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Study of structural features in Pittsburgh bituminous, Illinois #6 bituminous, rawhide sub-bituminous, and Texas lignite

Lagrone, Susan Ann, Ph.D.

Rice University, 1989
RICE UNIVERSITY

STUDY OF STRUCTURAL FEATURES IN PITTSBURGH BITUMINOUS, ILLINOIS #6 BITUMINOUS, RAWHIDE SUB-BITUMINOUS, AND TEXAS LIGNITE

by

SUSAN ANN LAGRONE

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

DOCTOR OF PHILOSOPHY

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April, 1989
Studies of the slow pyrolysis of coals using matrix-isolation Fourier-transform infrared spectroscopy (MI-FTIR) and electron spin resonance (MI-ESR) have given insight to coal structures. Evolution of light carbonyl compounds below 250°C and dealkylation reactions to form light hydrocarbons occurred from 150-400°C. CH₄ evolution continued to 800°C. Hydroxyl group decomposition evolved H₂O from 150°C to 700°C. Lower rank Texas Lignite produced the most H₂O, from 150-400°C, followed by Rawhide Sub-bituminous, Illinois #6 Bituminous, and Pittsburgh Bituminous. From analysis of CO₂ yields Texas Lignite contains 2.1 COOH groups per 100 C atoms, Rawhide 2.2, Illinois #6 and Pittsburgh 0.5. From CO yields Texas Lignite and Pittsburgh contain 9.13 and 4.28 ether groups per 100 C atoms respectively. Tar evolution began at 150°C with maximum production from 300-600°C.

H₂S evolved with the tar fraction at 300-500°C and, for Pittsburgh, this amount of H₂S constituted 90% of the organic sulfur content of the coal. Retention of organic sulfur in the chars or release of organic sulfur in other forms in tar may account for the difference in desulfurization of the other coals. CS₂ evolved from 800-1200°C. SO₂ from sulfate decomposition was most notable for Pittsburgh and Illinois #6, less so the lower rank coals. Nitrogen pyrolysis products were NH₃ at 300-700°C and HCN at 350-800°C. C₂H₂ was formed from 950-1400°C. Kaolinite reduction yielded SiO, Al₂O, and aluminum atoms complexed with CO at 1150-1500°C. At elevated temperatures further
evolution of H₂O and CO was observed probably due to secondary pyrolysis reactions or decomposition of inorganic hydroxides in the case of H₂O or to reduction of metal oxides (kaolinite) by char for CO.

Two distinct hydroxyl groups at 3626 cm⁻¹ and 3581 cm⁻¹ were detected in a N₂ matrix for tars evolved from 300-600°C. These groups were identified as phenolic hydroxyls and were most prevalent in Pittsburgh and Illinois #6. O-methylation of the carboxyl, aliphatic and phenolic hydroxyl groups in coal changed the pyrolysis behavior. New species were formed which were not produced in pyrolysis of untreated coals because of hydrogen bonding and decomposition of hydroxyl groups via water elimination reactions to form ether cross linkages. Tar evolution at 300-600°C remained unchanged for Pittsburgh and Illinois #6 but increased by 62.1% for Rawhide and 31.5% for Texas Lignite. Esters, aromatic ethers, and aliphatic ethers were observed in FTIR spectra of KBr methylated (CD₃I) coals. Pittsburgh and Illinois #6 contained phenolic-OH groups with some COOH groups and fewer aliphatic-OH groups. Rawhide and Texas Lignite contained more phenolic-OH than COOH and aliphatic-OH. Methanol and formaldehyde were produced from ester and aliphatic ether decomposition whereas methane and carbon monoxide evolved from aromatic ethers.

MI-ESR studies indicated peroxy radicals in evolved tars which can be attributed to surface peroxides. Pittsburgh and Illinois #6 tars displayed two radicals, one with average g values of 2.0366, 2.0071 and 2.0014 and the other 2.0302, 2.0098 and 2.0014. MI-FTIR studies showed a marked influence on the pyrolysis behavior of Pittsburgh for CaO and to a lesser extent MgO. The phenolic hydroxyl at 3626 cm⁻¹ was decreased when Pittsburgh was pyrolyzed with CaO and a large amount of water preceded the tar evolution. For all
additives tar was evolved at higher temperatures indicating their ability to change the mechanism of tar evolution.
To my husband Craig, my children, and my parents,
June and Wightman Cannon for their love and support
Gloria in excelsis Deo
ACKNOWLEDGMENTS

I gratefully acknowledge the support of the Department of Energy at Morgantown for funding of this work, Dr. Richard Neavel for supplying the coal samples used in most of these studies, Dr. M. R. Khan for the additive samples, Dr. Robert H. Hauge and Dr. C. Judith Chu for their assistance and my advisor Dr. John L. Margrave for his constant support.
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1.1 Introduction

Coal pyrolysis is the initial step in most coal conversion processes: gasification, liquefaction, and combustion. This step is greatly dependent on the properties of coal. Pyrolysis is a necessary and inseparable process in all areas of coal utilization and combustion; the most common pyrolysis product is coke.\(^1\) As coke is formed, gases and liquids are released. The pyrolysis process is especially important to coal processing and coal science as it is the basic method for producing coke. It has been suggested that devolatilization is important as a pretreatment step to further coal processing in order to obtain valuable liquids and gases prior to the main process which follows.\(^1\) By learning more of the structure of a coal and how it decomposes one can hopefully choose ways to pretreat the coal depending on what is desired. For example, if one wishes to maximize methane (CH\(_4\)) production then ways to minimize char yield and maximize char reactivity would need to be sought.\(^2\) Finding ways to increase the tar yield could lead to improvements in gasification reactors. Coaction of pyrolysis with oxidation, combustion, and gasification has also been of interest, specifically when pyrolysis interferes with other processes and affects the overall rates, yield, and properties of the products.\(^1\)

In regard to coal science by studying the pyrolysis products one may gain insight into coal structures. It is believed that many structural elements of the original coal are retained in the tar, the heavy molecular weight pyrolysis product. Orning and Greifer were the first to show that strong similarities exist between the infrared spectrum of parent coals and their respective tars.\(^3\) Since then others too have produced evidence supporting this idea.\(^4,5\) Investigation of other pyrolysis products can be used to suggest possible thermal decomposition mechanisms of functional groups in the original coal.

