

TWO-DIMENSIONAL HPLC AND GC-MS OF OILS FROM CATALYTIC COAL LIQUEFACTION

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ABSTRACT

We have employed normal-phase HPLC with photo diode array detector and GC-MS techniques to characterize the oils (hexane soluble fraction) from the catalytic and non-catalytic liquefaction of Wyodak subbituminous coal at 400 °C under 6.9 MPa H₂ pressure. The use of a dispersed Mo catalyst afforded much higher oil yield than the non-catalytic run. HPLC reveals that the oils from the catalytic runs contain more phenolic compounds and more of heavier components as compared to the oils from non-catalytic run. On the other hand, GC-MS shows that there is a significant amount of long-chain alkanes in the oils, ranging from C₁₁ to C₃₅. The analytical results from the two techniques appear to be complementary to each other. The oils contain some heavier components which are detectable by HPLC but undetectable by GC-MS. GC-MS of HPLC fractions of the oils from the catalytic run confirmed the presence of significant amount of phenols and indanols.

INTRODUCTION

Catalytic coal liquefaction is a potential route to alternate liquid transportation fuels and aromatic chemicals (Song and Schobert, 1993). However, the characteristics of the liquefaction products must be clarified before effective implementation. Certain coal-derived aromatic compounds can be used to make high-value chemicals through shape-selective catalysis (Song and Kirby, 1993, 1994; Song and Moffatt, 1993, 1994; Schmidt and Song, 1994). The non-fuel use of coal liquids could improve the economics of liquefaction significantly, although the majority of the coal liquids may be used for transportation fuels (Song and Schobert, 1993; Derbyshire et al., 1994).

The present work aims at clarifying the compositional characteristics and molecular components of oils from catalytic liquefaction of Wyodak subbituminous coal using a dispersed Mo catalyst. This paper reports on the oil analysis using normal-phase high-performance liquid chromatography (HPLC) with photo diode array (PDA) detector which allows continuous two-dimensional scanning analysis of HPLC elutes over UV wavelength range.

While reversed-phase HPLC is popular for analysis of a variety of samples that are soluble in water or polar organic solvents (Poole & Poole, 1991; Wise et al., 1993), normal-phase HPLC can be used for analyzing components dissolved in non-polar organic mixtures (Snyder et al., 1988). Reversed-phase HPLC is characterized by strong interactions between the polar mobile phase and various sample molecules. However, coal-derived oils are not soluble in the common solvent systems (such as water-acetonitrile) for reversed-phase HPLC. In normal-phase HPLC, sample-adsorbent (stationary phase) or solvent-adsorbent interactions are strong but sample-solvent interactions are relatively weak. Neutral organic solvent (hexane) and weakly polar solvent (methylene chloride) can be used for normal-phase HPLC, which are also good solvents for coal-derived oils. Some bonded-phase HPLC columns for normal-phase HPLC have become commercially available recently. The conventional monochromator UV detector has limited the amount of information that can be extracted from HPLC, since one particular wavelength may not be suitable for analyzing all the compounds in the complex mixtures (Snyder et al., 1988; Fetzer et al., 1993). PDA detector represent a recent development in the HPLC detection system, which allows sample analysis over UV range. Recently PDA has been demonstrated to be very useful in the analysis of PAHs in heavy liquids either by reversed-phase (Liu et al., 1992) or normal-phase HPLC (Clifford et al., 1994).

EXPERIMENTAL

Reagents and Materials. All the oils were derived from liquefaction of Wyodak subbituminous coal, which is one of the U.S. Department of Energy Coal Samples (DECS-8) maintained in the DOE/Penn State Sample Bank. Ammonium tetrathiomolybdate (ATTM) was dispersed as a catalyst precursor on to coal (1 wt% Mo on dmmf basis) by incipient wetness impregnation from its aqueous solution. ATTM is expected to generate molybdenum sulfide particles on coal surface upon thermal decomposition at ≥ 325 °C (Artok et al., 1993). The impregnated or the raw coal samples were dried in a vacuum oven at 100 °C for 2 h before use. The liquefaction was carried out in 25 mL tubing bomb reactors at 400°C for 30 min (plus 3 min heat up) under an initial H₂ pressure of 6.9 MPa. The oils are hexane-soluble fraction of liquefaction products. Detailed results of liquefaction may be found elsewhere (Song et al., 1993).

