

CHARACTERIZATION OF THE BENZENE METHANOL EXTRACTS FROM THE ARGONNE PREMIUM COAL SAMPLES

Y. J. Xia, P. H. Neill and R. E. Winans

Chemistry Division, Argonne National Laboratory,
9700 South Cass Avenue, Argonne, Illinois 60439

INTRODUCTION

The Argonne Premium Coal Samples represent a unique opportunity to study a set of pristine samples selected to represent the vast diversity of chemical structures exhibited by U.S. coals. In order to determine if there will be any non-oxidative changes in these coals during long term storage a project has been initiated utilizing a wide range of chemical and physical techniques. One of these techniques meant to focus on any changes which may occur in the volatiles and extractables is described in this paper.

We believe that the material that can be extracted from the coal will provide important information concerning any changes which may occur during long term storage. These materials are easily studied by well established techniques (1-5) and the suggestion has been made that they may be representative of the chemical structures found in the bulk coal (1-3).

EXPERIMENTAL

An overview of the experimental procedures is presented in Figure 1. In order to reduce exposure to atmospheric oxygen all transfers and weighings were performed in a glove box under nitrogen. The Argonne Premium Coal Samples (APCS) used in this study and their elemental analysis are given in Table 1. The preparation of the Argonne Premium Coal Samples has been described by Vorres and Janikowski (6). All of the samples were - 100 mesh except for APCS #2 and #6 which were not available in the smaller mesh size when the work was performed. The coals, excluding the low rank APCS #2 were dried before extraction at 100°C for 16 hours under vacuum then brought to constant weight. APCS #2 was extracted without drying due to possibility that drying would irreversibly modify its physical and chemical structure. The water content of this coal was determined in a separate experiment.

Each coal was extracted in 250 ml. of boiling benzene/methanol (31/69 w/w percent) for 48 hours under nitrogen. The extract was removed by vacuum filtration. The residue was washed with ca. 50 ml. of the benzene/methanol, dried at 100°C under vacuum to constant weight. The benzene/methanol was stripped from the extract at 70°C under vacuum in a rotary evaporator and the extract brought to constant weight.

The extract was then separated into nine fractions using the desorption column chromatographic technique developed by Farcasiu (7). In our application of this technique the extract was dissolved in 7 ml. of the benzene/methanol and coated on 6.65 grams of dried silica gel by evaporating the solvent. The coated silica gel was placed on the top of the column containing 26.8 grams of Aldrich Grade 12 silica gel. This silica gel had

been dried for 8 hours at 120°C and then rehydrated to 4 percent water. The sequential elution solvents in order of use and the classes of compounds reported finding in each fraction are presented in Table 2. A standard volume of 500 ml was used for each elution. In order to correct for silica gel dissolved in each of the fractions, blank elutions were performed under the same conditions as used for the actual separation. The solvent was striped from each fraction by rotary evaporation under vacuum, and the extract brought to constant weight.

Analysis of each fraction was by Gel Permeation Chromatography (GPC) and Gas Chromatography Mass Spectroscopy. The GPC separation in utilized three Ultra Styragel columns with exclusion limits of 1000, 500 and 100 angstroms connected in series to an refractive index and ultraviolet detector. The tetrahydrofuran mobil phase was pumped through the columns at a flow rate of 1 ml/min. Calibration for the conversion of retention times to molecular weight utilized a series of aromatic compounds ranging from naphthalene (128 g/mole) to erythromycin (734 g/mole). The GCMS separations were performed on a Kratos MS25 instrument with a 0V-1701 column.

Solvent swellings of the residues from the extractions were performed using the gravimetric technique utilized by Green et al. (8). Briefly ca. 1.1 grams of the residue from the extraction was placed in a desiccator with the benzene methanol swelling mixture in the base. The solvent mixture was frozen and the desiccator evacuated to remove the air. After thawing the freeze thaw cycle was repeated two more times. The swelling coefficients (weight of swollen coal/weight of unswollen coal) were determined after 36 hours.