The most commonly employed analytical techniques for studying the
thermal decomposition of coal are pyrolysis-GC and pyrolysis-MS or variations of these.⁶-⁹ The information obtained from this kind of work tells one what products are formed but not always at what temperature.⁹ A spectroscopic technique which is a bit more versatile than the above is Fourier transform infrared spectroscopy (FTIR). It takes advantage of the ability to use larger weight samples, more quickly analyze data, and identify heavy molecular weight tar materials. FTIR can be used as an on-line, in-situ monitor of time and temperature dependent yields of pyrolysis gas species.⁹,¹⁰ Furthermore, FTIR detects the devolatilization products without interference from carrier gases such as helium, oxygen, nitrogen, argon, etc. As expected this method affords quantitative data on organic and mineral composition of the coal, tar, and char.¹¹-¹⁵ Fourier transform infrared spectroscopy plays an important role in creating a kinetic model for coal thermal decomposition since it enables one to relate pyrolysis products to the organic structure of the parent coal. If one focuses on the solid products, char and tar, then the process is called carbonization.¹ Solomon has studied these solid products at successive stages during thermal decomposition using this analytical tool to elucidate the changes occurring in chemical bonds.¹⁶ Alternatively, if the focus is on the liberated matter the process is called devolatilization.¹ This area has also been widely explored and pyrolysis-FTIR has again been an important method for acquiring information on the amount, composition, and rate of evolution of gases.¹⁶ Usually some effort is made to relate the evolution of gases with the rate of change of chemical bonding within the coal. Other examples of how FTIR has been employed in the study of coal pyrolysis are evolved gas analysis-FTIR (FTIR-EGA)¹⁹, and matrix isolation -FTIR (MI-FTIR)¹⁶,¹⁷.

MI-FTIR is the tool used in the majority of this investigation and has been developed at Rice University by John L. Margrave and co-workers. It is capable
of isolating and analyzing the pyrolysis products at 12K in inert matrices as opposed to pyrolysis-FTIR in which the gases are merely sampled at various stages of the thermal decomposition. Better spectral characterization of pyrolysis products has been achieved especially in the hydroxyl regions. In earlier studies by other methods, water absorptions masked the absorptions of hydroxyl features present in the coal products. MI-FTIR also allows the comprehensive study of the gases in situ as well as the evolved tar. It is obvious that this technique while in no way replacing the methods previously used has contributed uniquely to the study of coal structures through analysis of pyrolysis products, especially the evolved tars.

In studying the slow pyrolysis of four coals using MI-FTIR much information has been obtained. This chapter describes the characterization of product spectra for four coals pyrolyzed from room temperature (RT) to 1500°C, along with comparisons to published work. Coal is viewed by some as a collection of functional groups which decompose independently to yield light gas species at rates independent of coal rank but dependent on the groups themselves. An effort is made to relate the evolution of light gas species quantitatively to the corresponding functional groups as portrayed in the original coal molecule. This requires a knowledge of the extinction coefficients for each evolved species. Once a weight (mg) is determined for each product, a comparison with published data provides a first approximation of the number of certain functional groups in coal.

1.2 Experimental

The Rice University multisurface matrix-isolation apparatus was used in studying the pyrolysis products of coal. A diagram of this machine is given in Figure 1. The rhodium-plated copper block has 80 deposition surfaces of which 60 have been used for pyrolysis studies over a wide temperature range. This
Figure 1. Matrix-Isolation FTIR Apparatus: (A) IBM-98 Vacuum FTIR, (B) Matrix-Isolation Apparatus, (V) Matrix-Isolation Chamber, (a) Multisurface Block, (e) Matrix Gas Inlet for Coal Chamber VII, (d) High Temperature Furnace with Water Cooled Shield, and (VIII) Pumping System for Chambers V and VI
block is easily rotated and/or translated allowing for efficient sequential sampling of the pyrolysis products, and it is cryogenically cooled using a helium closed-cycle refrigerator to 15K. This temperature allows efficient isolation of high temperature and reactive species in nitrogen. The pressure in the system measured by an ionization gauge was generally \( \sim 1.0 \times 10^{-7} \) torr but rose to \( \sim 10^{-5} \) torr during a pyrolysis experiment. The pyrolysis reactor is shown in detail in Figure 2. Its orientation with respect to the matrix isolation block can be found in Figure 1 (see chamber VII). Each coal sample was placed in a graphite cell the dimensions of which are given in Figure 3. The cell was supported by a platinum/platinum-10% rhodium thermocouple which was centered inside the furnace by a piece of alumina, the front end of the cell flush with the front end of the furnace. The furnace was made of a cylindrical piece of tantalum foil (1/2" o.d. and a 1mm i.d.) spot welded to an outer tantalum tube (3/4" o.d. and 20mm i.d.). This cylinder was then fitted onto a flange equipped with water-cooled leads to prevent its heat up during experiments and cable connectors to a variable transformer. The furnace length measured such that it placed the cell at the aperture of the matrix chamber. Inside the chamber the furnace was surrounded by a water-cooled copper jacket to minimize radiation to other parts of the apparatus. The coal chamber in Figure 1 could be isolated from the matrix block allowing samples to be evacuated independent of the remainder of the machine. Thus one could evacuate another sample while collecting data from a previous experiment. The vacuum in chamber VII was obtained with a fore-pump coupled to a 4" diffusion pump. A vacuum gauge measured pressure to 760 torr, a thermocouple gauge measured the pressure down to 10 microns, and an ionization gauge measured pressures to \( 10^{-7} \) torr. Each sample was evacuated slowly using the fore pump until the pressure read 50 microns. Then the chamber was opened to the diffusion pump and the
Figure 2. Pyrolysis Reactor for Slow Pyrolysis of Coal
Figure 3. Graphite Sample Cell
pressure was $< 10^{-5}$ torr. The small particle size of the coals used ($< 500$ mesh) caused sample loss if evacuation was too rapid; therefore, evacuation of sample was generally extended over an interval of 4-5 hours.

In a slow pyrolysis experiment the coal was placed in the graphite cell and resistively heated, the gaseous products being trapped in a nitrogen matrix at 15K. One deposition surface was used for every 30-100°C rise in temperature with a heating rate of 3-10°C/ min. The temperature range studied for each coal was from RT-1500°C. Each surface was later analyzed off-line with the IBM-98 FTIR spectrometer. The scan range used was 4000-500 cm$^{-1}$ with 1 cm$^{-1}$ resolution. Each spectrum corresponded to 100 scans spectrometer. The scan range used was 4000-500 cm$^{-1}$ with 1 cm$^{-1}$ resolution. Each spectrum corresponded to 100 scans. The elemental analysis for the four coals studied are found in Table I. The four coals in order of decreasing rank are:

1. Pittsburgh seam, high volatile A bituminous rank
2. Illinois #6 standard sample, high volatile C bituminous rank
3. Rawhide, sub-bituminous C rank, Wyoming
4. Texas lignite, lignite rank.