Various reagents were used as standards for confirmation of identification of HPLC and GC-MS peaks. The following reagents were purchased from Aldrich: phenol (99+%), 1,2,3,4-tetrahydro-1-naphthol (97%), tetralin (99%), 1-methylnaphthalene (98%), 9,10-dihydrophenanthrene (94%), and 1-naphthol (99+%). Sixteen polycyclic aromatic hydrocarbons were purchased from Supelco as a mixture defined as EPA Mixture 610. This mixture contains the following components: naphthalene,

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acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthrene, pyrene, benzo(a)fluoranthene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, and indeno(1,2,3,c,d)pyrene.

High Performance Liquid Chromatography (HPLC). The Waters HPLC system consists of U6K Universal Injector, 600E Powerline Multi-Solvent Delivery Module, and 991 Photodiode Array (PDA) Detector. The 600 Powerline Module serves as a system controller for setting up all solvent gradient conditions, injection and detection parameters and wavelength ranges. The PDA detector is capable of continuous monitoring and acquisition of all UV/VIS wavelengths from 190 to 800 nm. Through the use of computer, the 991 PDA operates exclusively with Millennium 2010 Chromatography Manager software system, which allows fully automated data acquisition, processing, and reporting as well as 3-D graphics. The resolution of the PDA detection is 4.7 nm.

The column used for HPLC was a Hypersil PAH-2 purchased from Keystone Scientific, Inc., which is a commercially available column (150 x 4.6 mm i.d.) made by Shandon Scientific, Inc., U.K. The Hypersil PAH-2 has been developed using tetrachlorophthalimidopropyl bonded silica. This type of column can be used for analyzing the polyaromatic compounds dissolved in organic mixtures such as crude oils and coal liquids. Classical n-alkyl bonded phases are not suitable for analyzing such non-polar mixtures.

For HPLC analysis, the oils were diluted in 50%-50% hexane-methylene chloride solution (approximate concentration: 1 mg/mL) and filtered through 0.2 µm membrane filter (Supeco Iso-Disc P-32) attached to a syringe. This assures that the solution to be analyzed is free of suspended micron-sized particles. For each HPLC analysis, about 10-20 µL of a sample solution was injected and the solvent elution was controlled by the gradient program, as shown in Table 1. Gradient elution was used: hold at 100% n-hexane for 20 min, from 100% hexane to 50% hexane-50% methylene chloride between 20 to 80 min, and to 100% methylene chloride between 80 to 100 min, followed by a 20 min hold at 100% methylene chloride. The flow rate of the mobile phase was 0.8 mL/min. The data acquisition of all the oils and standards were made in the UV wavelength range of 200 to 400 nm at the rate of 30 scans/minute. All the HPLC analyses were conducted at ambient temperature. HPLC fractions were collected for some representative samples and analyzed by GC-MS.

Gas Chromatography-Mass Spectrometry (GC-MS). The HPLC fractions of oil were analyzed on a HP 58901 GC coupled with an HP 5971A Mass Selective Detector (MSD). The column used for capillary GC was J&W DB-5 column: 30 m x 0.25 mm i.d. fused silica capillary column coated with 5% phenyl-95% methyl polysiloxane with a 0.25 µm film thickness. More analytical details may be found elsewhere (Song et al., 1994). In a typical GC-MS run, about 1 µL of the diluted methylene chloride solution of the sample was injected through the split/splitless injector in the splitless mode, with a 5 min delay of ionization to cut off the solvent. The GC oven in GC-MS was temperature-programmed as follows: 5 min isothermal holding at 40°C, subsequent heat-up to 280°C at 4°C/min, followed by isothermal holding at 280°C for 30 min.

