

DETERMINATION OF COMPOUND CLASS COMPOSITION OF OIL FRACTIONS OF SOME  
COAL LIQUIDS BY ANALYTICAL LIQUID CHROMATOGRAPHY

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ABSTRACT

A high-performance liquid chromatography method was developed to determine the amount of each of the compound classes (such as saturates, aromatics and polars) in the oil fraction (pentane soluble fraction) of coal liquids. The method utilizes bonded cyanosilane and aminocyanosilane columns and mixtures of benzene in *n*-hexane and tetrahydrofuran in methyl *tert*-butyl ether as mobile phases. A Tracor LC-rotating disc flame ionization detector was used to quantify the chromatographic peaks.

Oil fractions derived from different rank coals, liquefied at 385° and 445°C, were analyzed for their compound class compositions. The trends in the percentages of saturates, aromatics and polars varied with liquefaction temperature and coal rank.

INTRODUCTION

The products from coal liquefaction processes are so complex that it is almost impossible to completely analyze them. Therefore, following a practical approach widely used with petroleum, the coal liquids are divided into solubility classes such as: (i) oils - pentane soluble, (ii) asphaltenes - benzene soluble, pentane insoluble, and (iii) preasphaltenes - pyridine or tetrahydrofuran (THF) soluble, benzene insoluble.

To obtain data suitable for mechanistic considerations, it is essential that fractions or classes of compounds obtained from coal liquefaction processes be quantitatively analyzed in more detail. Such efforts have been made recently, but there remains much to be learned about the compositions of these three solubility classes of coal products. A commonly used method for separation and/or analysis of the coal liquids is based on liquid chromatographic fractionation in terms of major components such as saturates, aromatics, more polar aromatics (non-basic N, O, S - heterocyclics), monophenols, basic nitrogen heterocyclics, polyphenols, and non-eluted unidentified materials.

One method was developed in 1976 by Farcasiu (1); it has also been used recently by Winans et al. (2) to characterize materials extracted, using benzene-methanol as a solvent, from several Argonne Premium Coal Samples. To understand the liquefaction behavior of a number of coals, separations of oil, asphaltene and preasphaltene fractions of coal liquids have also been reported (3-12). However, these chromatographic techniques are laborious and time consuming. To the best of our knowledge, the high-performance liquid chromatography (HPLC) coupled with the LC-Flame Ionization Detector (FID) have not been used for characterization and/or quantitation of coal liquids.

The purpose of our investigation was to adopt an analytical HPLC technique for separation and quantitation of oil fractions (pentane-soluble) of coal liquefaction products in terms of three compound classes such as saturates, aromatics, and polars. To learn if our HPLC procedure was suitable for oil fractions of supposedly different compositions, we have analyzed the oil fractions obtained from the liquefaction of coals of different rank at two reaction temperatures (385°C and 445°C).

#### EXPERIMENTAL

The HPLC system consisted of two solvent delivery systems (Waters 6000A pumps), three Valco six-port valves, a Tracor 945 LC-FID and Nelson Analytical 3000 Chromatography System equipped with an ITT/XT computer and a Nelson Analytical Series 760 converter with a minimum detectable capability of 0.1 microvolt-second. Two analytical columns were used: a cyano column (Supelco 5  $\mu$ m LC-CN, 25 cm x 4.6 mm i.d.) and an amino-cyano column (Whatman 5  $\mu$ m PAC, 25 cm x 4.6 i.d.). Mixtures of benzene in *n*-hexane and tetrahydrofuran (THF) in methyl *tert*-butyl ether (MTBE) were used as mobile phases. HPLC grade commercial solvents were used as received. However, the mobile phases were always degassed through a vacuum system just before their use. Of the several solvent flow rates that were tried, 1.0 to 1.5 ml/min was found to be the most suitable.

Following Pearson and Gharfeh's HPLC procedure (13) for the determination of hydrocarbon types in crude oil residues, we have used a rotating disc flame ionization detector (Tracor 945 LC-FID) developed by Tracor Inc. (14). The FID appears to be one of the few detectors among the various detectors used so far in HPLC procedures which tolerate a change from a nearly non-polar to a highly polar solvent system and can at the same time, be unaffected when the pressure drifts due to back and forth switching of the valves during a run.

In a typical run, the total column effluent is applied onto a fibrous quartz belt mounted on a rotating disc. As the disc rotates in the heated housing, the volatile solvent is vaporized and removed from the housing with the help of a vacuum pump. Non-volatile solutes remain on the fibrous belt and are carried into the flame where they are combusted and detected.

