CROSSLINKING REACTIONS IN COAL PYROLYSIS

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INTRODUCTION

During coal pyrolysis, the break up of the coal macromolecular network is controlled by the relative rates of bond breaking, crosslinking and mass transport. Crosslinking reactions are important because the ultimate tar yield and tar molecular weight distribution are dependent on the extent of these reactions. Crosslinking, as measured by solvent swelling experiments, is observed to be rank dependent, with lignites crosslinking at lower temperatures than bituminous coals.

In a recent study of crosslinking, Suuberg et al. (1) observed that the crosslinking rate appeared to correlate with the evolution of CO_2. This correlation was confirmed by Solomon et al. (2,3). It appears that crosslinking may be related to the decomposition of carboxyl groups (whose concentration is rank dependent) to form CO_2. Recent research (4) has also demonstrated that substantial reductions in the crosslinking reactions can be achieved by ultra rapid heating. The high heating rate conditions for lignites produce melting and swelling of char, higher yields of soluble products, and product molecular weight distributions previously seen only for melting, easily soluble coals.

This paper describes a study of crosslinking behavior in which chars of a number of coals have been pyrolyzed under a variety of temperature histories and analyzed at intermediate extents of pyrolysis for solvent swelling behavior, functional group compositions and gas evolution. The behavior is consistent with the hypothesis that low temperature crosslinking is related to the decomposition of carboxyl groups to form CO_2.

EXPERIMENTAL

Coals Examined

Experiments were done with North Dakota (Zap), Big Brown Texas, and perdeutero-methylated Big Brown Texas lignites, Wellmore Kentucky #9, Pittsburgh Seam (high ash), Pittsburgh Seam (Argonne sample) bituminous coals and oxidized Pittsburgh Seam (high ash) bituminous coal. The ultimate analysis of each coal is given in Table I.

Char Preparation

The experiments described here were carried out on chars formed from the coals given in Table I. The chars were formed by heating in an inert gas within an entrained flow reactor (EFR) and a heated tube reactor (HTR) for a variety of residence times and maximum temperatures, or by heating in a Thermogravimetric Analyzer (TGA) at 30°C/min to 900°C where the volatiles are analyzed on-line by Fourier Transform Infrared (FT-IR) spectroscopy (TG-FTIR). A more detailed description can be found in Ref. 5.

Char Characterization

The chars were analyzed by quantitative FT-IR spectroscopy using the KBr pellet method (6,7). The chars were also analyzed using the solvent swelling techniques developed by J.W. Larsen and coworkers (8,9) to quantify and monitor the densities of covalent crosslinks inside the macromolecular framework of coal chars.

RESULTS AND DISCUSSION

Rank Dependence of Crosslinking Reactions

Measurements of the appearance of crosslinks during coal pyrolysis were recently reported by Suuberg et al. (1). Their results showed that lignites crosslink at temperatures (650 K) far below those where bituminous coals crosslink (800 K). This motivated the present study of systematically measuring the extent of crosslinking in coal pyrolysis.

Figure 1 shows the volumetric swelling ratio for Zap and Big Brown Texas lignites and Wellmore Kentucky #9, Pittsburgh Seam (Argonne sample) and Oxidized Pittsburgh Seam (high ash) bituminous coals measured as a function of temperature. The swelling ratio profiles are presented as (1-X) where X is the change in the solvent swelling ratio between the coal and char, normalized by the maximum change. The curves are quite different among the five samples. The lignites crosslink at much lower temperatures than the bituminous coals, while the oxidized bituminous coal is an intermediate case.

The extent of low temperature crosslinking correlates with the carbonyl concentration of the coal as measured by FT-IR. The carbonyl concentration is directly related to the concentration of carboxyl groups. The high rank coals have a very low concentration of carboxyl groups, as seen by a low intensity carbonyl band at 1700 wavenumbers, in Fig. 2. The oxidized Pittsburgh Seam coal and the low rank coals have much higher carbonyl peaks.