RESULTS AND DISCUSSION

The yields of benzene/methanol extractables are plotted versus carbon content in Figure 2. Excluding Wyodak subbituminous coal (APCS #2), the yields decreased with rank in a non-linear manner. The low extractability of Wyodak, relative to the trend defined by the higher rank coals, may be attributable to two factors. This coal contains a much higher oxygen content. Thus, the extractables from this coal should be more polar and exhibit a greater propensity towards intramolecular hydrogen bonding than extractables from coals of higher rank. The relatively non-polar benzene/methanol may be incapable of solvating the potentially extractible material. The solvent swelling coefficient (Figure 6) for this coal indicates that benzene/methanol does not show a disparity in its ability to gain access to the macromolecular structure. The Wyodak coal contained 30.4 ± 0.4 percent water which was the highest water content of all the coals studied. It was also the only coal which was not dried prior to extraction. The water from this coal could have modified the extraction potential of the benzene methanol enough to account for the observed yield. Reproducibilities of the extractions were quite good with standard deviations as indicated by the error bars on Figure 2. ranging from 0.0 to 0.22 percent of the mean extraction yield.

The percentage of the benzene/methanol extract in each of the LC fractions corrected for dissolved silica gel is presented in Figure 3. The solvent or mixture used to elute each of the fractions can be found in

Table 2. Only fractions 2, 5 and 6 appeared to show any rank dependence. Fraction 2 which Farcasiu (7) attributed to small non-polar aromatics was found to contain a homologous series of linear alkenes of even number dominance, having a maximum in their distribution near 20 carbons. This distribution is probably not inherent to the coal, but an artifact of the severe conditions used in removing the solvents from the extracts and LC fractions. Figure 4 presents the total extract in this fraction plotted with respect to carbon content for each of the coals studied. The opposite trend may occur, with a higher percentage of the extract from the higher heteroatom content lower ranked coals eluting in fractions 5 and 6. This trend of a higher percentage of the extractables eluting at higher eluent polarity for lower rank coal is illustrated in Figure 5 where yields are plotted versus fraction number for Upper Freeport and Wyodak coals. Although the trends can easily be seen the errors associated with the measurements are so large that no statistically valid conclusion can be drawn.

The average molecular weight from GPC for LC fractions 2-9 is presented in Figure 6. All of the retention times were within the linear portion of the calibration curve (128-734 grams/mole). One must be careful in assigning molecular weights for GPC retention times for compounds dissimilar to the calibration standards due to the basis of the GPC technique on molecular size rather than molecular weight (9). However, comparisons of intrafraction variation in molecular weight should be valid if similar material is eluted for each sample. The maximum in the molecular weight distribution increased up to fraction 7. Indicating a possible dependence of the LC fractionation technique on molecular size as well as functionality. Above fraction 6 the molecular weight appeared to decrease. Only a small amount of the total extract (<10%) was eluted in these two fractions. No valid intrafraction differences could be observed, due to the similarities in the mean molecular weight values and the relatively large errors associated with the measurements.

The swelling coefficient in benzene/methanol is plotted versus carbon content in Figure 7. It decreases with rank in a non-linear manner up to Upper Freeport coal (APCS #1) at 87.1 percent carbon. The Pocahontas 1v bituminous coal (APCS #5) at 89.6 percent carbon exhibited a statistically significant increase in its swelling coefficient. This break in the swelling trend corresponds to the break in the coalification pattern around 87 percent carbon attributed to a maximum in the macromolecular cross-link density by Larsen and Kovac (10). Standard deviations were found to be less than 0.4 percent of the swelling coefficient indicating a valid difference between the mean values for each of the coals studied.

