

Coal Oxidation and Thermal Chemistry

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I. Introduction

The physical and chemical properties and processing characteristics of most coals are extremely sensitive to storage conditions.(1-3) Both drying and the air induced oxidation are known to produce substantial changes to coal. Consequently, they have been the subject of study throughout the history of coal research. In this paper we discuss some of the recently obtained data indicating that these processes involve a few simple chemical transformations which are closely coupled by virtue of their kinetic behavior. In-situ FT-ir analysis used to examine the overall chemical changes is examined herein. Light and neutron scattering were used to examine the concomitant structural changes thereby providing some information on the location of some of the reactive functionality within the coal matrix. These studies will appear elsewhere.(4-7)

Drying is believed to result principally in the loss of adsorbed water, though some studies suggest that chemical alterations occur. That drying produces some alteration is evidenced by the routine use of drying prior to almost all coal studies or processing. The de-facto standardization leads to a coal having reproducible characteristics. Despite considerable study, similar standardized procedures to mitigate the effects of oxidations are not currently available.

Since oxidation of coal is generally believed to influence many coal properties, the resulting literature is extensive. The principal cause of changes associated with the "weathering" of coal is attributed to oxidation. From a utilization standpoint, air oxidation alters properties of the coal which, depending upon the particular end-usage of the coal, may either be detrimental or advantageous. For example, the heat content of coal decreases upon oxidation resulting in increased amounts of coal being needed in any particular application. However, oxidation increases the heteroatom content of the coal resulting in a greater number of sites available for chemical reaction and catalyst binding. Changes to the swelling and fluidity properties of coals are correlated to oxidation. This implies that oxidation alters the fundamental geometrical structure of the coal in addition to the chemical composition and will likely have a secondary effect on all coal chemical reactions through induced alteration of mass and thermal transport through the "semi-solid" coal.

In order to understand these complex reactivity/structure relationships, we have examined both the chemical and structural changes which occur when a sub-bituminous (Rawhide - SBB) and a bituminous (Illinois No. 6 - HvC) coal are reacted at low-temperature (<150°C). In brief we find that drying produces chemical alterations which compete with some of the chemical reactions which occur during the oxidation. Oxidation consists of at least two separate sets of reactions which are distinguishable by their time and/or temperature dependencies. Correlations between the reactivity studies and structural studies carried out with scattering methods suggests the species which react both thermally and oxidatively reside on void surfaces and are readily accessible to the environment.(7-9)

In this paper we review some of our evidence supporting the presence of multiple competing thermal and oxidation reactions. The correlated structural studies are available elsewhere.(8,9)

II. Experimental

Experimental procedures employed are described elsewhere.(4,5,7) As previously describes, samples employed for FT-ir studies are thin sections having a nominal thickness of 0.4 micro-meters and an area of approximately 1 mm². Analytical data representative of the samples are contained in Table 1. A two-dimensional matrix of these sections is prepared using serially cut sections to obtain the desired total sample area on an appropriate substrate.

III. Results and Discussion

We have found that several reactions take place at low-temperature when dry coal is either heated or exposed to oxygen. In order to examine the oxidation chemistry, it is first necessary to remove the effects of drying. We therefore discuss the thermally induced changes prior to dealing with the oxidation.

Drying Results in decarboxylation/decarbonylation

The effect of drying on thin-section samples of Rawhide (SBB) and Illinois No. 6 (Hv-C) coals were examined in a series of experiments. The coal thin-sections were dried at room temperature by subjecting them to a moderate vacuum ($>10^{-5}$ torr) for at least 12 hours. Observation of the hydroxyl stretching region indicates that the physisorbed water is removed within the first hour. We believe that such vacuum drying is able to remove most of the water for two reasons: 1) O'Rourke and Mraw found that room-temperature "drying" of coal using a highly desiccative environment was capable of removing greater than 98% of the adsorbed water from powdered samples of similar coals¹⁰ and 2) we find that subsequent drying by heating under vacuum at 100°C does not further reduce the hydroxyl stretching region intensity.

