REACTION OF PREMIUM WYODAK SUBBITUMINOUS COAL WITH POTASSIUM-CROWN ETHER REAGENT

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INTRODUCTION

Coal conversions typically involve reacting coal under severe conditions of temperature and pressure. As a result, bond cleavage is nonselective and often accompanied by retrogressive (bond forming) reactions. This has resulted in less than satisfactory results in deducing coal structure, coal behavior, and reactivity. Incorrect model of the basic structural units of the coal, and the nature of the linkages joining these units have been postulated. In our laboratory, we are studying the solubilization of coal at ambient temperatures and pressures using a site-specific reagent potassium-crown ether (K-CE), and the characterization of the soluble coal oligomer fragments (1,2). The small size and high reactivity of the solvated electrons generated by the K-CE reagent, promotes cleavage reactions at ether (3-5), ester (9), and diarylethane linkages (6,7), resulting in depolymerization and solubilization of coal. Reduction of aromatic rings to dihydro and tetrahydro analogs also occur (2,8). In this paper we report on the solubilization of a Wyodak premium subbituminous coal using K-CE reagent. The characterization of the solubilized coal fragments by IR, NMR, GPC, and microanalysis, is described.

EXPERIMENTAL

Material

Premium Wyodak subbituminous coal (-20 mesh, C=74%, H=5.1%, O=20%, S=0.5%) was obtained from the Argonne Premium Coal Sample Bank, Argonne National Laboratory, IL. Coal samples were used immediately upon opening the glass ampoule. -100 mesh coal used in our study was prepared by grinding the -20 mesh coal in a glove box under liquid nitrogen. The coal was then dried under vacuum for three hours and used immediately for the K-CE reactions.

Reaction of Wyodak Coal With K-CE Reagent

The stoichiometry of the reagents, and the experimental conditions for the coal-K-CE reaction followed established procedure as reported earlier (1,2). The work-up procedure for the reaction is shown in Figure 1.

NMR Spectroscopic Analysis

Proton NMR spectra was obtained from a Nicolet NTC-470 spectrometer (470 MHz) at ambient temperature. Coal samples (20 mg) were dissolved in 0.5 ml of chloroform-d (THF-1

fraction), or DMSO-d6 (THF-2 and alkali-soluble fractions). Proton decoupled ^{13}C NMR spectra were obtained from NTC-200 (50 MHz) at 45°C (22°C for THF-1 fraction). The sample concentration was 50 to 75 mg of sample per 1 ml of NMR solvent. For alkali-soluble fraction $NaOD/D_2O$ was used in the ^{13}C NMR experiment.

Gel Permeation Chromatography

Gel Permeation Chromatography (GPC) experiments were carried out on a Waters M-6000A pump with two ultrastyragel columns (500 A and 1,000 A) in tandem using THF eluent and a differential refractometer detector. Polystyrene standards were used to obtain a calibration plot. The molecular weight distribution of the THF-soluble coal samples were based on the elution time and the standard calibration plot.

RESULTS AND DISCUSSION

Solubility Studies

The work-up of the coal/K-CE reaction mixture and the extraction of coal into different soluble fractions (THF-1 fraction, alkali-soluble fraction, and THF-2 fraction) are shown in Figure 1. The percent coal solubilized in the various fractions is summarized in Table 1.

Our previous report (2) suggests that the solubility of K-CE treated coal is related to the stoichiometries of the reactants. We found that when the ratio of potassium to coal was decreased, the solubility of coal decreased significantly. We also found that successive K-CE reactions with coal solubilized additional coal. A total solubility of up to 70% was obtained after a coal sample was consecutively treated with K-CE reagent for three to four times. These results suggest that the diffusion of the solvated electrons into the coal matrix is an important factor in determining the solubility of coal, (the amount of soluble coal oligomer fragments formed) after the K-CE reaction.