Big Brown Texas lignite shows a slightly slower rate of crosslinking than Zap lignite. Schobert et al. (10) compared the ESCA spectra of Big Brown Texas and Beulah Zap lignites and found that the carboxylic peak to be less pronounced in the Big Brown spectrum. Spackman (11) has also reported that Big Brown Texas lignite had a lower carboxylic content than the North Dakota Zap lignite. When both lignites are heated at 30°C/min to 600°C, Big Brown Texas lignite evolves less CO_2 (8%) than Zap lignite (11.3%). The area corresponding to the carbonyl peak in the FT-IR spectrum of Big Brown Texas lignite is also less (1.29) than for the Zap lignite (1.69). These observations are consistent with the hypothesis that early crosslinking reactions in lignites occur with loss of carboxyl groups and evolution of carbon dioxide and the extent of crosslinking is directly related to the amount of these labile carboxyl groups present in coal. Bituminous coals which do not have a large concentration of these groups do not undergo early crosslinking reactions. A major contribution of hydroxyl groups in early crosslinking reactions is not likely because bituminous coals have a larger concentration of hydroxyl groups than the carboxyl groups and do not crosslink at low temperatures.

Heating Rate Dependence of Crosslinking Reactions

An important observation was made that crosslinking reactions could be minimized by carrying out the pyrolysis at a very high heating rate. In Fig. 3, the effect of heating rate on tar yield and volumetric swelling ratio in pyridine for North Dakota (Zap) lignite is compared for rapid pyrolysis (20,000°C/s) and slow pyrolysis (0.5°C/s). It can be clearly seen that the lignite starts to crosslink prior to the tar evolution in slow pyrolysis, whereas crosslinking occurs simultaneously with tar evolution in rapid pyrolysis. The tar yield obtained during rapid pyrolysis is higher than that obtained at low heating rate by more than a factor of two. Figure 4 compares scanning electron micrographs of lignite chars produced at 800°C with heating rates of 600°C/s and 20,000°C/s. The 600°C/s char shows little evidence of fluidity while the 20,000°C/s char shows fluidity, bubbling, and swelling. This is believed to be due to reduced crosslinking reactions.

Chemical Modification of Crosslinking Reactions

In order to test the hypothesis of low temperature crosslinking in lignites due to carboxyl groups, slow pyrolysis (heating rate, 0.5 K/s) of Big Brown Texas and perdeutero-methylated Big Brown Texas lignites were carried out in the TG-FTIR. The sample of perdeutero-methylated Big Brown Texas lignite was provided for this study by Dr. Ron Liotta. The gas evolution rate profiles (in arbitrary units) for gas species CO, CO_2, paraffins, CH_4, and H_2O are shown in Figs. 5a-5e, respectively, for Big Brown Texas and perdeutero-methylated Big Brown Texas lignites. The amount of gas species evolved is proportional to the area under the curve. It can be seen that during the pyrolysis stage (Time < 2000 s) the amount of CO_2, CO, and H_2O evolved is less for the perdeutero-methylated coal while the amount of CH_4 evolved is slightly more.

The amount of paraffin evolved (which is related to the amount of tar evolved) is also higher for the perdeutero-methylated coal. The weight loss profile for these two coals is shown in Fig. 5f. The initial weight loss profile (Time < 800 s, T < 300°C) is different while the rest of the weight loss profile during the pyrolysis stage (800 < Time < 2000 s; 300 < T < 900°C) seems to be very similar. The increase in weight at 2040 sec is due to noise in the balance and is not a real effect. CO, CO_2, and H_2O evolution is lower and CH_4 and paraffin (300 < T < 900°C) is higher for the perdeutero-methylated coal. Hence the difference in the weight loss profiles of the two lignites.

The effect of reduction in crosslinking reactions observed in pyrolysis of perdeutero-methylated coal is not only on the total amount of tar evolved but also on the molecular weight distribution of the tar. Figure 6 compares the FIMS spectra for raw and perdeutero-methylated Big Brown Texas lignites. The average molecular weight is substantially increased from that of the unmethylated coal and now resembles that of a bituminous coal.

