay minerals catalyze transfer of hydrogen from hydroaromatics to aromatics. Thus the significance of f_a in the equation may lie in the fact that it indicates the number of C atoms available for accepting H atoms and hence (presumably) for generating free radicals in the solvent (admittedly this term may be not very significant since the range of values of f_a is small).

In comparing the yields and composition of the products of liquefaction experiments, it might be considered desirable to subtract out the components derived from the solvent. The aromatic fraction of the oil (HPLC fraction 2) can be corrected as follows:

$$\% \text{ aromatics (corr.)} = \% \text{ aromatics (HPLC)} \times \frac{100 - \% \text{ artifacts}}{100}$$

Consequential changes are needed in other figures characterizing the product distribution. Thus:

$$\begin{aligned} \% \text{ hexane-sol. oil (corr.)} &= \% \text{ sat.} + \% \text{ arom. (corr.)} + \% \text{ polars} \\ \% \text{ benzene-sol. total liquids (corr.)} &= \% \text{ oil (corr.)} + \% \text{ asph.} \\ \% \text{ gases (corr.)} &= \% \text{ conversion} - \% \text{ total liquids (corr.)} \end{aligned}$$

The corrected and uncorrected yields of various fractions obtained from the liquefaction of coals listed in Table 1 are shown in Table 4. From the table, it is clear that the adjustment of the figures for hexane-soluble oils and for the aromatic HPLC fraction makes a quite appreciable difference to the data and ought to be determined before product distributions for any batch system are evaluated.

CONCLUSION

An important fraction by weight of the whole aromatic fraction of the oils obtained from the liquefaction of coal using tetralin as the hydrogen-donor solvent was made up of binaphthyls and related compounds. The concentrations of these artifacts were affected by the coal characteristics. Both clay minerals and pyrite seem to independently catalyze one or more of the types of artifact formation from tetralin. This is a somewhat unexpected effect of coal characteristics on the composition of liquefaction products. Other donor solvents, such as partially hydrogenated phenanthrene or a commercial recycle oil, are obviously likely also to undergo changes during processing, whose magnitude and nature will vary with the feedstock, and whose effects on product composition will be appreciable.

ACKNOWLEDGEMENT

The coals used in this study were kindly supplied by Dr. William Spackman, Professor of Palaeobotany and Director of the Coal Research Section in this College. This work was supported by Contract No. DE-AC22-81-ET 10587 from the U.S. Department of Energy.

REFERENCES

1. Epperly, W. R., "EDS Coal Liquefaction Process Development, Phases IIIB/IV", Technical Progress Report, DoE, FE-2893-1F (1978).
2. Whitehurst, D. D., Mitchell, T. O., and Farcasiu, M., "Coal Liquefaction", Academic Press, New York (1980).
3. Bertsch, W., Anderson, E., and Holzer, G., *J. Chrom.*, 126, 213-224 (1976).
4. White, C. M., Sharkey, Jr., A. G., Lee, M. L., and Vassilaros, D. L., in "Polynuclear Aromatic Hydrocarbons", Ed. Jones, P. W., and Leber, P., Ann Arbor Science Pub. Inc., Ann Arbor, MI. (1979).
5. White, C. M., and Lee, M. L., *Geochim. Cosmochim. Acta*, 44, 1825-1832 (1980).
6. Schultz, R. V., Jorgenson, J. W., Maskarinec, M. P., Novotny, M., and Todd, L. J., *Fuel*, 58, 783-789 (1979).
7. Cronauer, D. C., Jewell, D. M., Shah, Y. T., Modi, R. J., and Sheshadri, K. S., *Ind. Eng. Chem. Fundam.*, 18, 368-376 (1979).
8. Cronauer, D. C., Jewell, D. M., Shah, Y. T., and Modi, R. J., *ibid.*, 153-162 (1979).
9. Ruberto, R. G., *Fuel Proc. Tech.*, 3, 7-24 (1980).
10. Gerstein, B.C., Murphy, P.D., and Ryan, L.M., in "Coal Structure", ed. R.A. Myers, Academic Press, New York, p. 112 (1982).
11. Grob, K., and Grob, K., Jr., *J. High Res. Chro.*, 57 (1978).
12. Whitehurst, D. D., Farcasiu, M., and Mitchell, T. O., EPRI Annual Technical Report No. AF-480-RP-410-1 (1977).
13. Abdel-Baset, M., in "The Relation of Coal Characteristics to Coal Liquefaction Behavior", by Given, P. H., Spackman, W., Davis, A., Walker, P. L., and Lovell, H. L., Report No. 2 to RANN Division of Nat. Sci. Foundation, under Grant No. GI-38974, pp. 50-52.
14. Curran, G. P., Struck, R. T., and Gorin, E., *Ind. Eng. Chem. Proc. Des. Dev.*, 6, 166 (1967).
15. Franz, J. A., and Camaioni, D. M., *Fuel*, 59, 803-805 (1980).
16. Philip, C. V., and Anthony, R. G., *Preprints ACS Fuel Div.*, 24(3), 204-214 (1979).
17. Given, P.H. and Yarzab, R.F., in "Analytical Methods for Coal and Coal Products", ed. C. Karr, Academic Press, New York, Vol. 2, pp. 3-41 (1978).