The operational logic of the HPLC system is shown in Figure I. During Step I, pump A (1.0 ml/min) with benzene solution in hexane was turned on. The switching valves were set in such a way that the mobile phase went first to the cyano column, then to an amino-cyano column and finally to the detector (see Figure I). This arrangement allowed the polar molecules to be retained by the cyano column and the aromatics to be retained by the amino-cyano column. About 3 to 4 minutes after the emergence of a saturates peak from the amino-cyano column, the system was switched to Step II. In Step II, the cyano column was isolated. Pump A was switched off and pump B with THF in methyl *tert*-butyl ether (MTBE), was operated at a flow rate of 1.0 ml/min. This arrangement allowed the retained aromatics to be backflushed from the amino-cyano column. Once the saturates and aromatics have been eluted, the system was switched to the final operation Step III where polars were backflushed from the cyano column using the THF/MTBE mobile phase. Upon completion of the separation, the system was brought back to its initial

conditions by reequilibrating the columns with benzene-hexane mixture. A typical chromatogram is shown in Figure II.

Liquefaction runs were made at two temperatures, 385° and 445°C, for 15 min. or 45 min. using tetralin as a solvent and a hydrogen atmosphere (800 psig, ambient). Typically 5g of dried coal and 7.5 g of tetralin were used for a run (see (15) for more experimental details). At the end of the experiment the reactor products were quantitatively removed and separated into three solubility classes through Soxhlet extractions. The oils were used for our HPLC analyses.

#### RESULTS AND DISCUSSION

A number of coals were used in this study (Table 1). They were selected to cover the rank range, based upon %C(daf) or vitrinite reflectance, that is present in the western Kentucky coals. A Breckinridge sample, an unusual coal that approaches the properties of a cannel coal, was also included in the study.

It was pointed out earlier that the FID detector could tolerate the solvent changes and the pressure drifts employed in the study. However, it is necessary to determine a relative response factor (ions produced/unit mass) for the various compound classes of the oil. In order to accomplish this, it was important to have aliphatics, aromatics and polars with compositions that are similar in chemical compositions as those of these components in the investigated oil fractions. The oil fractions obtained from coal liquefaction runs contained about 90-95% tetralin, the solvent used in this reactions; the preparative liquid chromatography of these samples over silica gel was not fruitful. Therefore, the oil fraction of a sample (V-1064) from the first stage reactor of the Wilsonville, Alabama coal liquefaction plant was used to carry out a larger scale separation.

The LC separation was performed using freshly activated silica gel (400°C overnight) and hexane, benzene and THF as the mobile phases. Hexane was used to elute the aliphatics from the column and 15% benzene in hexane was used to elute the aromatics. Finally, the column was backflushed with THF to obtain a polar fraction. The aliphatic, aromatic and polar fractions were tested for completeness of separation with the analytical HPLC procedure described in this report and were found to be of acceptable purity (>98%). A GC of the aliphatic fraction showed that it contained C<sub>15</sub> - C<sub>37</sub> hydrocarbons; these were mostly normal alkanes. Alkanes with a carbon number greater than C<sub>37</sub> are present in very small amounts. Other components were not detected in any significant amount.

The absolute response factors for saturate, aromatic and polar fractions were obtained from the slopes of the linear plots (Figure III) of the peak areas versus their mass (over a range of concentration of 0-20 µg/µl). Their relative response factors, as area/mass, are in the ratio of 1:2.16:1.23 for saturates : aromatics : polars.

The precision and reproducibility of the data were established by making six repeated measurements on the separation of one of the oils used in this study. The maximum uncertainties in the weight percentages of saturates, aromatics and polars were determined to be within 2%, 2% and 4-5% respectively.

Finally, the oil fractions obtained from the liquefaction of eight coals at 385° and 445°C were analyzed. The results are presented in Table 2. The following observations may be made for the data in Tables 1 and 2:

- (a) The relative aliphatic percentages decrease with an increase in reaction temperature for all the coals studied with the exception of Breckinridge coal sample which shows the opposite effect but this is what should be anticipated for this type of coal.
- (b) The aromatic percentages remained almost constant with the increase in temperature for most of the coals including the Breckinridge sample.
- (c) The polar percentages increased with an increase in temperature for all the coals except the Breckinridge sample.
- (d) Aliphatic, aromatic and polar percentages do not show a systematic trend with the coal rank. However, the data at 445°C (see Table 2) show that aliphatics tend to decrease with decreasing coal rank.
- (e) With the exception of the Breckinridge sample, the aliphatics, aromatics and polars are generally in the ratio of 1:2:5 (Table 2).
- (f) Irrespective of the liquefaction temperature, the oil fractions from the Breckinridge coal contain extremely large amounts of aliphatics (45.8% and 55.4%) small amounts of aromatics (7.8% and 7.9%) and polars (46.4% and 36.7%) compared to those of other coals (aliphatics, 9-18%; aromatics, 19-28% and polars, 55-69%).