An example of the effect of heating such a dried Illinois No 6 coal sample for ca 6 hours under vacuum is shown in Fig. 1. Only the region of the ir spectrum indicating carbonyl content (C=O stretch and -C-O-H modes) is shown. The difference spectrum clearly indicates loss of carbonyl intensity at ca 1707 cm⁻¹. This region of the spectrum does not uniquely identify the specific carbonyl species lost. We assign the loss to hydrogen bonded or dimerized aliphatic carboxylic acids based upon several lines of reasoning. These will be discussed subsequently.

The observed frequency loss at ca 1707 cm⁻¹ is generally assigned (9) to the C=O stretch in dimers of aliphatic carboxylic acids in which the aliphatic chain is contains more than 3 carbons.(11) It can also be assigned to a variety of ketone and aldehyde species. It is unusual for aromatic carbonyls to absorb at such a high frequency. This fact together with surface functionality information obtained from neutron small-angle scattering (8) makes an assignment to aromatic carbonyl functionality less plausible. Despite the possibility that the absorption is due to non-carboxylic acid carbonyl species, the weight of the evidence summarized below is in favor of the carboxylic acid assignment. A more complete discussion of alternate assignments is available elsewhere.(6)

A spectral loss is observed at 1285 cm⁻¹ which is observed to follow the same kinetics as the 1707 cm⁻¹ loss feature. Therefore these two absorptions probably result from different vibrational modes of the same species. When present in addition to a carbonyl stretch, the 1285 cm⁻¹ mode is diagnostic for carboxylic acid dimers. We have attempted to determine whether the reactive functionality was located on the void surface or inside the organic matrix by performing solvent permeation studies and examining the induced structural changes and permeability restrictions using neutron and light scattering techniques. Neutron scattering measurements suggest that aliphatic carboxylic acid species are present on the void (pore) surface.(8) In view of our spectroscopic assignments above, we believe the thermally reactive carboxylic acid species to be located at the pore surface.

Restricted mobility of both of reactant and product molecules within the coal matrix is expected. Indeed, higher temperature pyrolysis of coal shows that different chemical transformations occur when carried out under vacuum as compared to a closed atmosphere.(12) This is understandable when the overall reaction is the result of secondary reactions of some initially formed reactive intermediate. We investigated this by carrying out the same thermal reaction in a closed cell under a static helium atmosphere. The overall thermal reaction was unchanged. Only minor changes in some of the relative intensities of the absorption losses were seen. This indicates that mass transport limited secondary reactions are not important under these conditions. Therefore the thermal reaction is either 1) bimolecular between two topologically adjacent portions of the matrix or 2) sequential with the first step being the formation of a reactive species by a unimolecular decomposition followed by reaction with a nearby portion of the matrix surface. The available data does not uniquely determine either possibility.

Available functional group analysis of the Illinois No. 6 coal used for the experiments discussed above indicates that only a relatively small amount of carboxylic acid functionality (0.5 COOH per 100 carbon atoms) is present. We are not currently able to quantify the number of carbonyl groups which we observe since an extinction coefficient for these vibrations is not available for species present in a similar environment. Therefore we were particularly interested in observing the thermal behavior of a lower rank coal containing a larger carboxylic acid content. Rawhide coal containing ca 3.2 COOH per 100 carbon atoms was used.

In contrast to that observed for the Illinois coal, a significant loss of intensity which could be assigned to a loss of C=O species was not seen. There are several possible explanations: 1) carboxylic acid species are unreactive; 2) the predominant carboxylic species are not dimers and the carboxylic acid species which do react form some other carbonyl containing species (e.g., ketones or aldehydes); or 3) the absorptivity of the affected carbonyls is small. We discount 3) since observed C=O stretching intensities are strong in liquid, polymer and solid systems. In order to distinguish between 1) and 2), we employed pyridine as a spectroscopic titrant for acid functionality.