Table 1
Selected Characteristics of Coals Used

PSOC No.	Province*	ASTM Rank	% C dmmf	% S dry	% MM, [†] dry	f _a ^{**}	
833	Fort Union Bed, Mont.	3	Lig	70.43	0.55	16.26	0.68
791	A Pit, Texas	6	Lig	72.13	0.81	20.78	0.55
785	Lower Wilcox, Texas	6	sbb	73.21	1.06	14.29	0.54
240A4	Big Dirty, Wash.	5	sbb	74.34	0.39	17.82	--
240A1	Big Dirty, Wash.	5	sbb	75.11	3.36	33.98	--
866	G Seam, Colo.	4	HVC	76.97	0.50	22.22	0.64
548	Wolf Creek, Colo.	4	HVC	78.98	0.52	13.11	0.64
680	Indiana No. 6, Ind.	2	HVC	80.61	3.58	14.23	--
854	Juniata C, Colo.	4	HVB	81.64	0.40	6.71	0.63
739	Kentucky No.12, Ky.	2	HVB	83.29	2.72	15.05	0.70
773	Ohio No.6, Ohio	1	HVB	83.29	2.83	9.30	0.75
808	Croweburg, Okla.	2	HVA	84.71	3.20	6.57	0.73
821	Pittsburgh, W. Va.	1	HVA	84.92	2.56	6.00	0.70
801	Stigler, Okla.	2	MV	88.35	4.65	13.83	0.79

* Key to province numbers: 1, Eastern or Appalachian; 2, Interior; 3, North Great Plains; 4, Rocky Mountain; 5, Pacific; 6, Gulf.

** Data from ¹³C nmr, kindly provided by Professor B. Gerstein, University of Iowa, now published by him (10).

† Calculated by a modification of the Parr formula (Given and Yarzab, 17).

Table 2
Identification of Peaks in Specific Ion Chromatograms
of Figure 3

Figure 3(a):	1. 1,1'-binaphthyl 2. 1,2'-binaphthyl 3. 2,2'-binaphthyl
Figure 3(b):	1. 1,2,3,4-tetrahydro-1,1'-binaphthyl 2. 1,2,1',2'-tetrahydro-2,2'-binaphthyl 3. 1,2,3,4-tetrahydro-2,2'-binaphthyl 4. 1,2,3,4-tetrahydro-2,1'-binaphthyl (three other unidentified peaks)
Figure 3(c):	1. 1,2,3,4,1',2',3',4'-octahydrobinaphthyl 2. 1,2,3,4,1',2',3',4'-octahydro-1,2'-binaphthyl 3. 1,2,3,4,1',2',3',4'-octahydro-2,2'-binaphthyl

Table 3
Concentrations of Solvent Artifacts in the
Aromatic HPLC Fraction of Some Coals

percent of total fraction

PSOC No. C	Binaphthyls	Tetrahydro- binaphthyls	Octahydro- binaphthyls	Binaphthyl derivatives (total)	$\Sigma \phi-\nu$ *	$\Sigma C_{n-\nu}$	Total artifacts
833	15.6	7.6	15.8	38.9	1.9	5.5	46.3
791	17.7	13.3	13.4	44.4	0.7	7.8	52.9
785	10.3	12.4	15.6	38.3	0.7	5.4	44.4
240A4	14.0	20.2	8.4	42.5	1.5	3.5	47.5
240A1	19.1	22.4	16.7	58.2	1.2	4.4	63.8
866	16.0	12.5	15.1	43.6	1.8	6.7	52.0
548	8.7	9.7	10.4	28.8	2.2	15.5	46.6
680	6.1	7.9	9.5	23.5	3.9	11.1	38.5
854	12.6	12.7	9.7	35.4	3.5	4.2	42.7
739	7.1	6.7	7.7	21.6	2.8	11.1	35.5
773	7.1	9.4	7.1	23.5	3.9	9.3	36.8
808	3.9	4.5	5.9	14.3	3.3	15.5	33.0
821	5.7	6.9	10.6	23.2	3.4	5.5	32.0
801	4.9	6.2	5.7	16.8	4.1	38.2	59.0