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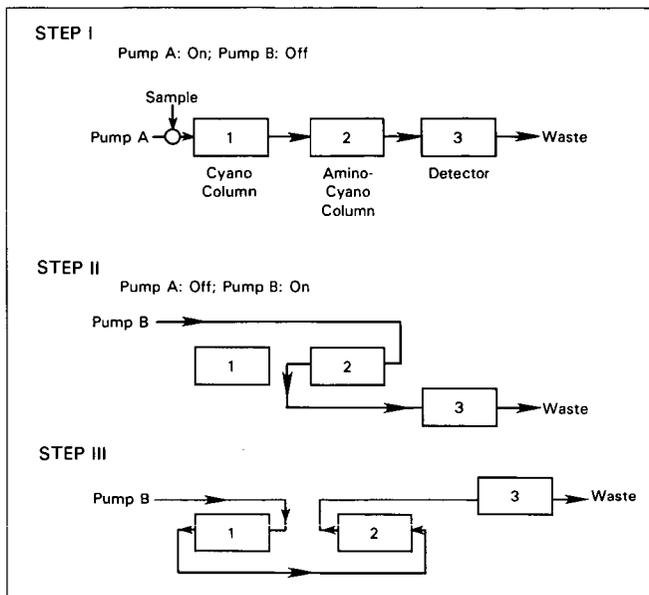
**Table 1. Coal Analysis.**

|                         | <b>W. Ky. #9<br/>71154</b>  | <b>Breckinridge<br/>71160</b> | <b>W. Ky. #9<br/>71148</b>  | <b>W. Ky. #9<br/>71072</b> |
|-------------------------|-----------------------------|-------------------------------|-----------------------------|----------------------------|
| 1. Ash (As-Received)    | 30.03                       | 6.36                          | 14.87                       | 9.04                       |
| 2. Volatile Matter, daf | 47.83                       | 74.28                         | 46.10                       | 42.90                      |
| 3. Fixed Carbon, daf    | 52.17                       | 25.72                         | 53.90                       | 57.10                      |
| 4. Sulfate S, daf       | 0.00                        | 0.01                          | 0.17                        | 0.14                       |
| 5. Pyritic S, daf       | 1.47                        | 1.23                          | 1.35                        | 0.53                       |
| 6. Organic Sulfur, daf  | 2.27                        | 0.55                          | 1.70                        | 1.91                       |
| 7. Total Sulfur, daf    | 3.74                        | 1.81                          | 3.22                        | 2.57                       |
| 8. Carbon, daf          | 84.99                       | 80.66                         | 79.59                       | 79.19                      |
| 9. Hydrogen, daf        | 6.16                        | 8.51                          | 5.62                        | 5.44                       |
| 10. Nitrogen, daf       | 1.98                        | 2.13                          | 1.90                        | 2.00                       |
| 11. Oxygen, daf         | 3.13                        | 6.90                          | 9.67                        | 10.80                      |
|                         | <b>W. Ky. #11<br/>71064</b> | <b>W. Ky. #11<br/>71081</b>   | <b>W. Ky. #11<br/>71077</b> | <b>W. Ky. #9<br/>71095</b> |
| 1. Ash (As-Received)    | 9.56                        | 4.43                          | 9.06                        | 14.80                      |
| 2. Volatile Matter, daf | 47.47                       | 43.23                         | 41.74                       | 43.73                      |
| 3. Fixed Carbon, daf    | 52.53                       | 56.77                         | 58.26                       | 56.27                      |
| 4. Sulfate S, daf       | 0.06                        | 0.17                          | 0.75                        | 0.68                       |
| 5. Pyritic S, daf       | 1.06                        | 0.64                          | 2.09                        | 4.48                       |
| 6. Organic Sulfur, daf  | 3.11                        | 2.21                          | 3.35                        | 3.27                       |
| 7. Total Sulfur, daf    | 4.23                        | 3.01                          | 6.19                        | 8.43                       |
| 8. Carbon, daf          | 78.80                       | 78.28                         | 76.96                       | 76.63                      |
| 9. Hydrogen, daf        | 5.85                        | 5.52                          | 5.37                        | 5.10                       |
| 10. Nitrogen, daf       | 1.70                        | 1.70                          | 1.63                        | 1.70                       |
| 11. Oxygen, daf         | 9.42                        | 11.49                         | 9.85                        | 8.14                       |