The present results showed that the diffusion of the solvated electrons is, indeed, an important factor in determining the solubility of the coal, especially the alkali-soluble fraction, in the coal/K-CE reactions. As shown in Table 1, when the coal particle size was changed from -20 mesh to -100 mesh, the alkali-soluble fraction increased from 25% to 47%, whereas the THF-1 and THF-2 fractions did not change significantly. A smaller particle size of coal provides more surface area which allows more of the solvated electrons to react with the aryl ether, ester, and aryl ethane linkages of the coal macromolecule. The alkali-soluble fraction increased two fold on going from a -20 mesh coal particle size to -100 mesh, while the THF-1 and THF-2 fractions were not affected as much. These results suggested that the cleavage of the aryl ether and ester linkages was a predominant reaction during the coal/K-CE reaction.

The alkali-soluble fraction was also subjected to THF extraction. The results are summarized in Table 2. It was interesting to note that the THF extractability of the alkali-soluble fraction from the second K-CE reaction (72%) was higher than that of the first K-CE reaction (55%). During the second K-CE treatment, greater reduction of the polar groups of the coal structure, such as aromatic hydroxyl group to a corresponding less polar dihydro-ketone group, would account for the observed higher solubility in THF.

Elemental Analysis

Elemental compositions of the soluble fractions, the insoluble fractions, and the original premium Wyodak coal are shown in Table 3. The results show that there was an overall increase of the hydrogen content. This hydrogen uptake suggested that Birch-Huckel type

reductions, and cleavage of aryl methylene linkages and ether linkages occurred during the K-CE reaction (7).

THF-1 and THF-2 fractions show relatively high H:C ratios indicating that these fractions are rich in aliphatic material. The THF-1 extraction step (Figure 1) extracted the non-polar hydrocarbon material, that arose from the cleavage of the macromolecular network or was present as trapped molecules. THF-2 step extracted hydrocarbon material containing some polar functionality like OH, or COOH groups (confirmed by high field proton NMR spectroscopy) discussed in the next section. Under alkaline conditions, they are present in salt form (i.e., $-O^-M^+$), and therefore, not extracted during the THF-1 extraction. However, these compounds were not acidic enough (contained more hydrocarbon groups, to make it alkali-soluble). Acidification of the residue converted the salts into the free acid form (O^-–M^+ to -OH) and this rendered the hydrocarbon material THF extractable.

An oxygen balance of the K-CE reaction is shown in Table 3. The result showed that there was no significant increase or uptake of oxygen during the reaction. This was important to establish because of the distinct presence of a number of oxygen functionalities like carboxylic groups, phenolic -OH groups, and carbonyls in all the extracts. Therefore, the appearance of these oxygen functionalities arose by chemical transformations (cleavage reactions, reductions) of the original oxygen functionalities.

Gel Permeation Chromatography Analysis

GPC was carried out on all the THF-soluble fractions including THF-1 fraction, THF-2 fraction, and THF extract of the alkali-soluble fraction. GPC experiments were expected to yield information on the size (molecular weights and molecular weight distribution) of the various clusters being held together by K-CE cleavable linkages. The absolute molecular weights of the coal extracts were not determined. The results of the GPC analysis are summarized in Table 4.

The results show that K-CE reagent is dismantling the coal macromolecule into low molecular weight, non-polar, hydrocarbon material (THF-1), large (34,000-42,000 and 900-1400) polar oligomer fragments (THF extract of the alkali-soluble fraction), and a second hydrocarbon fraction (MW 1300-2200) containing few polar (-OH) functionalities. The results also suggested that upon second consecutive treatment of the coal sample, the size of the resulting coal oligomer fragments are slightly larger than that of the first K-CE reaction. A definite confirmation of these results would require the determination of the absolute molecular weight of the coal extracts.

Infrared Spectroscopy

Infrared spectra of the soluble fractions were obtained and compared to that of the original untreated coal. IR spectra of THF-1 and THF-2 fraction both showed strong absorption at the aliphatic C-H stretching regions, which corresponds well with the finding of the microanalysis. The carbonyl absorption bands (1725 and 1700 cm^{-1}) are found in the IR spectra of all the soluble fractions. These carbonyl absorptions are attributed to the functional groups such as ketone and carboxyl which arose from the reduction of the phenolic OH and the cleavage of the ester groups (2,9).