RESULTS AND DISCUSSION

HPLC of Oils

Figures 1 and 2 show the 3-dimensional HPLC plots for oils from non-catalytic and catalytic runs, respectively, where the signal intensity (Z axis) is plotted against the UV wavelength (X, 247-390 nm) and retention time (Y). The use of a dispersed molybdenum sulfide catalyst increased oil yield from 10 to 46 wt% (based on dmmf coal). Apparently, the dispersed catalyst not only improved coal conversion, but also altered the compositional features of oils, as can be seen from the 3-D HPLC plots. The 3-D plots indicate that oils from the catalytic run contain more components that have either larger aromatic ring-size or are more polar, as compared to the non-catalytic runs.

To assist in the peak assignments, we performed HPLC analysis of two standard mixtures. Figure 3 shows 3-D plot for a standard containing 16 PAHs. The UV spectra of some peaks eluted before 20 min in the PAH mixture are in the similar wavelength range as those peaks in the real sample of oil from catalytic coal liquefaction. However, it becomes clear that the intense peaks in the 30-65 min range in the oil from catalytic runs (Figure 2) are not due to condensed PAHs (Figure 3). Figure 4 shows a maxiplot (maximum UV absorbance corresponding to each retention time unit) for the PAH standard mixture, in which the peaks were identified based on the information from the column supplier (Keystone Scientific, 1994).

As oxygen compounds are also possible products, we also analyzed the HPLC profiles of several pure polar compounds. Figure 5 gives a maxiplot for the phenolic mixture containing phenol, 1-naphthol, 1,2,3,4-tetrahydro-1-naphthol, and 1-indanol as well as aromatic hydrocarbons including tetralin, 1-methylnaphthalene, and 9,10-dihydrophenanthrene. The results with phenolic standards are very useful in understanding the differences between oils from non-catalytic and catalytic runs. Some major peaks around 60 min in the 3D-plot in Figure 2 have UV spectra similar to those of phenolic compounds.

The sample retention in normal-phase HPLC is governed by adsorption to the stationary phase. As PAHs are electron-donors, the chemically bonded electron-acceptor stationary phase (PAH-2 phase) allows the selective retention of PAHs in non-polar mobile phases. It is interesting to note that all the phenolic compounds interact so strongly with the tetrachlorophthalimidopropyl bonded-phase that their retention times (Figure 5) are longer than those of all the 16 PAHs (Figure 4). These results also indicate that, for HPLC analysis using PAH-2 column, one should be very careful in determining the ring size of aromatic compounds solely based on normal-phase HPLC. The most illustrative example is that the retention time of phenol, a single-ring compound, is even longer than that of a six-ring PAH, indeno(1,2,3,c,d)pyrene.

The HPLC results seem to imply that, as compared to the oils from non-catalytic run (Figure 1), the

oils from the catalytic runs (Figure 2) contain more phenolic compounds and more of heavier components. At first glance, these HPLC results are surprising, as a good catalyst was used in the liquefaction. The present HPLC results, however, are in agreement with our earlier work on GPC. We have analyzed the molecular size distribution of coal-derived oils using HPLC operating in the GPC mode with polystyrene gel column (Song et al., 1988, 1989). The GPC results suggested that the oils from catalytic runs have more components with larger molecular sizes.

GC-MS of HPLC Fractions

To clarify the molecular components and to identify the HPLC peaks, we have collected eleven HPLC fractions of the oils derived from catalytic liquefaction. Figure 6 shows the maxplot together with the number and retention time ranges of individual HPLC fractions. We have analyzed all the HPLC fractions using GC-MS. The results are summarized below.

GC-MS shows that all the HPLC peaks and fractions represent a mixture rather than a single component. Fraction 1 (2-3.5 min) is a co-elute of monoaromatic compounds with long-chain alkanes, ranging from C₁₁ to C₃₅. The aromatic compounds include alkylbenzenes, indanes, and tetralins. The HPLC peak intensity for this fraction does not include long-chain alkanes. Fraction 2 (3.5-6.0 min) consists of naphthalene, methyl-naphthalene, and alkylbiphenyls (or acenaphthenes). Fraction 3 (6-8.0 min) corresponds to a small peak in the HPLC and contains C₂-naphthalenes and other two-ring compounds. In Fraction 4 (8-10.5 min) we detected phenanthrene and a C₄-alkyl-substituted phenanthrene. Fraction 5 (10-13.5) contains many three-ring compounds, phenanthrene and its derivatives. Fraction 6 (14-18 min) seems to give a very noisy GC-MS total ion chromatogram (TIC), but some compounds in this fraction are three-ring compounds. Fraction 7 (14-18 min) contains four-ring compounds including fluoranthene (m/z: 202) and pyrene (m/z: 202). Fraction 8 (21-30 min) contains several peaks with same molecular ion of m/z 216, and are probably methylfluoranthene and methylpyrene.