CONCLUSIONS

Significant differences have been observed in the total amount of material extracted from the Argonne Premium coal samples and the swelling coefficients of the resulting residues. Each generally decreased with increasing carbon content as would be expected. Differences were observed in the amount of the extract proportionating into each of the LC fraction. A higher percentage of the extract from coals of lower rank appeared to elute in the more polar fractions, although the experimental procedure will have to be refined before one can be sure that this conclusion is valid. There did not

appear to be any significant differences between the infrafraction maximum in the molecular weight profile for any of the samples. The data reported in this paper represents baseline values for the benzene/methanol extractables from the Argonne Premium Coals. The next phase of the project will involve the repetition of these experiments in order to determine if any changes are occurring during storage.

ACKNOWLEDGMENTS

The coal analyses were provided by I. Fox and P. C. Lindahl of the Argonne Analytical Chemistry Laboratory.

This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under contract number W-31-109-ENG-38.

REFERENCES

1. R. Hayatsu, R. E. Winans, R. G. Scott, L. P. Moore and M. H. Studier, *Nature (London)*, 275, 116 (1987).
2. R. Hayatsu, R. E. Winans, R. G. Scott, L. P. Moore and M. H. Studier, *Fuel*, 57, 541 (1978).
3. M. H. Studier, R. Hayatsu, and R. E. Winans, in "Analytical Methods for Coal and Coal Products", Karr C., ed., Vol. 2, pp. 43-74, Academic Press, NY (1978).
4. T. J. Palmer and M. Vahrman, *Fuel*, 51, 22 (1972).
5. Z. Mudamburi and P. H. Given, *Org. Geochem.*, 8, 441 (1985).
6. K. Vorres and S. Janikowski, *ACS Fuel Division Preprints*, 32(1), 492 (1987).
7. M. Farcasiu, *Fuel*, 56, 9 (1977).
8. T. Green, J. Kovac, D. Brenner, and J. W. Larsen, in "Coal Structure", R. A. Meyers, ed., pp. 199-282, Academic Press, NY (1982).
9. B. Brule, *ACS Fuel Chemistry Division Preprints*, 26(2), 28 (1981).
10. J. W. Larsen and J. Kovac, *ACS Symp. Series*, 71, 36 (1978).

TABLE 1. Composition of the Coals used in this Study.

APCS No.	Coal	% Carbon (dmmf)	Composition
1	Upper Freeport mv bituminous	87.1	C ₁₀₀ H _{75.8} N _{1.48} S _{0.26} O _{2.58}
2	Wyodak subbituminous	72.0	C ₁₀₀ H _{95.0} N _{1.19} S _{0.26} O _{21.3}
3	Illinois #6 hvC bituminous	77.8	C ₁₀₀ H _{87.9} N _{1.54} S _{1.30} O _{8.8}
4	Pittsburgh No. 8 hvA bituminous	83.4	C ₁₀₀ H _{84.9} N _{1.69} S _{0.40} O _{6.03}
5	Pocahontas lv bituminous	89.6	C ₁₀₀ H _{62.9} N _{1.15} S _{0.17} O _{3.26}
6	Utah Blind Canyon bituminous	75.7	C ₁₀₀ H _{111.0} N _{1.59} S _{0.20} O _{15.16}

TABLE 2. The sequence of solvents used for the elutions of the various LC fractions, and classes of compounds eluted as reported by Farcasiu (7).

Fraction No.	Solvent	Major Components
1	Hexane	Saturates
2	Hexane/15% benzene	Aromatics
3	Chloroform	Polar aromatics, Non-basic N,O,S-heterocyclics
4	Chloroform/10°C diethyl ether	Monophenols
5	Diethyl ether/3% ethanol	Basic nitrogen heterocyclics
6	Methanol	Highly functional molecules (>10 wt% heteroatoms)
7	Chloroform/3% ethanol	Polyphenols
8	Tetrahydrofuran	Increasing O content and increasing basicity of nitrogen
9	Pyridine/3% ethanol	Increasing O content and increasing basicity of nitrogen
10		Non-eluted, unidentified materials

Figure 1. Overview of the experimental procedure.