Effects of Minerals on Crosslinking Reactions

Several investigators (12-15) have studied the role of exchangeable cations in gasification and pyrolysis of low rank coals. The ion-exchange technique as outlined by Schafer (16,17) is used to exchange cations with ammonium ions or load the coal with a certain cation (e.g. calcium) in different amounts.

Tyler and Schafer (13) found that the removal of cations from Gelliondale coals increased the yields of both tar and total volatile matter. The converse was also observed in that the addition of Ca^{2+} ions to an acid-form coal reduced the yields. The reversibility of the phenomena shows that the increase in yields on cation removal is not the result of any permanent chemical modification or degradation of the organic structure of the coal during the acid treatment (2N HCl at room temperature).

This motivated the study of effect of minerals on crosslinking reactions. As calcium has been the cation most extensively studied and low rank coals have a large amount of calcium cations attached to the carboxylate anions, Indian Head Zap lignite was used in this study. Two techniques were used to remove the calcium cations, the details of which can be found elsewhere (18,19). In the first technique, calcium ions were ion exchanged with 1N ammonium acetate for three 24 hour periods. The calcium content after ion exchange was reduced from 1.66 to 0.2%. In the second technique, demineralization with HCl and HF was used. The calcium content after demineralization decreased to 0.01%.

The swelling ratio profiles presented as (1-X) where X is the change in the solvent swelling ratio between the coal and char normalized by the maximum change

for ion exchanged Zap lignite, demineralized Zap lignite and Zap lignite are compared in Fig. 7. The crosslinking behavior for ion-exchanged Zap lignite is similar to raw lignite and shows early crosslinking. It should be noted here that the calcium has not totally been removed by the ion-exchange technique in this study.

The crosslinking behavior of demineralized Zap lignite is strikingly different from that of Zap lignite. It shows a shift to a higher temperature for the same loss in swelling due to crosslinking reactions. Both the raw and demineralized Zap lignites were pyrolyzed in the TG-FTIR apparatus. The tar evolved was higher (daf basis) and the CO and CO_2 evolutions were lower for the demineralized case. An increase in tar evolution is expected due to reduced crosslinking reactions. When pyrolysis of two lignites were carried out at high heating rate (5000 K/s) in the entrained flow reactor, the tar yield was increased from 14% (for raw lignite) to 22% due to demineralization. Similar increase in tar yield has been found for increase in heating rate during pyrolysis which has been discussed in the section entitled "Heating Rate Dependence of Crosslinking Reactions". This further supports the idea of reduced crosslinking due to demineralization.

It should be noted that the increase in tar yield due to the removal of calcium found by Tyler and Schafer (13) was for coals whose cations were removed by acid treatment. Both the lignite and the demineralized lignites were exhaustively extracted by pyridine in a soxhlet apparatus to determine whether any depolymerization of lignite had occurred. The amount of pyridine extractable material was 0% for the raw lignite and 2.6% for the demineralized lignite. The volumetric swelling ratio in pyridine was 2.4 for the raw lignite and 2.5 for the demineralized lignite. Both results show that a very small degree of depolymerization had occurred, if any, due to the demineralization procedure employed to remove the cations. Hence the increase in tar amount and shift of the crosslinking curve to a higher temperature for the same amount of loss in swelling due to crosslinking for demineralized Zap lignite appears to be due to the reduced mineral content.

Effect of Oxidation on Crosslinking Reactions

To further study the role of carboxyl groups in crosslinking, Pittsburgh Seam bituminous coal was oxidized in an oven in air to add carboxyl groups to the coal and see whether the oxidized coal behaved like a lignite in slow heating rate pyrolysis. After 239 hours of oxidation, a large increase in the absorption of IR due to carbonyl band at 1700 wavenumbers is observed which is shown in Fig. 2. There is a slight change in the OH band at 3300 wavenumbers, a large decrease in the aliphatic C-H at 2900 wavenumbers. This was consistent with the findings of other (20-22) investigators.