We detected significant amount of phenolic compounds in the fractions between HPLC retention time of 30 to 60 min. Beginning with fraction 9 (30-38 min), phenols and indanols were observed. Fraction 10 (38-45 min) contains mainly C₁-, C₂-, C₃- and C₄-phenols. Fraction 11 (50-60 min) is the dominant phenolic fraction. It contains phenol, C₁-, C₂-, C₃-phenols and indanol, C₁- and C₂-indanols. These GC-MS results in combination with HPLC results clearly revealed that the oils from catalytic liquefaction of Wyodak subbituminous coal using a dispersed molybdenum sulfide catalyst contain more phenolic compounds (30-65 min range in HPLC) and more heavier components (70-110 min range in HPLC), as compared to oils from the non-catalytic run at 400°C for 30 min under 6.9 MPa H₂. The HPLC retention times for peaks with this sample are not exactly the same to those for the PAH and phenolic standards (due to some difference in instrumental conditions).

In addition, the fact that a catalytic run gives more phenolic compounds also provides further evidence that the initial reaction involves the cleavage of O-C bonds in coal. The stabilization of the radicals from these bond cleavages by hydrogen transfer can produce phenolic compounds, otherwise these highly reactive radicals would seek self-stabilization through retrogressive cross-linking reactions. The use of a dispersed Mo catalyst facilitates the transfer of hydrogen to radicals.

It should be mentioned that Clifford et al. (1994) analyzed several coal liquefaction process streams (oils) by normal-phase HPLC. They detected many polyaromatic compounds but did not observe oxygen compounds in their samples. The samples they analyzed represent highly 'upgraded' products, because they were derived from two-stage catalytic liquefaction of coals in Wilsonville pilot plant and HRI pilot plant. The present samples, however, were derived from primary (one-stage) liquefaction of Wyodak subbituminous coal under mild conditions (400°C, 30 min).

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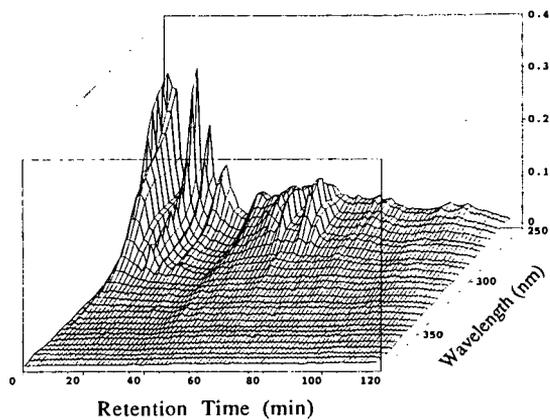


Figure 1. 3-D HPLC plot of oils from non-catalytic liquefaction of Wyodak subbituminous coal.

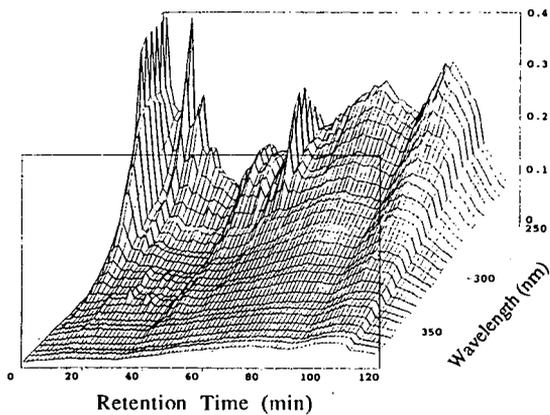


Figure 2. 3-D HPLC plot of oils from catalytic liquefaction of Wyodak subbituminous coal.