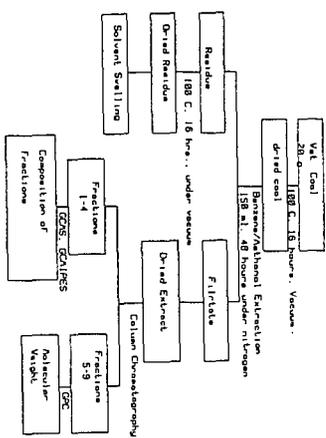


Figure 2. Variation of benzene/fractional extractables with carbon content, APCS No. in brackets.

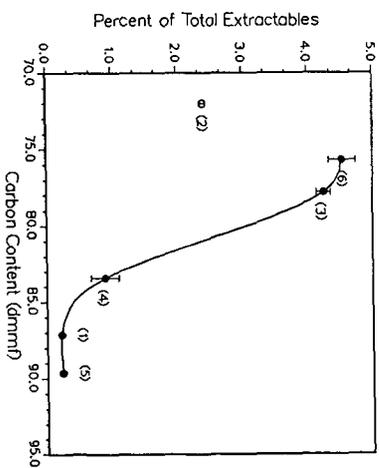


Figure 3. Average percentage of total extractables in LC fractions for APCS #1 - #4.

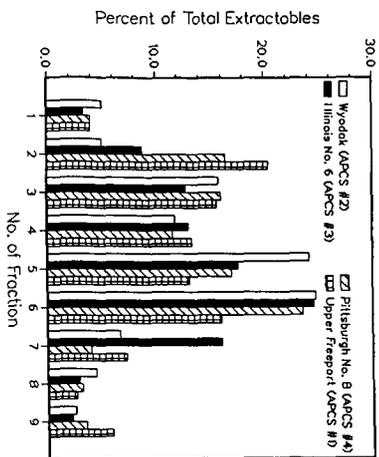


Figure 4. Variation in the percentage of the total extractables in liquid chromatographic fraction with respect to carbon content, the APCS no. is in brackets.

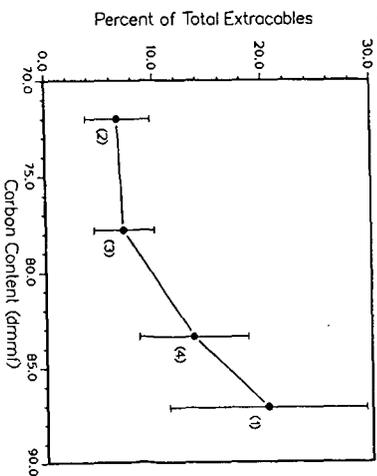


Figure 5. Percentage of total extractables in LC fractions 1-9 for APCS #1 and #2.

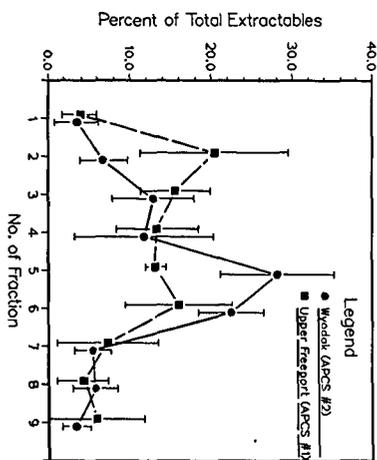


Figure 6. The variation in molecular weight (GPC) with fraction number for APCS 1-4.

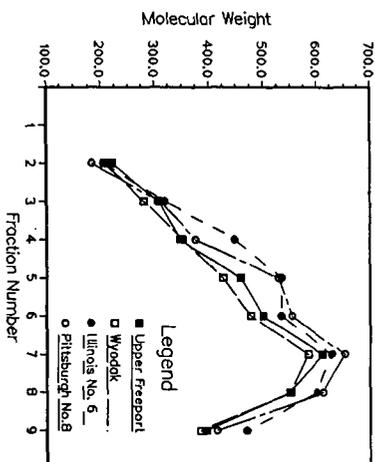


Figure 7. Variation of swelling coefficient in benzene/methanol with carbon content, APCS No. in brackets.