The chars of the oxidized coal formed at intermediate temperatures were swelled in pyridine to determine the crosslink densities. These results are shown in Fig. 1. The oxidized coal shows earlier crosslinking, as seen by the decrease in swelling ratio (decrease in value of (1-X)) at temperatures above 300°C. The decrease is not as large as that for the lignites because the concentration of carboxyl groups formed during oxidation is not as large as that found in the lignites. The height of the shoulder peak at 1700 wavenumbers corresponding to carbonyl band for oxidized coal is smaller than both the Zap lignite and the Big Brown Texas lignite.

The on-line FT-IR spectra of the gas evolution products from the raw coal and the oxidized coal were taken during pyrolysis and are shown for different temperatures during pyrolysis in Fig. 8. There is a larger amount of CO evolution at low temperatures for the oxidized coal than for the raw coal. This was also

found by Ignasiak et al. (21) in their study of pyrolysis of oxidized bituminous coals. The amount of CO_2 and CO evolved were higher for the oxidized bituminous coal. This is consistent with the larger carbonyl peak in the FT-IR spectrum of the oxidized coal. The amount of tar evolution (as seen from absorption of C-H band at 2900 wavenumbers) at temperatures between 400°C and 550°C is greater for the raw coal than the oxidized coal. This is consistent with the findings of Furimsky et al. (20). The tar, as it flows out of the pyrolysis chamber of the TG-FTIR into the FT-IR cell, forms an aerosol which causes scattering and results in increased absorption at high wavenumbers. The scattering is maximum at temperatures between 450 and 500°C and is also found to be greater for the raw coal than the oxidized coal.

CONCLUSIONS

1. For the low rank coals, the amount of tar obtained in a pyrolysis process increases with the increase in the heating rate.

2. The initial crosslinking reactions in low rank coals appear to be due to the presence of carboxyl groups. High rank coals which do not have these groups in large concentration do not show this kind of behavior in pyrolysis.

3. Chemical modification of carboxyl groups in lignites by methylating results in increased tar yield and molecular weight distribution of tar looks like that of a bituminous coal.

4. Demineralization of the lignite results in decrease in the rate of crosslinking reaction and increase in tar yield and the increase is higher when pyrolysis is carried out at a higher heating rate. The amount of CO and CO_2 evolution is also decreased due to demineralization. These results are consistent with ion exchanged minerals playing an important role in the crosslinking reactions.

5. Oxidation of bituminous coal results in early crosslinking during pyrolysis due to the presence of carboxyl groups introduced during the oxidation process.

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TABLE I

ULTIMATE ANALYSES OF COALS USED (%DAF)

	C	H	N	S	O (diff)
Zap N. Dakota Lignite	66.5	4.8	1.1	1.1	26.5
Big Brown Texas Lignite	72.4	5.5	1.4	1.2	19.5
Wellmore Kentucky #9 Bituminous	86.0	5.4	1.5	1.2	5.9
Pittsburgh Seam #8 Bituminous	82.1	5.6	1.7	2.4	8.2
Pittsburgh Seam #8 (Argonne sample) Bituminous	83.3	5.9	1.6	2.3	6.9