Several of the ring-based carbon vibrations of pyridine are sensitive to the existence and strength of any hydrogen-bonds formed with the unpaired electrons on the nitrogen. Such spectroscopic information has been used for investigations of acidic functionality on surfaces.(13) We show the dependence of some of the pyridine-based vibrations on thermal treatment in Fig. 2. Absorptions at 1485 and 1465 cm^{-1} characterize pyridine which is hydrogen bonded to two types of sites which differ in the strength of the hydrogen bond formed. Only one type of hydrogen bonded pyridine is seen prior to thermal treatment (1485 cm^{-1}). After thermal treatment two pyridine binding sites are seen. The original 1485 cm^{-1} absorption is narrower following thermal treatment. Therefore thermal treatment has converted part of the acid functionality associated with the 1485 cm^{-1} vibration to an acid center characterized by the 1465 cm^{-1} absorption and having a greater hydrogen bond strength than the original species. It is generally believed that the only significant acidic functionality present is phenolic and carboxylic.(1) Concomitant spectroscopic changes indicating phenolic reaction (e.g., 1600 cm^{-1} loss) is not observed. In addition the frequency loss (1485 cm^{-1}) indicates that the original species bound to pyridine have similar hydrogen bond strength. Therefore we assign the acid group loss to carboxylic species. Since corresponding loss in the C=O stretching region does not occur, we conclude that a reaction of the type



occurs. If the species which reacts with the carboxylic acid is a part of the "solid" matrix, a new covalent "cross-link" will be formed at the expense of one hydrogen-bonded "cross-link".

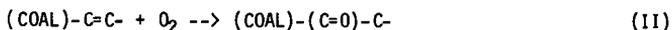
Oxidation of thermally treated coal at 100°C produces new oxygen functionality

The effect of O₂ oxidation of Illinois No. 6 coal at 100°C was examined. An example of the spectroscopic changes resulting from O₂ oxidation at 100°C is shown in Fig. 3 for a sample which had been thermally treated at 100°C to remove the reactive carboxylic acid species. The dependence of the oxidation changes on prior treatment (thermal, closed cell or ambient oxidation) was examined. The principal changes could be attributed to the same oxidation reactions indicating that the 100°C oxidation is reasonably independent of sample history.

The principal changes observed are absorption increases which occur in regions attributable to oxygen functionality on carbonaceous substances. Intensity increases in the carbonyl stretching region (1650 to 1750 cm⁻¹) indicates aldehyde, ketone or carboxylic acid formation. The observation that most of the intensity increase is broadly centered at 1670 cm⁻¹ suggests that oxygen addition to aromatic or unsaturated carbon residues has taken place. Intensity increases occur in the "ether" region (1000 to 1150 cm⁻¹) which, though not diagnostic for ether formation, are suggestive.

The reaction of coal with O₂ to form thermally unstable hydroperoxide intermediates has been frequently proposed as the principal air and/or O₂ oxidation reaction. Definitive spectroscopic evidence showing hydroperoxides has not been reported. Compelling non-spectroscopic evidence is reported by deVries, et al.(14) Our spectroscopic changes are consistent with the formation of all of the expected decomposition products of transient hydroperoxides with the exception of alcohols. Hydroperoxide decomposition proceeds by two parallel pathways: one leads to carbonyl formation while the other leads to alcohol formation. deVries found, and our data supports, the conclusion that the alcoholic pathway is not important in coal oxidation.

We do not believe that significant numbers of carboxylic acids are formed either. An increase in intensity in the OH stretching region associated hydrogen-bonding is not seen. Nor does acid group titration using pyridine indicate a change in the number of acidic groups as a result of oxidation. The principal reaction can be summarized as

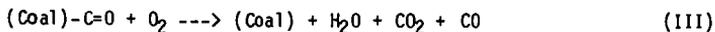


where we have indicated the reaction having occurred with unsaturated carbon as noted above.