NMR Spectroscopy Analysis

Proton NMR spectra of the soluble fractions are shown in Figure 2. The spectra of THF-1 and THF-2 fractions (Figure 2A and Figure 2C) confirmed that hydrocarbon material is more abundantly in the THF fractions than in the alkali-soluble fraction. Strong signals at 1.3

ppm and at 1.0 ppm correspond to the methylene protons of long chain polymethylenes and the parafinic methyl protons respectively. Broad signals at 9-10 ppm and 11-13 ppm corresponding to the phenolic protons and carboxylic protons respectively are found in the spectra of the alkali-soluble fraction and the THF-2 fraction. The broad signals disappeared from the spectra upon the addition of D_2O to the NMR samples thus confirming the presence of these acidic protons. The disappearance of the 4.0 ppm strong broad signal on addition of D_2O to the NMR sample, suggested the presence of aliphatic alcohols. These aliphatic alcohols could arise from the cleavage of the ester linkage of the coal macromolecule.

^{13}C NMR spectra of the alkali-soluble fractions from first and second K-CE reactions are shown in Figure 3. It is interesting to note an increase in the intensity of the peak centered around 110 ppm (corresponding to olefinic carbons) in the spectrum of the alkali-soluble fraction from the second K-CE reaction. The results suggest that during the second K-CE treatment, more of the aromatic ring of the coal oligomer fragments were reduced to the corresponding dihydroaromatics. The spectrum of the alkali-soluble fraction from second K-CE reaction also showed a sharp decrease in the intensity of the alkane carbons resonances.

The proton and ^{13}C spectra of the soluble fractions obtained from the K-CE treated premium Wyodak coal were compared with the proton and ^{13}C spectra of similar fractions of the K-CE treated regular Wyodak coal obtained from Electric Power and Research Institute (EPRI), and stored under water. The spectra are compatible, i.e., the same distinct structural characteristics are observed in the soluble fractions from both the premium Wyodak and regular Wyodak coals.

SUMMARY

In this paper we have shown that a total of 53% premium Wyodak coal was solubilized into THF- and alkali-soluble fractions after the first K-CE reaction. The alkali-soluble fraction accounted for 89% of the total solubles. This result is consistent with our previous findings using the regular Wyodak coal obtained from EPRI. The results showed that a decrease in the coal particle size increased the amount of alkali-soluble coal formed. The oxygen balance, based upon the results of the elemental analysis, showed that the oxygen functionalities (phenolic and carboxylic OH groups and carbonyl groups) found in all the soluble fractions arise by chemical transformations (cleavage reactions, reductions) of the original functionalities.

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REFERENCES

1. S. L. Huang, K. Wood, and R. Narayan, Amer. Chem. Soc., Div. Fuel Preprints, *31*(4), 85 (1986).
2. S. L. Huang, and R. Narayan, Amer. Chem. Soc., Div. Fuel Preprints, *32*(1), 32 (1987).
3. B. Weinstein and A. H. Fenselan, J. Org. Chem., *34*,126 (1969).
4. J. A. Marshall, and N. H. Anderson, J. Org. Chem., *30*, 1291 (1965).

5. D. H. Eargle, Jr., J. Org. Chem., *12*, 1918 (1967).

6. L. Schanne and M. W. Haenel, Tet. Letter, *44*, 4245 (1979).

7. C. J. Collins, H. P. Hombach, B. E. Maxwell, N. C. Woody, and B. M. Benjamin, J. Amer. Chem. Soc., *102*, 851 (1980).

8. R. A. Benkeser, M. L. Burrows, J. J. Hazdra, and E. M. Kaiser, J. Amer. Chem. Soc., *28*, 1094 (1963).

9. S. L. Huang, and R. Narayan, "Reduction of Benzyl Benzoate by K-CE Reagent," to be submitted to J. of Amer. Chem. Soc.