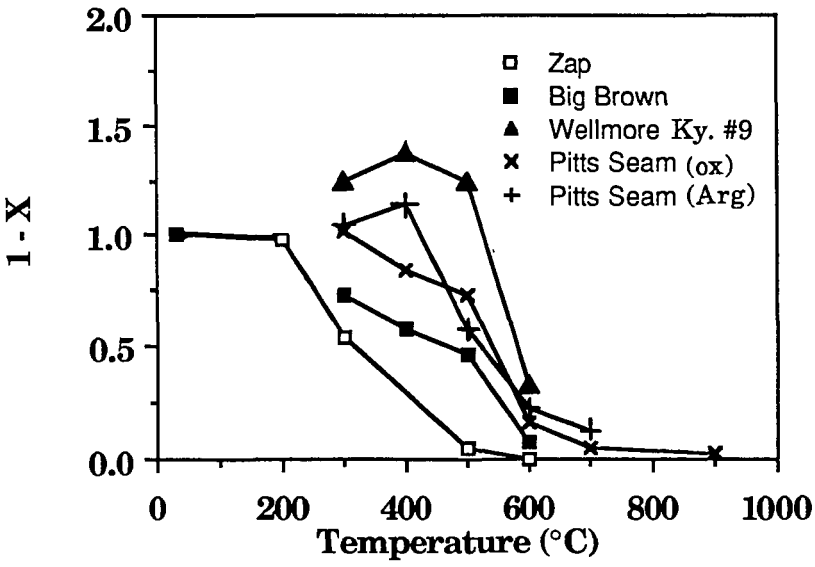

Figure 1. Comparison of Swelling Data of Zap Lignite, Big Brown Texas Lignite, Wellmore Bituminous Coal, Pittsburgh Seam Bituminous (high ash) Oxidized Coal and Pittsburgh Seam (Argonne sample) Bituminous Coal in a TG-FTIR at Various Final Temperatures (Heating Rate = 0.5 K/s).

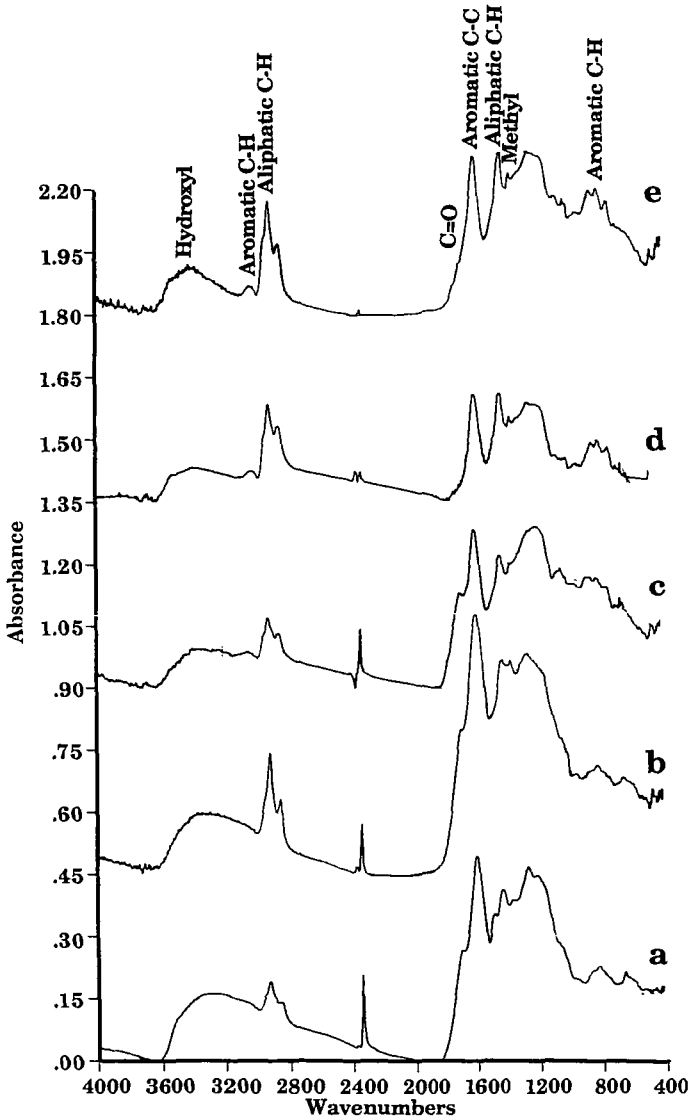

Figure 2. Comparison of the FT-IR Spectra of a) Zap Lignite, b) Big Brown Texas Lignite, c) Pittsburgh Seam Bituminous (high ash) Oxidized Coal, d) Pittsburgh Seam (Argonne) Bituminous, and e) Wellmore Coals Dry, Mineral Matter Corrected.