A new oxidation reaction is found at room-temperature

The effect of lengthy O₂ on Illinois No. 6 coal was examined spectroscopically. While some changes were seen, they were of low intensity and difficult to resolve. Since the 100°C oxidation and the thermal decarboxylation are obviously independent reactions, we expected the room-temperature oxidation to have no effect on any thermal chemistry. This did not prove to be correct. Lengthy room-temperature oxidation eliminated all evidence of the thermal decarboxylation reactions. The room-temperature oxidation reactions, though not resulting in any striking absorptivity changes, have a dramatic reactivity effect.

We propose the existence of a hitherto unrecognized reaction which is competitive with the thermal decarboxylation reaction. The reaction is summarized as:



We have examined the kinetic behavior of this new oxidation reaction and find that the reaction is rapid by 50 to 60°C. On the other hand, the thermal decarboxylation

reaction is negligible below 60 to 70°C. Therefore there is a temperature "window" from approximately 50 to 80°C in which the reactions will compete and the overall spectroscopic and chemical changes are extremely sensitive to temperature and atmosphere. In addition we predict that any experiment employing a temperature-jump encompassing this temperature "window" will be heating rate dependent. Such a temperature-jump is routinely employed in coal drying procedures. A survey of the literature examining the low-temperature oxidation of coal reveals many statements that the coal used must be carefully predried under precisely defined conditions (see, for example, deVries, et al.(14) and the discussion and references in 7). We take this to be a consequence of the need to control these competing reactions. The sensitivity to the pre-oxidation conditions suggests that the reactivity differences arising from the thermal and room-temperature oxidation are significant even though the i.r. spectroscopic changes are relatively weak and non-specific.

Oxidation Mechanism

Based upon the above evidence with additional confirmation from studies not included herein, we propose the following "mechanism" for the low-temperature oxidation of coal. The oxidation at any moderate temperature is comprised of a combination of the reactions observed in the single-step procedures which we have discussed and summarized as I-III. Thermal decomposition results in loss of carboxylic acid functionality (I). These can be partially replenished during oxidation by the formation of a variety of new carbonyl species (II) resulting from the decomposition of transient hydroperoxide intermediates. The variety of carbonyl species formed is larger than lost due to the thermal decomposition. If the oxidation is allowed to proceed for a long time, the net change in carboxyl absorbance can approach zero. Consequently the net result of the thermal oxidation is to convert carboxylic acid functionality into a more extensive variety of oxygenated species. The oxygen-to-carbon ratio will be less sensitive to these changes than might be expected on first consideration since carbon may be lost through the production of CO and CO₂ and the change of carbonyl functionality will depend upon both the length of time allowed for reaction and the heating rate. A second oxidation reaction (III) occurs at a significant rate slightly above room temperature. Over some temperature ranges, this reaction occurs simultaneously with the thermal decomposition reaction (I) and is either competitive or involves a common intermediate species. Since the absorbance changes associated with II are relatively weak, reaction I will dominate the i.r. difference spectra when it is present.

Sensitivity to water content

We have observed that the relative contribution of the three indicated reactions is sensitive to water. This has not been systematically explored in our experiments. Similar dependencies have been reported.(14,15) deVries, et al.(14) point out that water will influence the hydroperoxide decomposition reactions. Marinov finds evidence for multiple reactions in the low-temperature chemistry of coal.(15) Marinov further finds that water is both a product and a reactant in the low-temperature chemistry of coal. Comparison of the conditions employed by Marinov and ourselves indicates that the two sets of observed reactions may be the same. Therefore water is likely involved in two or more of the reactions which we observe and will lead to extremely complex time-temperature-water content dependencies.

The conditions which we have employed and those of the other cited studies were carried out in the temperature range and using coals which are subject to "spontaneous" ignition. These complexities associated with water content will be one of several factors which will contribute to the initiation of such an uncontrolled oxidation. We believe that our results are suggestive of several new approaches which might be beneficial in preventing "spontaneous" ignition and, more generally, improving the stability of dry coal. Hydroperoxide oxidation is not important until relatively high temperatures and is endothermic in model compounds. Our identification of two additional reactions which occur at much more modest

temperatures and are competitively coupled provides specific reaction-types which might be amenable to control. It is likely that interrupting either reaction will to improved coal stability and may even be effective in reducing or eliminating a key reaction leading to spontaneous ignition.