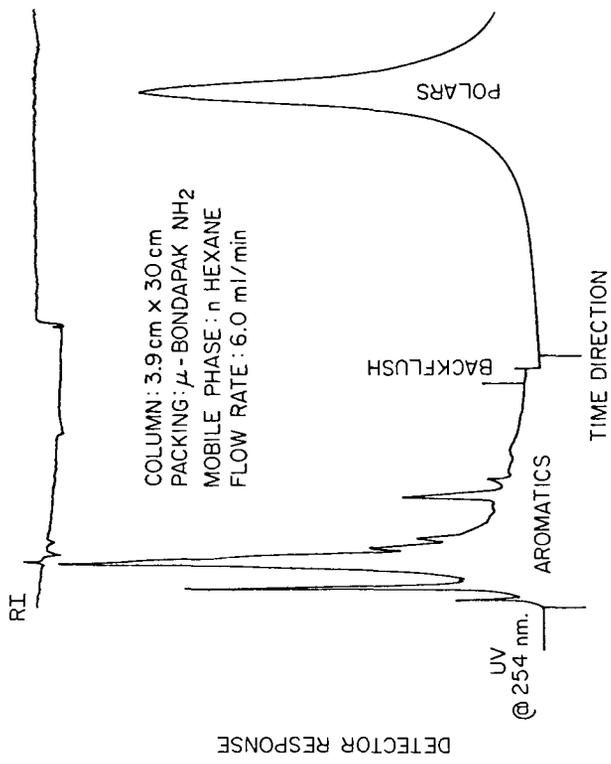
* Total phenyl-naphthalenes.

** Total alkyl-tetralins and naphthalenes.

Table 4
 Product Distributions from Coal Liquefaction,
 Corrected for Artifacts from Solvents

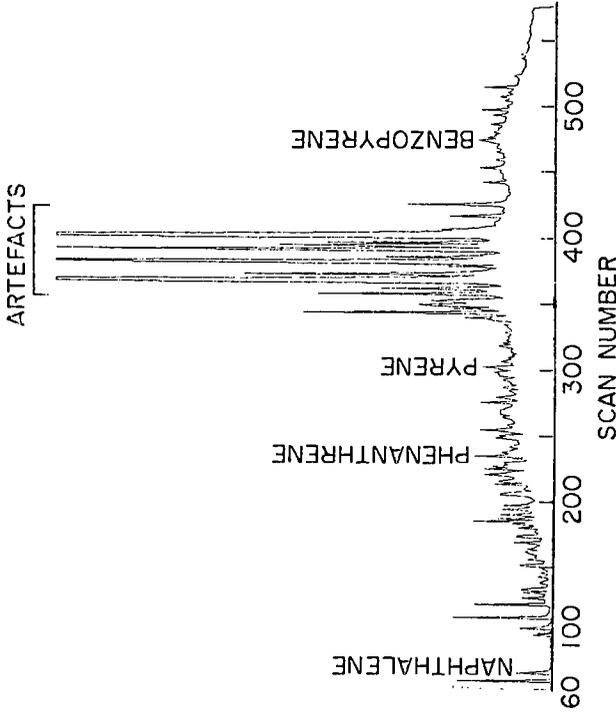
(% of dmmf coal)