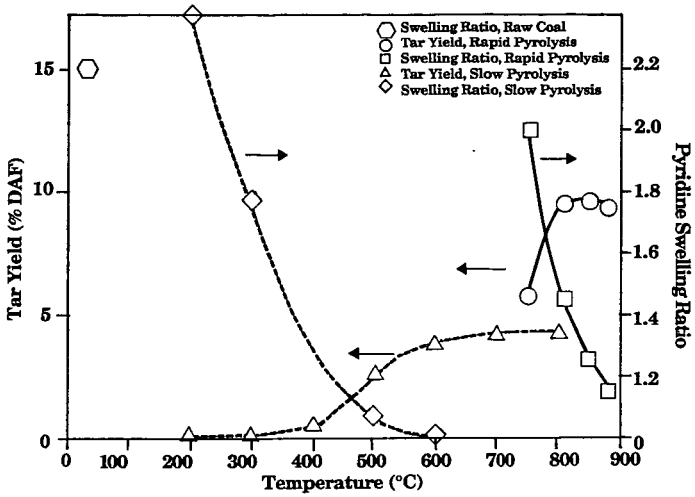

Figure 3. Effect of Temperature on Tar Yield and Pyridine Swelling Ratio of Char for Rapid Pyrolysis of Zap Lignite in Carbon Dioxide (solid line) and Slow Pyrolysis of Zap Lignite in Helium (dashed line).

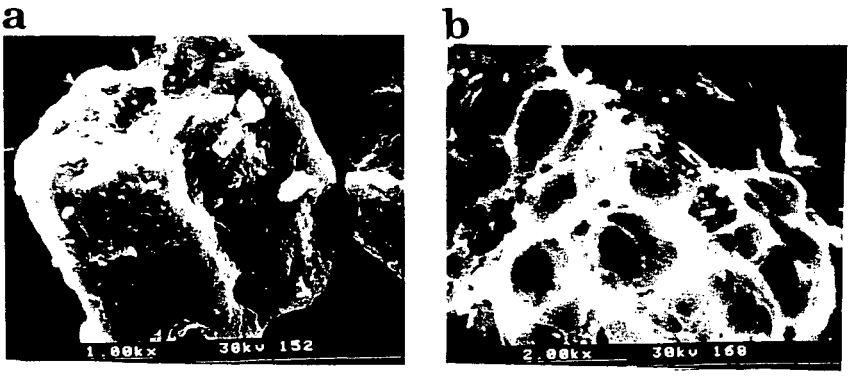

Figure 4. Scanning Electron Micrographs of North Dakota Lignite Chars. a) 600°C/sec Heating Rate and b) 20,000°C/sec Heating Rate.