All coal samples were ground with a mortar and pestle in a glove bag under a nitrogen pressure and subsequently sifted through a series of sieves, the 500 mesh (25μ) size being collected for use. For quantitative comparisons a weight of 30.50mg was used.

Another important part of this apparatus used in the coal work was a quartz crystal microbalance. There were three crystals mounted onto the matrix block capable of measuring thickness(weight) of a gaseous product deposited at ambient temperature or 15K. First the quartz crystal was used for determining extinction coefficients of model coal vapor species. The crystal was held at 15K, the same temperature as the deposition surfaces in the pyrolysis experiments.
Table I

Elemental Analysis of Four Coals

<table>
<thead>
<tr>
<th></th>
<th>Texas Lignite</th>
<th>Rawhide Sub-bituminous</th>
<th>Illinois#6 Bituminous</th>
<th>Pittsburgh Bituminous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture (wt%)</td>
<td>21.1</td>
<td>15.4</td>
<td>10.3</td>
<td>7.6</td>
</tr>
<tr>
<td>Ash (wt%)</td>
<td>9.35</td>
<td>8.64</td>
<td>9.28</td>
<td>6.04</td>
</tr>
<tr>
<td>Mineral matter (wt%)</td>
<td>6.9</td>
<td>7.1</td>
<td>10.9</td>
<td>7.8</td>
</tr>
<tr>
<td>Vol. matter (wt%)</td>
<td>48.2</td>
<td>47.3</td>
<td>41.6</td>
<td>37.2</td>
</tr>
<tr>
<td>Carbon (wt%)</td>
<td>68.0</td>
<td>68.3</td>
<td>70.9</td>
<td>78.9</td>
</tr>
<tr>
<td>Hydrogen (wt%)</td>
<td>4.99</td>
<td>4.84</td>
<td>5.08</td>
<td>5.25</td>
</tr>
<tr>
<td>Nitrogen (wt%)</td>
<td>1.06</td>
<td>0.82</td>
<td>1.18</td>
<td>1.28</td>
</tr>
<tr>
<td>Sulfur, total (wt%)</td>
<td>0.96</td>
<td>0.92</td>
<td>3.94</td>
<td>2.29</td>
</tr>
<tr>
<td>Sulfur, pyritic (wt%)</td>
<td>0.04</td>
<td>0.01</td>
<td>1.17</td>
<td>0.69</td>
</tr>
<tr>
<td>Sulfur, organic (wt%)</td>
<td>0.92</td>
<td>0.91</td>
<td>2.77</td>
<td>1.60</td>
</tr>
<tr>
<td>Oxygen, organic (wt%)</td>
<td>18.3</td>
<td>18.2</td>
<td>9.4</td>
<td>5.6</td>
</tr>
<tr>
<td>Density (g/ml)</td>
<td>1.44</td>
<td>1.45</td>
<td>1.37</td>
<td>1.33</td>
</tr>
<tr>
<td>Btu/lb</td>
<td>11720</td>
<td>11710</td>
<td>12857</td>
<td>14312</td>
</tr>
</tbody>
</table>

Samples supplied by Exxon Research and Engineering Company. Analysis based on moisture free coal. Ash contents of samples supplied may not be same as those indicated.
and the following gaseous products were studied: CO, CO₂, H₂O, CH₄, H₂S, CS₂. The pure gases were directed toward the crystal via the coal chamber (see Figure 1) at specific concentrations as regulated by a needle valve. Basically one measures the thickness deposited (KÅ) per time(min) by detecting changes in the resonant frequency of the quartz crystal. At each concentration the pure substance was co-deposited with nitrogen for 10 minutes to mimic slow pyrolysis conditions. A reading of the amount of nitrogen used(constant) was recorded at the end so as not to overload the crystal before all measurements could be made. Equation I shows how molar ratios of concentrations were calculated.

$$\text{molar ratio concentration} = \frac{\text{(moles of pure substance/moles of nitrogen)}}{[(\text{KÅ/min}) \times 1000/60] / (\AA/\sec)} \times \frac{\text{MW(N₂)}}{\text{MW(GAS)}}$$

Now from an integrated peak area program available on the IBM computer the area (absorbance) for the pure substance could be determined and plotted vs. the concentration in KÅ. For example the peak area for CH₄ at each concentration(KÅ) was obtained by integration of the C-H bending mode at 1320-1290 cm⁻¹. Graphs for the pure gases studied can be found in the Appendix. A measured weight of elemental silver was vaporized and used as the standard for calibration of geometric factors, configuration of the furnace and the sample cell distance from the matrix surface. With an average value of 5.4 x 10⁻¹ mg vaporized/KÅ deposited any gaseous product can be related quantitatively to the amount vaporized from the coal. Calculation of total peak area for a vapor species during the pyrolysis experiment can then be related to a total thickness(KÅ) using the above plots and ultimately converted to a weight(mg) by applying the experimentally determined conversion factor of 5.4 x 10⁻¹ mg/KÅ. The results for these calculations can be found in Table II as well as a comparison of the sum of tar, char and volatile products analyzed to the
Table II
Slow Pyrolysis Products of Four Coals in Milligrams