PSOC No.C	Total conversion	Total liquids		Gases (by diff.)		Asphal- tenes	Hexane-sol. oil		Sat. HPLC frac.	Polar HPLC frac.	Aromatic HPLC fraction	
		uncorr. corr.	corr.	uncorr. corr.	corr.		uncorr. corr.	uncorr. corr.				
833	50.3	28.4	24.8	21.9	25.6	16.2	10.3	8.6	0.1	6.5	3.7	2.0
791	57.8	39.7	35.6	18.1	22.2	21.4	18.4	14.3	0.2	10.4	7.8	3.7
785	57.5	38.3	34.9	19.3	22.6	21.5	16.8	13.4	0.8	8.4	7.6	4.2
240A4	59.3	38.5	35.9	20.8	23.4	25.1	13.4	10.8	0.6	7.3	5.5	2.9
240A1	70.1	45.1	40.6	25.0	29.5	22.2	18.0	13.4	0.4	10.4	7.2	2.6
866	49.1	37.3	34.7	11.8	14.4	25.7	11.6	9.0	0.2	6.3	5.2	2.5
548	52.0	42.5	39.2	9.5	12.8	24.8	17.8	14.4	0.6	9.9	7.3	3.9
680	56.9	49.3	47.1	7.6	9.8	33.3	15.9	13.8	0.1	10.1	5.8	3.6
854	53.3	44.0	42.4	9.2	10.9	31.7	12.3	10.7	0.8	7.6	4.0	2.3
739	52.0	43.6	42.0	8.4	10.0	31.4	12.3	10.7	0.9	6.8	4.6	3.0
773	55.4	47.7	46.1	7.7	9.4	35.9	11.8	10.1	0.4	6.9	4.5	2.9
808	45.4	40.2	39.0	5.2	6.4	29.2	11.0	9.8	0.3	6.8	4.0	2.7
821	58.4	52.2	50.5	6.2	7.9	39.1	13.2	11.4	0.5	7.2	5.5	3.7
801	28.5	25.0	21.3	3.6	7.3	15.7	9.3	5.5	0.3	2.7	6.2	2.5



LIQUID CHROMATOGRAPHIC SEPARATION OF A VACUUM-STRIPPED OIL INTO SATURATE, AROMATIC AND POLAR FRACTIONS

Figure 1



CAPILLARY GAS CHROMATOGRAM OF AROMATIC FRACTION FROM PSOC-739 (hvB, KENTUCKY #12)

Figure 2

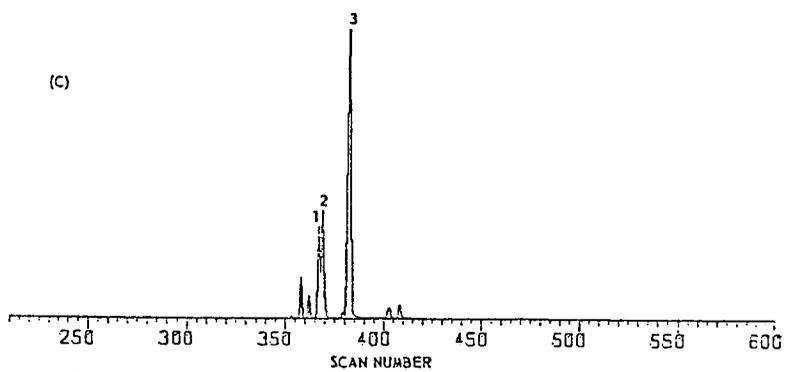
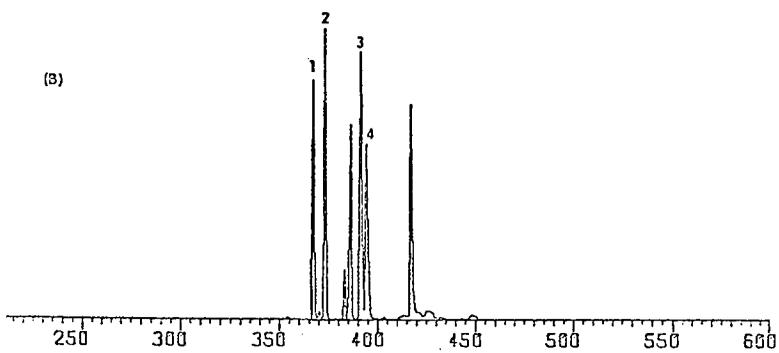
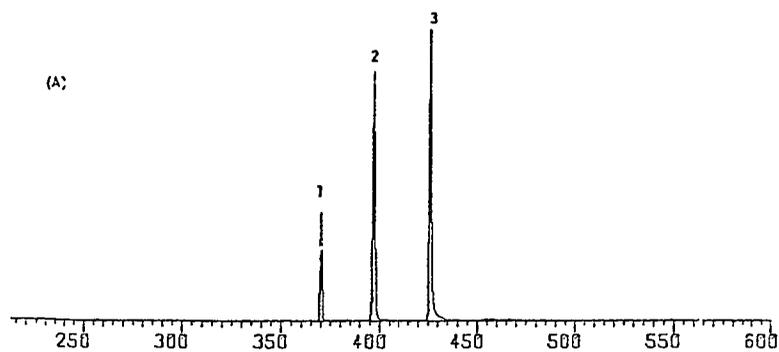


Figure 3 SINGLE ION CHROMATOGRAMS FOR HPLC FRACTION 2 FROM PSOC-739 (KENTUCKY NO. 12)
 (A) $m/e = 254$, (B) $m/e = 258$, (C) $m/e = 262$