Table 1. Solubility of Premium Wyodak Subbituminous

	THF-1 Fraction (%)	Alkali-Soluble Fraction (%)	THF-2 Fraction (%)	Total
One K-CE Reaction[a]	7	25	2	34
Total of Two K-CE Reaction[a]	9	29	6	44
One K-CE Reaction[b]	4	47	2	53

a. Particle size of coal was -20 mesh.

b. Particle size of coal was -100 mesh.

Table 2. THF Solubility of Alkali-Soluble Fractions and Total Solubility in THF for Wyodak Subbituminous[a]

	% THF Solubility of Alkali-Soluble Fraction	Total % THF Solubility for Wyodak
First K-CE Reaction (20 mesh)	55 (out of 21%)	24
Second K-CE Reaction (20 mesh)	72 (out of 14%)	15
First K-CE Reaction (100 mesh)	53 (out of 47%)	31

a. THF extraction of untreated Wyodak coal was negligible.

b. This includes THF-1 and THF-2 fractions, and THF fraction of alkali-soluble.

Table 3. Elemental Analysis of Premium Wyodak Subbituminous and Soluble Fractions[a] (Moisture and ash-free values)

Coal Samples	C	H	O	N	S	H/C	Yield %[c]	Empirical Formula
Wyodak[b] Subbituminous	74	5.1	20	0.40	0.50	0.83		$C_{100}H_{83}O_{20}$
THF-1 Fraction	77.9	8.9	12.9	0.20	0.36	1.37	7.38	$C_{100}H_{137}O_{12}$
Alkali-Soluble Fraction	71.2	4.9	22.3	0.98	0.59	0.82	25.01	$C_{100}H_{82}O_{23}$
THF-2 Fraction	74.6	7.4	16.8	0.54	0.63	1.19	2.45	$C_{100}H_{119}O_{17}$
Insoluble Fraction	72.1	5.4	21.1	0.89	0.52	0.90	57.82	$C_{100}H_{90}O_{22}$
Total Yield	--	--	--	--	--	--	92.66	$C_{92.7}H_{85.6}O_{19.8}$
Normalized to C_{100}	--	--	--	--	--	--	--	$C_{100}H_{92}O_{21}$

a. The results reported here are from first K-CE reaction.

b. These values are from the Argonne National Laboratory reported data.

c. The solubility % yield from first K-CE reaction.

Table 4. GPC Results of THF Soluble Fractions

	Molecular Weight Distribution		
	Number Average $\bar{M}_n$	Weight Average $\bar{M}_w$	Peak Mol. Wt.
First K-CE Reaction[a]			
THF-1 Fraction	414	1441	1117
THF-2 Fraction	986	4029	2244
Alk-THF Fraction	23,990	27,170	33,880
	532	1457	930
Second K-CE Reaction[a]			
THF-1	641	1981	906
THF-2	1079	4059	1319
Alk-THF Fraction	32,345	35,030	42,204
One K-CE Reaction[b]			
THF-1 Fraction	522	1606	956
THF-2 Fraction	1310	4070	1784
Alk-THF Fraction	20,080	24,860	35,714
	1062	2553	1395

a. The coal particle size was -20 mesh.

b. The coal particle size was -100 mesh.