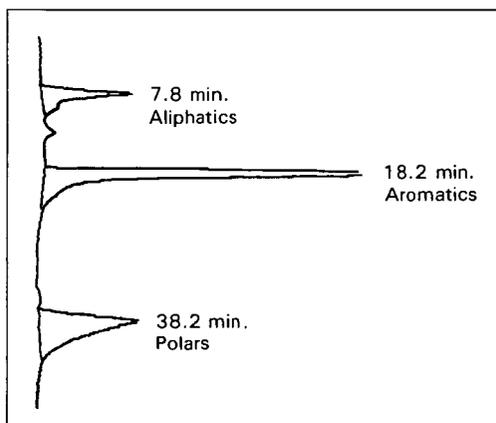
Oxygen by difference.

**Table 2.** HPLC Analysis of Oil Fractions at 385°C and 445°C.

| Coal Number        | C (daf) | Weight %         |          |        |                   |          |        |
|--------------------|---------|------------------|----------|--------|-------------------|----------|--------|
|                    |         | 385°, 15 minutes |          |        | 445°C, 15 minutes |          |        |
|                    |         | Aliphatic        | Aromatic | Polar. | Aliphatic         | Aromatic | Polar. |
| 71154 (W. Ky. #9)  | 84.99   | 13.2             | 24.1     | 62.7   | 12.8              | 23.3     | 63.9   |
| Breckinridge       | 80.66   | 45.8             | 7.8      | 46.4   | 55.4              | 7.9      | 36.7   |
| 71148 (W. Ky. #9)  | 79.59   | 15.0             | 20.4     | 64.6   | 11.5              | 20.3     | 68.2   |
| 71072 (W. Ky. #9)  | 79.19   | 18.4             | 21.6     | 60.0   | 12.1              | 19.7     | 68.2   |
| 71064 (W. Ky. #11) | 78.80   | 13.9             | 19.3     | 66.8   | 10.2              | 20.3     | 69.5   |
| 71081 (W. Ky. #11) | 78.28   | 11.0             | 24.3     | 64.7   | 9.7               | 20.5     | 69.8   |
| 71077 (W. Ky. #11) | 76.96   | 12.2             | 25.5     | 62.3   | 9.2               | 24.5     | 66.3   |
| 71095 (W. Ky. #9)  | 76.63   | 16.6             | 28.2     | 55.2   | 8.8               | 22.0     | 69.2   |



**Figure I.** Operation of HPLC system.



**Figure II.** A typical chromatogram of an oil fraction separation.

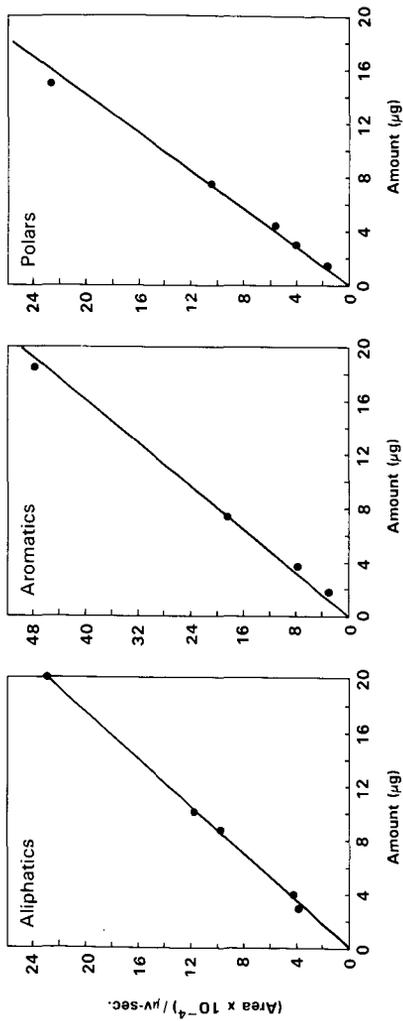


Figure III. Calibration plots of aliphatics, aromatics, and polars.