<table>
<thead>
<tr>
<th></th>
<th>Texas Lignite</th>
<th>Rawhide Sub-bituminous</th>
<th>Illinois#6 Bituminous</th>
<th>Pittsburgh Bituminous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal (dry wt in mg)</td>
<td>30.50</td>
<td>30.50</td>
<td>30.50</td>
<td>30.50</td>
</tr>
<tr>
<td>Char</td>
<td>9.80</td>
<td>12.53</td>
<td>13.56</td>
<td>16.38</td>
</tr>
<tr>
<td>Tar</td>
<td>2.21</td>
<td>1.31</td>
<td>2.92</td>
<td>3.94</td>
</tr>
<tr>
<td>CO₂</td>
<td>3.42</td>
<td>3.64</td>
<td>0.82</td>
<td>0.85</td>
</tr>
<tr>
<td>CO</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>12.84</td>
<td>13.18</td>
<td>11.76</td>
<td>6.73</td>
</tr>
<tr>
<td>Low temperature</td>
<td>7.54</td>
<td>8.11</td>
<td>4.52</td>
<td>3.54</td>
</tr>
<tr>
<td>High temperature</td>
<td>5.30</td>
<td>5.07</td>
<td>7.24</td>
<td>3.19</td>
</tr>
<tr>
<td>H₂O</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>3.12</td>
<td>2.49</td>
<td>1.54</td>
<td>1.34</td>
</tr>
<tr>
<td>Low temperature</td>
<td>2.27</td>
<td>1.74</td>
<td>1.16</td>
<td>0.98</td>
</tr>
<tr>
<td>High temperature</td>
<td>0.85</td>
<td>0.75</td>
<td>0.38</td>
<td>0.36</td>
</tr>
<tr>
<td>LT/HT ratio</td>
<td>2.67</td>
<td>2.32</td>
<td>3.05</td>
<td>2.72</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.65</td>
<td>0.58</td>
<td>0.90</td>
<td>1.33</td>
</tr>
<tr>
<td>CS₂</td>
<td>0.01</td>
<td>0.01</td>
<td>0.05</td>
<td>0.02</td>
</tr>
<tr>
<td>H₂S</td>
<td>0.13</td>
<td>0.11</td>
<td>0.62</td>
<td>0.47</td>
</tr>
<tr>
<td>Char + tar +</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>volatile species</td>
<td>32.18</td>
<td>33.85</td>
<td>32.17</td>
<td>31.06</td>
</tr>
<tr>
<td>% deviation</td>
<td>5.5</td>
<td>11.</td>
<td>5.5</td>
<td>1.8</td>
</tr>
</tbody>
</table>
measured weight of starting material. The greatest percent error is seen for Rawhide (11%) with the remaining coals showing 5.5% or less. These reasonable deviations indicate this technique is applicable to coal characterization.

Secondly, the quartz crystal was used to measure the amount of tar condensable at room temperature. For these studies the coal was vaporized as before except the temperature ranged from RT-600°C and the crystal was kept at room temperature. The only condensable product was the heavy molecular weight tar fraction since all other species were pumped away. This type of experiment is useful in comparing the amounts of tars for all coals, as illustrated in Figure 4 showing the concentration (KÅ) as it relates to temperature.

1.3 Results and Discussion

KBr Spectra

Identification and band assignments for infrared spectra of various coals have been extensively investigated by Painter et. al.11-14 The FTIR spectra of these coals in KBr are shown in Figure 5. The broad absorptions in the O-H stretching region from 3800-2000 cm⁻¹ are assigned to hydroxyl functional groups as well as adsorbed water in the coal.18,19 This broad absorption was stronger for Texas Lignite and Rawhide sub-bituminous than for the higher ranked coals, Illinois#6 and Pittsburgh bituminous, indicative of a higher moisture content for the lower ranking coals (see elemental analysis Table I). The absence of aromatic hydrogen stretching and bending modes at ~3100 cm⁻¹ and 800-900 cm⁻¹ respectively for Texas Lignite and Rawhide are also indicative of their lower rank.18 Of the two bituminous coals Pittsburgh is slightly higher in rank due to its pronounced aromatic stretching and bending modes and its higher carbon content of 78.9%. Of the four coals studied
Figure 4. Tar Evolution Measured as a Function of Temperature
Figure 5. FTIR Spectra as KBr Pellets of (a) Illinois #6 Bituminous, (b) Pittsburgh Bituminous, (c) Texas Lignite and (d) Rawhide Sub-bituminous
Illinois#6 had the highest kaolinite \( \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \) concentration as seen by the intense absorption at \( \sim 1000 \text{ cm}^{-1} \). A shoulder at \( \sim 1700 \text{ cm}^{-1} \), most noticeable for Rawhide sub-bituminous, was due to the presence of carbonyl and carboxyl functional groups in the coal.\(^{13}\)

**Matrix Isolation FTIR Spectra**

Matrix isolation FTIR spectra of gaseous pyrolysis products of the four coals studied are shown in Figures 6, 7, 8 and 9. Differences in pyrolysis behavior of the coals are discernable from these three-dimensional FTIR plots. Evolution of pyrolysis products occurred at approximately the same temperatures for each coal thereby implying that the devolatilization mechanism of a particular functional group is rank insensitive. Solomon has observed that, excluding anthracites, decompositions of certain functional groups and primary evolution of light gases (CO, CO\(_2\), H\(_2\)O, HCN, CH\(_4\), C\(_2\)H\(_6\)) are rank insensitive\(^{20}\). The major differences among the coals were found in the amounts of pyrolysis species produced.

**Hydrocarbon Evolution**

Traces of small carbonyl compounds such as acetone, formaldehyde, formic acid, and acetic acid were observed at low temperatures, \(< 250^\circ\text{C}\). Low molecular-weight hydrocarbons (ethane, ethene, and propene) were identified during coal depolymerization around 150-400\(^\circ\text{C}\). Similar evolution at these temperatures were noted by Jüntgen and Van Heek.\(^1\) The source of these light hydrocarbons may be aliphatic side-chain groups and interlamellae linkages cracked at higher temperatures.\(^6\) Methane evolution was seen to increase sharply with production of the other hydrocarbon gases (300\(^\circ\text{C}\)). From Table II Pittsburgh bituminous produced the greatest amount of methane followed by Illinois#6 with lesser amounts from Texas lignite and Rawhide sub-bituminous. A possible explanation for these observations can be found from its
Figure 6. Matrix-Isolation FTIR Spectra of Pittsburgh Bituminous
Figure 7. Matrix-Isolation FTIR Spectra of Illinois #6 Bituminous
Figure 8. Matrix-Isolation FTIR Spectra of Rawhide Sub-bituminous
Figure 9. Matrix-Isolation FTIR Spectra of Texas Lignite
Figure 10. Comparison of C-H Stretching Region for Matrix-Isolated Tar (Left) and the Original Coals as KBr Pellets (Right)
matrix-isolated tar spectra and KBr spectra (Figure 10). Comparison of the relative intensities of CH$_2$ and CH$_3$ absorptions in evolved tar shows Pittsburgh bituminous to possess greater amounts of -CH$_3$ groups in the evolved tar followed by Illinois#6. Texas lignite and Rawhide contain approximately equal amounts of CH$_3$ groups. KBr spectra of the original powdered coals show the same trend for methyl groups in coal. The concentration of methyl groups in the original coal correlates with the observed amount of methane by pyrolysis of each coal. Other investigators$^{1,6,7}$ agree that methane is from dealkylation of the coal as are the other hydrocarbons. Yet methane evolution continues past that of the other hydrocarbons, specifically up to temperatures around 800°C with traces up to 1500°C suggesting possibly another source for methane. Fitzgerald and Van Krevelen suggest this source of methane could be from char autohydrogenation reactions:

$$C + 2H_2 \rightarrow CH_4; \quad T>500^°C$$

However, Campbell suggests for most in-situ experiments the source of methane appears to be coal pyrolysis reactions.$^6$