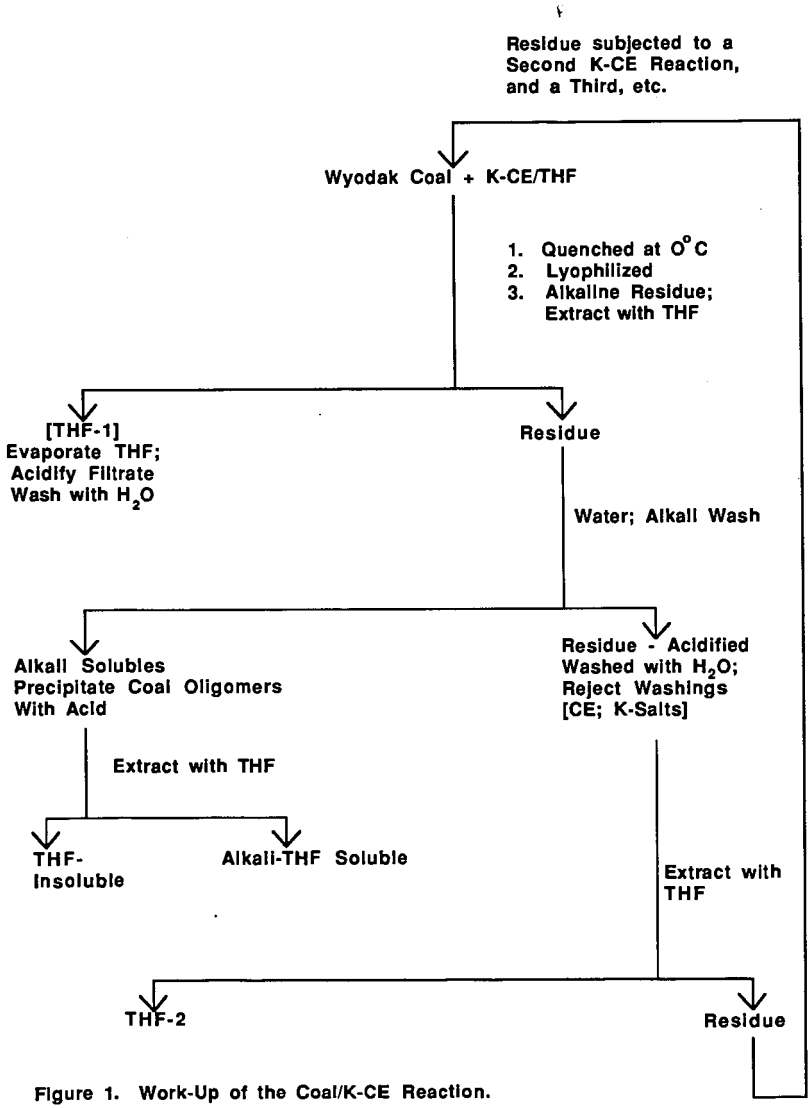

Figure 1. Work-Up of the Coal/K-CE Reaction.