V. Conclusions

Analysis of FT-ir difference spectra obtained when coal is subject to different oxidation and thermal conditions indicates that thermal oxidation consists of at least three reactions all of which occur in a low-temperature (25 - 100°C) oxidation region. Reaction types (I-III) account for the observed data. Two of the reactions involve oxygen directly; the third is a thermal decarboxylation or decarbonylation reaction which proceeds in the absence of oxygen. Oxidation at 100°C results in the formation of a variety of oxygenated species. The principal products are believed to be carbonyl species which result from the decomposition of thermally unstable hydroperoxides formed by oxygen addition to some species in the coal. In contrast, oxidation at 25°C results in a net loss of absorbance which we interpret as a loss of carbonyl species. The thermal process results in significant i.r. absorption loss at frequencies which are characteristic of carboxylic acid species. Since carbonyl species can either be lost or gained depending upon which pathway dominates, the time-temperature profile employed in oxidation studies will have a significant effect on the overall composition of the oxidized coal. Commonly employed coal pre-drying procedures prior to oxidation is expected to alter the composition of the final oxidized coal since such pre-drying is similar to the thermal step examined in this work.

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Table I

Analytical data for coals representative of the samples utilized⁽¹⁾

PARAMETER	ILLINOIS No. 6	EMWIDE
Rank	HR-C	SAB-C
S Carbon (DMF)	29.44	73.40
H/C	0.944	0.836
O/C	0.999	0.201
COON (per 100 carbon)	0.5 ⁽²⁾	3.2 ⁽³⁾
Organic S (DMF)	3.08	0.93
Phenolic OH (per 100 carbon)	4.5 ⁽²⁾	4.4 ⁽³⁾
Total S (Dry)	3.94	0.92
Pyritic S. (Dry)	1.17	0.01
Mineral Matter	10.94	7.00

1. All analysis (except as noted) are from data from similar samples contained in the Coal Characterization Library of the Exxon Coal Research Laboratory, Baytown, Texas. Sample to sample variations are expected as well as differences due to sample preparation. The numbers, therefore, are useful only in addressing trends.

2. R. Liotta, G. Brons, J. Amer. Chem. Soc., 1981 103, 1725-1742.

3. Analyses were kindly provided by Dr. R. Liotta and obtained from samples representative of those utilized.

Fig. 1 - FT-ir difference spectrum of Illinois No. 6 coal subjected to vacuum drying at 100°C showing absorption losses relative to the coal before heating.

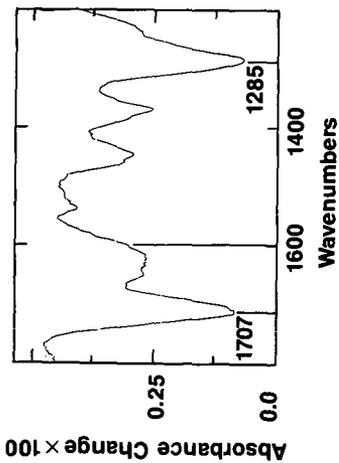


Fig. 2 - Pyridine adsorbed on Rawhide coal (A) before and (B) after having been subjected to vacuum drying at 100°C. The 3 indicated absorptions are pyridine specific.

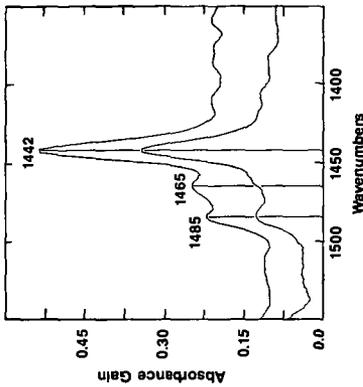


Fig. 3 - FT-ir difference spectrum of Illinois No. 6 pretreated by vacuum drying at 100°C and subjected to O₂ treatment at 100°C. Absorption increases of the oxidized coal as compared to the dried (100°C) starting coal are shown.