**CO$_2$ Evolution**

The evolution of CO$_2$ is thought to be primarily from the carboxyl groups(-COOH) present in coal. This decomposition occurred at temperatures ranging from 65-450°C in good agreement with other published data. Comparison of CO$_2$ evolution for the four coals showed a marked decrease with increase of rank due to the reported lack of -COOH groups in bituminous coals.$^{21}$ Interestingly no clear C=O stretching absorption at $\sim$1700 cm$^{-1}$ can be observed other than a shoulder for the two low rank coals. The absence of C=O stretching modes could be attributed to the existence of metal chelates from a complexation of the carboxyl functional groups with metal ions such as calcium ions present in coal. Results from O-methylation studies have shown an
enhancement of the C=O absorption at 1700 cm\(^{-1}\), presumably due to the elimination of metal chelates and the formation of esters from the methylation of carboxyl groups present originally in the coal. KBr spectra of the O-deuterated coal clearly shows the lack of -COOH groups in the bituminous coals and the larger amounts in the low rank coals. Some have reported a second source of CO\(_2\) (570-800°C) resulting from the decomposition of inorganic carbonates\(^{22}\) present in the minerals(calcite, dolomite, and ankerite).\(^{6,7,14}\) The CO\(_2\) at these temperatures is contributed to this latter source. A residual amount of CO\(_2\) is evolved throughout the remainder of the pyrolysis.

Although not all the CO\(_2\) can be attributed to the carboxyl functional group a rough approximation can be obtained for the amount of this group in original coal. Table III lists the organic oxygen functional group distributions of Illinois#6 and Rawhide as determined by \(^{13}\)C NMR spectroscopy by Levine et. al.\(^{23}\) Attar suggests that esters are found in peat and low rank coals in small amounts and essentially not at all in higher ranking coals.\(^{14}\) With this in mind it is supposed for Illinois#6 that there are 0.5 carboxylic acid groups per 100 C atoms. From the limitation described earlier, that all the CO\(_2\) is generated from decomposition of carboxylic acid functional group, an approximation can be found to the amount of this functional group originally present in Illinois#6 and Rawhide. From Table II Illinois#6 produced 0.82 mg CO\(_2\) and contains 0.5 -COOH groups / 100 C atoms yielding a ratio of 1.64 mg CO\(_2\) per -COOH / 100 C atoms. From Table II Rawhide produced 3.64 mg CO\(_2\) which when compared to the above ratio indicates Rawhide contains 2.2 -COOH groups / 100 C atoms. Thus of the 3.2 groups / 100 C atoms for Rawhide 2.2 are carboxylic acid and 1.0 is ester. For Pittsburgh this gives 0.5 -COOH groups / 100 C atoms and for Texas lignite 2.1 -COOH groups / 100 C atoms. This interpretation of course assumes the ester functional group does not decompose as CO\(_2\).
<table>
<thead>
<tr>
<th>Functional Group</th>
<th>No. per 100 C atoms</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Illinois#6</td>
<td>Rawhide</td>
<td></td>
</tr>
<tr>
<td>Ether (-O-)</td>
<td>5.5</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>Hydroxyl (-OH)</td>
<td>4.5</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>Carboxylic acid or Ester</td>
<td>0.5</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>Total Oxygen</td>
<td>11.0</td>
<td>21.0</td>
<td></td>
</tr>
</tbody>
</table>
**CO Evolution**

All four coals exhibited two well defined maxima for evolution of CO. The first maxima occurred at ~650°C while the second occurred at ~1350°C. Similar studies\(^6,7,14\) have shown two maxima in this low temperature region, one around 420-547°C the second around 670-747°C. Several sources are attributed to CO production, mainly ether linkages, ketone groups (quinones), and heterocyclics. Fitzgerald and Van Krevelen\(^7\) suggest that CO produced below 497°C is from decomposition of ether linkages and carbonyl groups while that evolved above 497°C is from degradation of heterocyclic compounds. It is also proposed that CO could be formed from a secondary pyrolysis as in the Boudouard reaction:

\[
\text{CO}_2(\text{mineral decomposition}) + C(\text{s})(\text{char}) \rightarrow 2\text{CO} \quad T > 727°C.
\]

Taylor and Bowen\(^24\) investigated the kinetics for CO\(_2\) reaction with char (627-777°C) and reported an appreciable rate for this reaction at high temperatures. This was perhaps one source of CO at the observed temperature maxima around 1350°C and this is supported by the absence of CO\(_2\) at these temperatures. Attar has proposed that CO, CO\(_2\), and H\(_2\)O may react with other gaseous species in secondary pyrolysis reactions such as the water shift reaction:

\[
\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}.\]

Both CO and H\(_2\)O are formed at temperatures > 900°C whereas CO\(_2\) is not in appreciable amounts. Also Campbell has reported presence of H\(_2\) at temperatures > 600°C.\(^6\) Though these sources may contribute to high temperature CO, another source seems to be the reduction of metal oxides by the remaining char. Matrix-isolated FTIR spectra showed that the evolution of SiO, Al\(_2\)O, and Al-CO complexes (pyrolysis and reduction products of kaolinite)
appeared to be closely coupled to high temperature CO evolution. These observations suggest reduction of the metal oxides could be an important source of CO at higher temperatures.