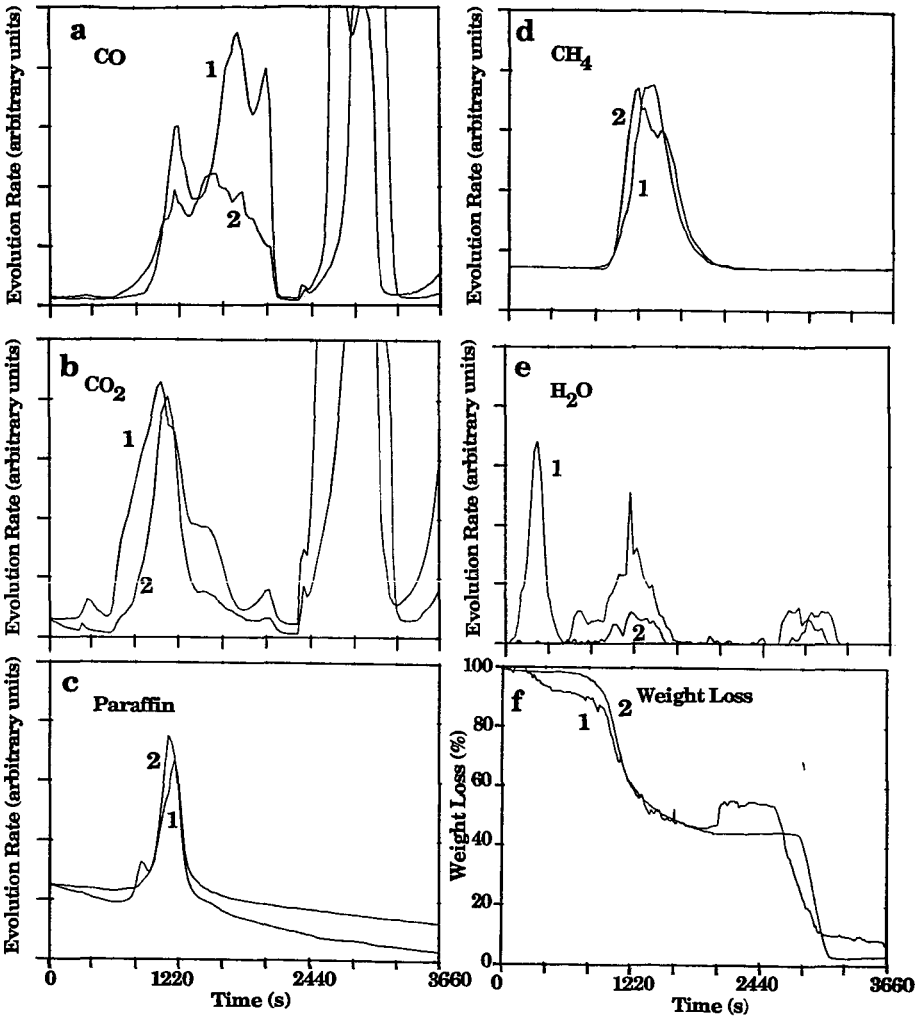

Figure 5. Thermogravimetric/Evolved Gas Analysis of Big Brown Texas and Perdeutero Methylated Big Brown Texas Lignites. a-e) Evolution Rate in Arbitrary Units for Individual Gas Species, and f) Measured Weight Loss. (Heating Rate = 0.5 K/s). 1 = Big Brown Texas Lignite and 2 = Perdeutero Methylated Big Brown Texas Lignite.

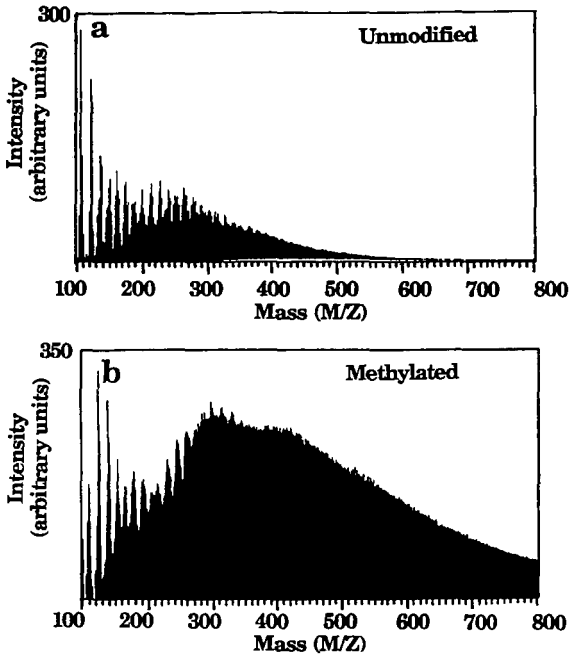

Figure 6. Comparison of FIMS Spectra for Raw and Perdeutero-methylated Big Brown Texas Lignite.