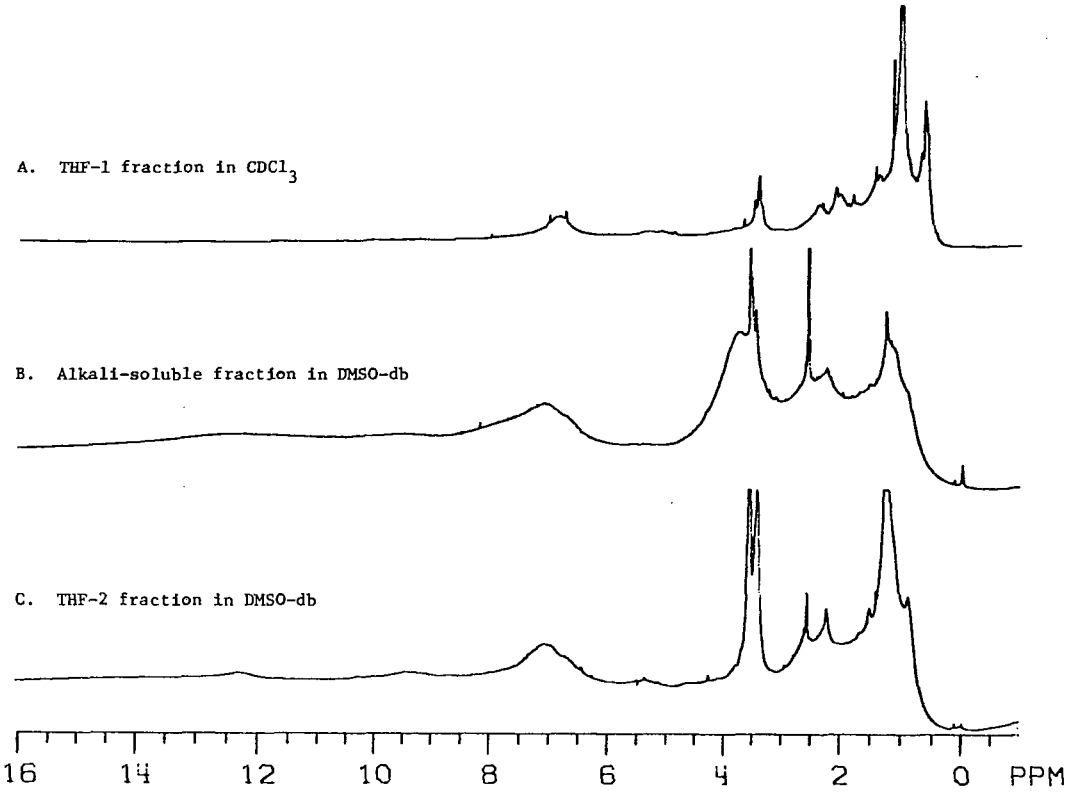

Figure 2. 470 MHz ^1H NMR spectra of soluble fractions of K-CE treated premium Wyodak coal.

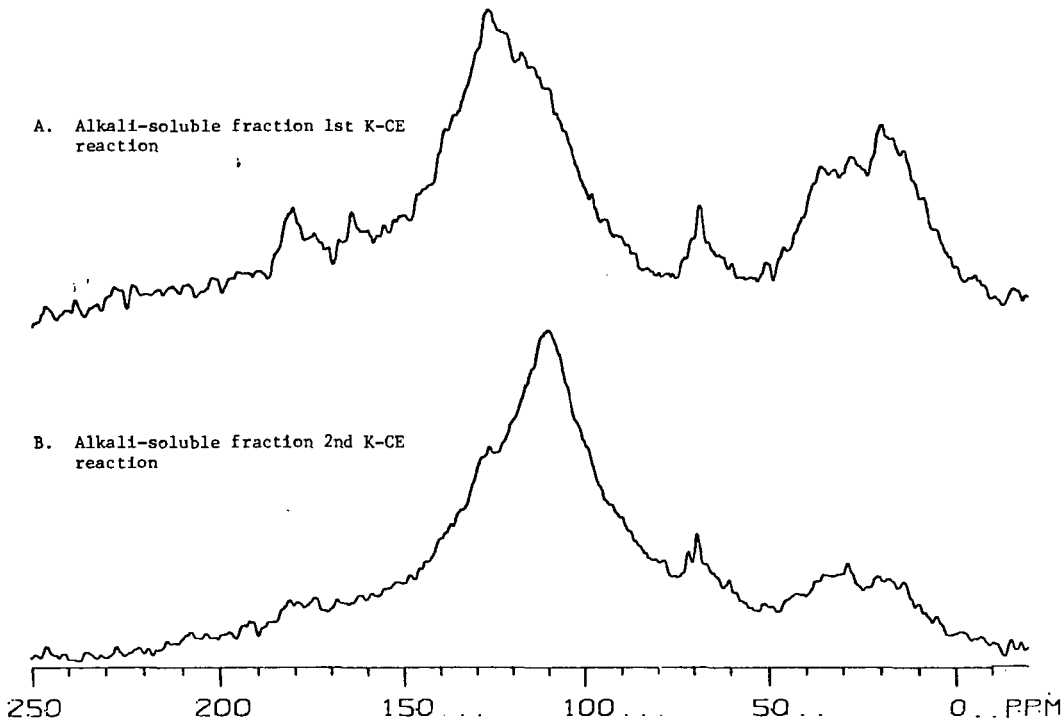

Figure 3. Proton decoupled ^{13}C NMR spectra (50 mHz) of alkali-soluble fractions in $NaOD/D_2O$