Table IV shows evolution of CO and how it relates to the number of ether functional groups in two coals. The only ratio corresponding to the ether functional group ratio was the low temperature CO weight implying the predominant source of CO below 900°C was decomposition of ether functional groups. If all the CO produced at the lower temperatures (<900°C) were coming from ethers then an approximation for the number of ether functional groups in original coal can be made. From Table III Illinois#6 contains 5.5 ether groups / 100 C atoms and from Table II produces 4.52 mg CO giving a ratio of 0.823 mg CO per ether functional group/ 100°C. Rawhide shows a ratio of 0.828 mg CO per ether functional group/ 100°C. Using the average ratio, the number of ether functional groups for Texas Lignite is 9.13 and for Pittsburgh bituminous is 4.28. This estimation of ether groups of course is based on the assumption that the amount of carbonyls is negligible compared to ether groups. Attar has noted that the quantity of carbonyls in raw coals is small compared to ether oxygen.14

H2O Evolution

The rate of evolution of water during coal pyrolysis needed to be studied according to Attar14. What was known about the source of water during pyrolysis was that it initially came from physically drying the coal at temperatures around 100°C. It was generally believed that the next source of water was the decomposition of thermally unstable hydroxyls at temperatures around 380-450°C1,14. For all coals studied except the lowest rank lignite, water peaked at a range of 330-420°C. Lignites having larger oxygen content were found to release more water, CO, and CO2 especially at lower temperature.1 This explains the evolution of water from lignites over the range
Table IV
Carbon Monoxide Evolution

<table>
<thead>
<tr>
<th></th>
<th>Rawhide</th>
<th>Illinois#6</th>
<th>Raw/Ill#6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ether$^{23}$</td>
<td>9.8/100 C</td>
<td>5.5/100 C</td>
<td>1.78</td>
</tr>
<tr>
<td>CO Total Wt.</td>
<td>13.18 mg</td>
<td>11.76 mg</td>
<td>1.12</td>
</tr>
<tr>
<td>CO (&lt;900°C)</td>
<td>8.11 mg</td>
<td>4.52 mg</td>
<td>1.79</td>
</tr>
<tr>
<td>CO (&gt;900°C)</td>
<td>5.07 mg</td>
<td>7.24 mg</td>
<td>0.70</td>
</tr>
</tbody>
</table>
169-404°C. Attar suggested that the water evolving at these temperatures constituted the major portion of the coal oxygen.\textsuperscript{14} Table V shows a comparison of the amount of water released during pyrolysis with the number of hydroxyl groups per 100 carbon atoms for two of these coals. From the Table, the total weight of water evolved during pyrolysis decreased significantly on going from low rank to high rank coals as expected with decreasing oxygen content.\textsuperscript{1} The most marked increase is noted at the lower temperatures or at a sufficient temperature for thermal decomposition of hydroxyls. As Levine found the number of hydroxyls for Rawhide and Illinois\#6 to be approximately the same, one might expect the amount of water to be similar too. Yet that was not the case; in fact Rawhide yielded 1.5 times more water than Illinois\#6. This ratio indicates that there are differing thermal stabilities for the hydroxyl groups known to be present in coals. Aliphatic hydroxyls have been reported in brown coals but Tingey and Morrey\textsuperscript{21} reported that fresh bituminous coals contain little aliphatic hydroxyls. From methylated coal work it was found that the relative amounts of hydroxyl groups(-COOH, R-OH, O-OH) differed for each coal. More specifically the higher ranked coals, Pittsburgh and Illinois\#6, contained far less aliphatic hydroxyl groups than phenolic. On the other hand the sub-bituminous coal, Rawhide and the brown coal Texas lignite contained only a few more phenolic than aliphatic hydroxyls. In addition, phenolic hydroxyls were shown to be thermally more stable than any of the other hydroxyls present as they were the only hydroxyls observed in the evolved tars. These observations lead one to consider the aliphatic hydroxyls as the source decomposing via water elimination reactions to form new ether cross linkages. Thus, the two lower ranked coals containing more aliphatic hydroxyls yielded more water than the higher ranked ones.
<table>
<thead>
<tr>
<th></th>
<th>Tx. Lig.</th>
<th>Rawhide</th>
<th>Illinois#6</th>
<th>Pittsburgh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxyl&lt;sup&gt;23&lt;/sup&gt;</td>
<td>4.8/100 C</td>
<td>4.5/100 C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water Total Wt. (mg)</td>
<td>3.12</td>
<td>2.49</td>
<td>1.54</td>
<td>1.34</td>
</tr>
<tr>
<td>Low Temp. Water (&lt;700°C)</td>
<td>2.27</td>
<td>1.74</td>
<td>1.16</td>
<td>0.98</td>
</tr>
<tr>
<td>High Temp. Water (&gt;700°C)</td>
<td>0.85</td>
<td>0.75</td>
<td>0.38</td>
<td>0.36</td>
</tr>
</tbody>
</table>
From Table V it is clear that the amount of water evolving at temperatures higher than 800°C was small and decreased with rank. Attar has noted that CO, CO₂, and H₂O can react with other gases¹⁴ and so a possible source for this water is secondary pyrolysis in which CO₂ is reduced by hydrogen yielding water and CO.²⁵ Campbell²⁶ has reported hydrogen evolution occurring over a wide temperature range, 600-1027°C. However, most of the water and CO evolve later than these temperatures. Not much work has been done on water evolution in the temperature range 950-1450°C and other possibilities exist. Decomposition of tightly bound etheric oxygen has been characterized by several groups.¹⁴,²⁷ The temperatures for this decomposition ranged from 450-700°C and the products were mainly CH₄, CO, with some H₂O, and H₂. Thus this does not explain the high temperature water observed. The source of this water is still not clear.

**Tar Evolution**

From slow pyrolysis of the four coals to 600°C, Figures 11, 12, 13, and 14, the tar was seen to evolve beginning at ~300°C and was completely finished by 600°C. Campbell also noted tar evolution between 247-547°C using a similar heating rate, 3.3K/min.⁶ Solomon et al. pyrolyzed coal and an ethylene polymer and found the major weight loss at 450-500°C for tar. His flash pyrolysis of this sample showed evolved tar to be similar in structure to the original starting material¹⁰ (Figure 15). This likeness between pyrolyzed tar and original coal was first noted by Orning and Greifer ³ and has also been shown by others.⁴,⁵ All of this seems to indicate that the evolved tar may be minimally disturbed fragments of the original coal matrix. Solomon has proposed from work on this polymer that the mechanism for tar evolution is linked to the breakage of weak methylene (-CH₂-CH₂-) bridges present in coal. Scission of this bond allows the heavy molecular weight tar to escape with little
Figure 11. Matrix-Isolation FTIR Spectra for Tar Evolution of Pittsburgh Bituminous
Figure 12. Matrix-Isolation FTIR Spectra for Tar

Evolution of Illinois #6 Bituminous
Figure 13. Matrix-Isolation FTIR Spectra for Tar

Evolution of Rawhide Sub-bituminous
Figure 14. Matrix-Isolation FTIR Spectra for Tar Evolution of Texas Lignite
Figure 15. Comparison of FTIR Spectra of Various Tars and Their Coals
change in structure.