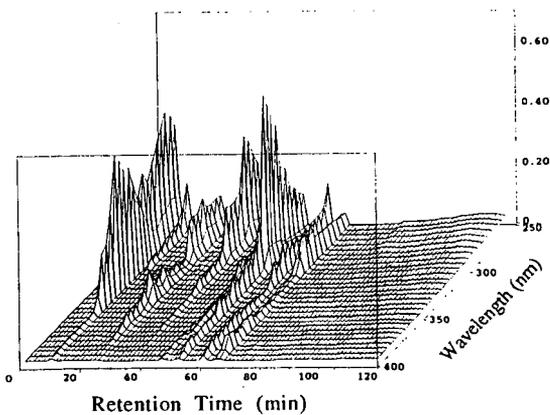


Figure 3. 3-D HPLC plot of a mixture of 16 polynuclear aromatic hydrocarbons (PAHs).

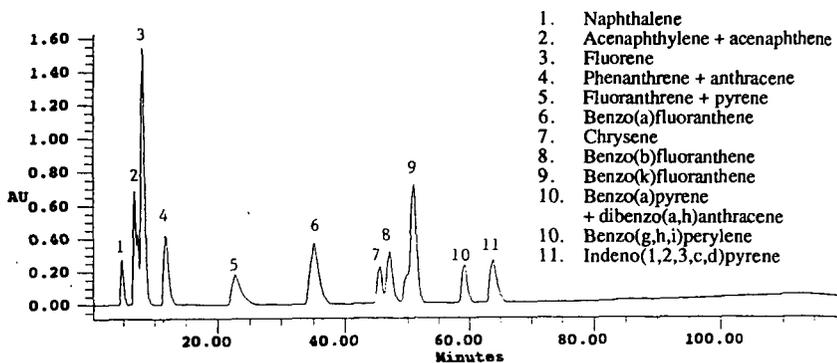


Figure 4. HPLC maxplot of PAH standard containing 16 PAHs.

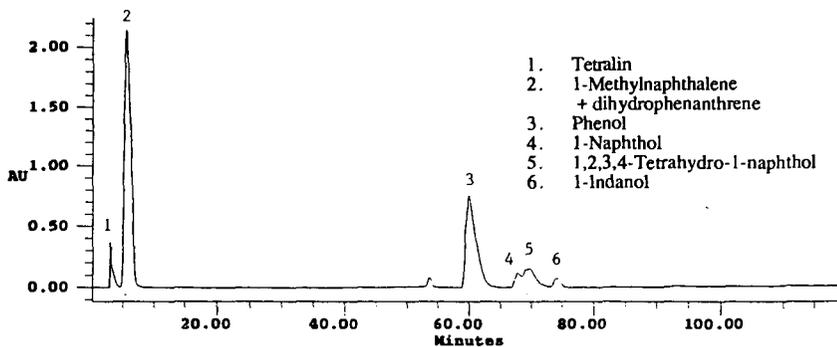


Figure 5. HPLC maxplot of phenolic standard mixture.

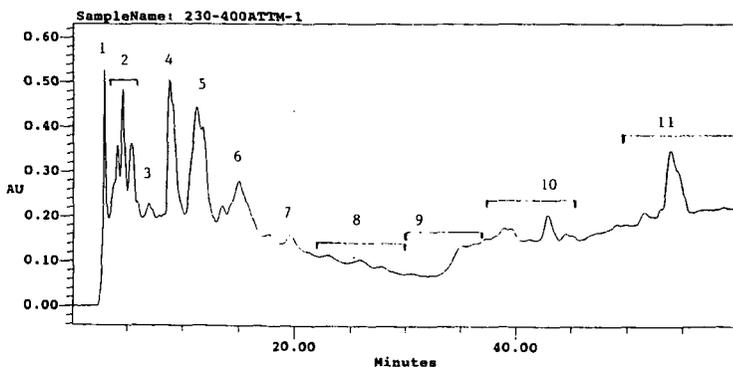


Figure 6. Expanded HPLC maxplot of oils from catalytic liquefaction at 400°C for 30 min. The number and accompanying lines indicate the retention time range of HPLC fractions collected.