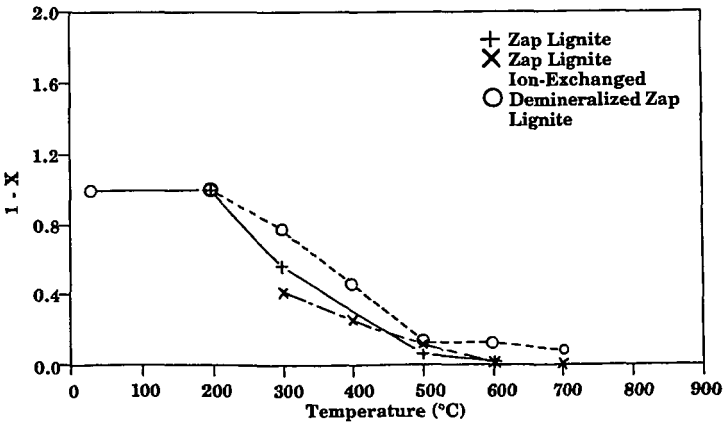

Figure 7. Effect of Removal of Ca by Ion Exchange or Demineralization on Crosslinking Behavior of Zap Lignite.

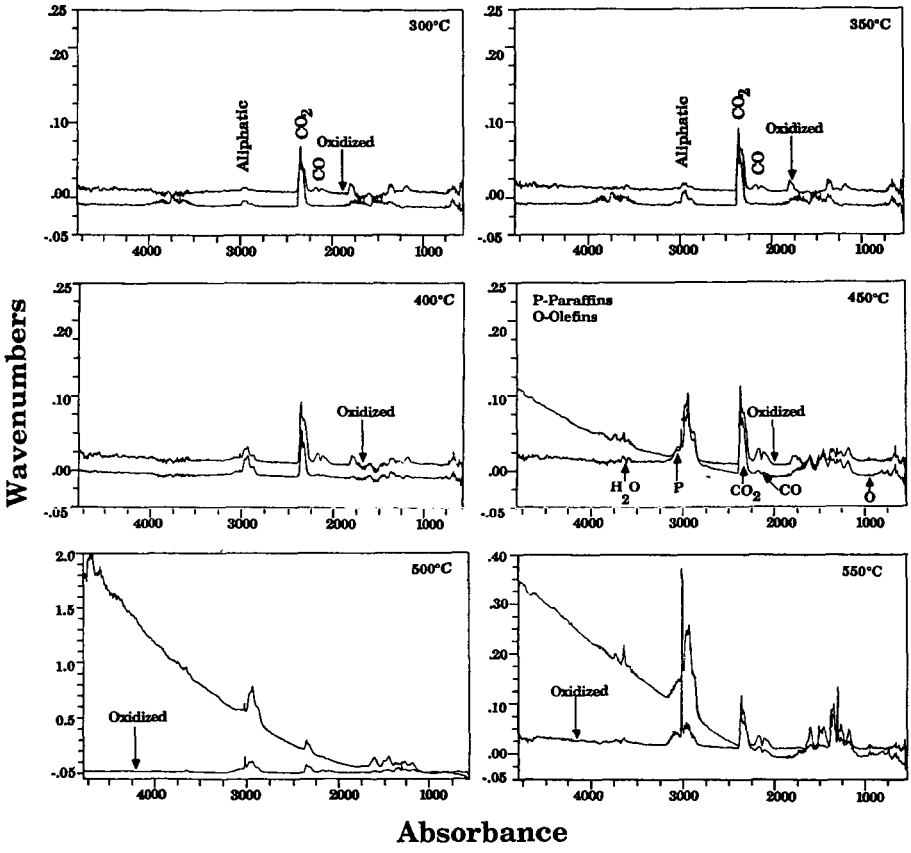

Figure 8. FT-IR Spectra of Evolved Products from Pyrolysis of Pittsburgh Seam Bituminous (high ash) Coal and Pittsburgh Seam Bituminous (high ash) Oxidized Coal.