Total amounts of tar for each coal were obtained from the room temperature quartz crystal studies as described earlier. The highest reading in KÅ was converted to a weight in mg using the conversion factor $5.4 \times 10^{-1}$ mg/KÅ. The calculated weight percents of room temperature condensable tar for each coal were as follows: Pittsburgh had a value of 13% tar by weight, Illinois #6 yielded 9.6%, Rawhide yielded 4.3%, and Texas Lignite yielded 7.2%. The values for Pittsburgh and Illinois #6 can be compared to those reported by Khan, specifically, 17.7% and 11% respectively. From experimental results it is concluded that tar evolution is greater for high rank coals than low rank coals.

Sulfur

Sulfur dioxide was seen to evolve along with the tar but maximized at a slightly higher temperature of 550°C. Attar and Corcoran suggested some of the inorganic sulfur is present in the original coal as sulfates (Fe, Ba and Ca). Paris has observed that weathered coals may contain more sulfates due to oxidation of the pyrite. The observance of SO$_2$ in the FTIR spectra suggests these sulfates as probable sources. Pittsburgh evolved the most SO$_2$ followed by Illinois #6 with the two lower ranked coals showing only traces. A similar evolution was noted for hydrogen sulfide and carbonyl sulfide from 300-500°C. Campbell has reported organic sulfides evolved between similar temperatures, 297-497°C. He noted that in this temperature range the sulfur : carbon ratio in the char decreased implying that organic sulfur was preferentially released with the tar phase. Attar et al. attributed the source of H$_2$S to thiols as they readily decompose to H$_2$S at temperatures of 350-450°C. These temperatures correspond to the observed evolution of H$_2$S for the four coals studied. Carbonyl sulfide was thought by Attar to be the product of a secondary reaction of H$_2$S with CO$_2$. Tabulated results of the weight (mg) of sulfur in the evolved
products (from Table II) compared to the weight of sulfur (mg) in the original coal (Table I) can be found in Table VI. Weight of sulfur in H₂S did not correspond exactly to the weight of organic sulfur, which implies organic sulfur was released in other forms. As discussed above H₂S may be producing COS thereby accounting for some of this difference.

Braye et al. have noted the sulfur in coal tars to be mainly thiophenic and because of their extreme thermal stability, they may evolve undisturbed in tar. This could account, in part, for loss of organic sulfur. These authors also noted that the added presence of FeS₂ caused this thiophenic concentration in the tar to decrease. Given and Jones indicated that reduction of pyrites during pyrolysis occurred around 550-650°C. Since evolution of CS₂ occurred at much higher temperatures, around 800-1200°C, the CS₂ was not believed to be coming directly from decomposition of pyrites. Rather the reduction of pyrites influenced the relative distribution of thiophenic structures in tar. Further evidence was given by Solomon who stated that CS₂ was released from thiophenes upon breakage and rearrangement of the aromatic ring structure. Indeed Illinois#6 produced the most CS₂ and contained the greatest amount of pyrites followed by Pittsburgh and the two lower ranking coals. However the amount of CS₂ was very small (< 0.04 mg S) and did not account for the difference between organic sulfur and sulfur products. Perhaps any other organic sulfur present remained in the char as aliphatic or aryl sulfides and thiophenes.

Pittsburgh has the smallest residual weight of sulfur (0.03mg) of all the coals, implying few thiophenic groups in original coal. Attar and Hendrickson also observed a small thiophenic sulfur content for a Pittsburgh coal.
<table>
<thead>
<tr>
<th></th>
<th>Texas Lignite</th>
<th>Rawhide Sub-bituminous</th>
<th>Illinois #6 Bituminous</th>
<th>Pittsburgh Bituminous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight of S (CS₂)</td>
<td>0.01</td>
<td>0.01</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>Weight of S (H₂S)</td>
<td>0.12</td>
<td>0.10</td>
<td>0.58</td>
<td>0.44</td>
</tr>
<tr>
<td>Weight of organic S</td>
<td>0.28</td>
<td>0.28</td>
<td>0.84</td>
<td>0.49</td>
</tr>
<tr>
<td>Weight of S (FeS₂)</td>
<td>0.01</td>
<td>&lt; 0.01</td>
<td>0.36</td>
<td>0.21</td>
</tr>
<tr>
<td>Weight of organic S - weight of S(H₂S)</td>
<td>0.16</td>
<td>0.18</td>
<td>0.26</td>
<td>0.05</td>
</tr>
</tbody>
</table>
**Nitrogen Evolution**

Nitrogen containing products observed during pyrolysis were NH$_3$ around 300-700°C and HCN around 350-800°C with traces up to 1200°C. Not much seems to be known about nitrogen in coal. Pohl and Sarofim proposed that the nitrogen in coal was in heterocyclic rings (pyridines and pyrroles) with perhaps small amounts of nitrogen in side groups.\(^{33}\) Denitrogenation proceeds slower than desulfurization and so requires more hydrogen. Removal of nitrogen from amines, amides, and nitriles proceeds faster than removal of nitrogen from pyridines and quinoline.\(^{14}\) Campbell noted the preferential retention of nitrogen in char at low temperatures and its concentration in char decreased only slightly with evolution of HCN and NH$_3$.\(^{6}\) Table VII shows a comparison of HCN evolution for the four coals. Pittsburgh and Texas lignite evolved less HCN than the Illinois #6 for comparable nitrogen wt %. This could mean greater retention of nitrogen in char for Pittsburgh and Texas Lignite. It is also possible that this lower production of HCN was due to a smaller amount of ring nitrogen in Pittsburgh and Texas Lignite; Solomon\(^{10}\) has suggested HCN is produced upon breakage and rearrangement of aromatic rings. The possibility that there was a greater amount of nitrogen containing side groups in the coals decomposing to NH$_3$\(^{34}\) cannot be ignored. Extinction coefficient studies could make a contribution to the study of nitrogen.

**Evolution of other species >900°C**

Other species identified were acetylene (C$_2$H$_2$) and products related to the pyrolysis and reduction of kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$). Acetylene evolved around 950-1400°C and kaolinite reduction occurred around 1150-1500°C. The high temperature gas species from kaolinite reduction and pyrolysis are SiO, Al$_2$O, and aluminum atoms which were detected by complexation with CO.\(^{17,35}\)
<table>
<thead>
<tr>
<th></th>
<th>Texas Lignite</th>
<th>Rawhide Sub-bituminous</th>
<th>Illinois #6 Bituminous</th>
<th>Pittsburgh Bituminous</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCN peak area</td>
<td>0.84</td>
<td>0.78</td>
<td>1.30</td>
<td>0.95</td>
</tr>
<tr>
<td>Nitrogen wt %</td>
<td>1.06</td>
<td>0.82</td>
<td>1.18</td>
<td>1.28</td>
</tr>
<tr>
<td>Peak area / wt%</td>
<td>0.79</td>
<td>0.95</td>
<td>1.10</td>
<td>0.74</td>
</tr>
</tbody>
</table>
1.4 Summary

Devolatilization of coal initially yielded small carbonyl compounds below 250°C as well as H₂O, CO₂, and CO with tar evolution around 300-600°C. Water below about 700°C was from decomposition of hydroxyl groups in coal other than phenolic. The source of water above 700°C is not yet identified although reduction of kaolinite(Al₂Si₂O₅(OH)₄) or other inorganic hydroxides may produce this water. Carbon dioxide was mainly from carboxylic functional group degradations though possibly small amounts were from reduction of inorganic carbonates in coal. Through quantitative analyses of FTIR spectra, it has been shown that Pittsburgh and Illinois#6 have 0.5 (-COOH) functional groups/100 C atoms; Rawhide has 2.2 (-COOH) functional groups/100 C atoms, 1.0 ester functional groups/100 C atoms; and Texas lignite has 2.1 (-COOH) functional group/100 C atoms. This establishes the general trend for lower ranked coals to contain greater amounts of carboxyl functional groups.

Two distinct sources were observed for carbon monoxide. The first was from ether functional groups (<900°C) and a second source (>900°C) was probably due to secondary pyrolysis reactions, specifically reduction of metal oxides by the remaining char. Quantitative analyses of FTIR spectra yielded 0.826 mg of CO per ether functional groups/100 C atom which showed Texas lignite to contain 9.13 ether functional groups/100 C atoms and Pittsburgh bituminous to contain 4.28 ether functional groups/100 C atoms. Light weight hydrocarbons, C₂H₄, C₃H₆, C₂H₆, and CH₄ were related in evolution at low temperatures as they were produced from the dealkylation of the coal. Methane however appeared different in that it reached maximum amounts at slightly higher temperatures, possibly indicating a second source in addition to dealkylation.

Organic sulfur was initially released with the tar fraction predominately as H₂S and at higher temperatures (800-1200°C) as CS₂, presumably from
thiophenic groups. Nitrogen products identified were ammonia, NH₃ and hydrocyanic acid, HCN. Ammonia was probably from side groups such as alkyl amines and amides. Hydrocyanic acid is probably from ring nitrogen degradation. At temperatures above 900°C the major products were acetylene along with the pyrolysis and reduction species from kaolinite: SiO, Al₂O, and aluminum atoms.
REFERENCES


2.1 Introduction

The objective of this investigation was to study the hydroxyl functional groups of those molecules involved in the mechanism of tar evolution during coal pyrolysis processes. Strong similarities exist between the infrared spectra of coals and their respective tars suggesting that the tar molecules are similar in structure to the parent coal\textsuperscript{1,2} and contain similar functional groups characteristic of the parent coal. Clarification of the structure of tar molecules should lead to a better understanding of the parent coal structure. This chapter is centered on the identification and characterization of tar hydroxyl functional groups.

Hydroxyl functional group determination in coals has been undertaken both spectroscopically as well as through a combination of chemical and spectroscopic means. One spectroscopic method of hydroxyl determination relied on the measurement of the broad hydroxyl absorption region between 3600-2000 cm\textsuperscript{-1}(3). This broad absorption range was complicated by the presence of KBr/water absorptions as well as absorptions attributed to hydrogen-bonded hydroxyl groups. A second method of hydroxyl functional group determination involved the measurement of intensities of infrared bands (carbonyl stretching at 1770 and 1740 cm\textsuperscript{-1}) assigned to products of acetylation reactions of coal\textsuperscript{4}. Both methods involved indirect determination of hydroxyl functional groups in the parent coal matrix. Studies of coal pyrolysis processes using matrix-isolation techniques have the advantage of physically isolating the individual tar molecules and other gaseous products in an inert matrix. The matrix-isolated tar should be free of hydrogen bonding thus facilitating the identification of hydroxyl functional groups.

2.2 Experimental

The experiments were designed so that tar molecules and other gaseous
products of coal pyrolysis could exit the reaction zone rapidly and be trapped with inert nitrogen gas on a cold matrix surface. Matrix-isolation studies of tar molecules produce better resolved FTIR spectra than those in a coal matrix, making structural characterization of the tar molecules a more definite possibility. The coals were pyrolyzed in the same manner as previously described with the exception that one matrix surface was used for every 40-100°C incremental rise in temperature over a 10 minute period, i.e., a heating rate of 4-10°C/minute. Tar evolution was observed within the same temperature range (150-600°C) for the four coals studied, the actual experimental temperature range studied was from room temperature to approximately 620°C. Between 70 and 80 mg of each coal was used for pyrolysis. This amount of coal was chosen because it yielded more intense tar absorptions facilitating spectral analysis.

Pure compounds containing various kinds of hydroxyl groups were also isolated in a nitrogen matrix at 15K. This aided characterization of the tar-OH species found to survive the vaporization process. The concentrations of these species are given below: 0.0373% Benzoic acid/ N2, 0.00513% Phenol/N2, and 0.0173% 2-Naphthol/N2.

2.3 Results and Discussion

Isolation of the individual tar molecules in an inert gas matrix at 15K produced better resolved infrared spectra than have been observed in the FTIR spectra of tars in a coal matrix, thus making structural characterization of the tar molecules highly feasible. FTIR spectra for pyrolysis of Pittsburgh Bituminous can be found in Figure I and those spectra for the remaining coals in the Appendix. The evolution of tar molecules began at temperatures as low as 130°C and continued until maximum evolution was reached at 400-470°C. Absorptions characteristic of high molecular-weight hydrocarbon (tar)
Figure 1. MI-FTIR Spectra of Pittsburgh Bituminous
molecules are broad bands at 3000-2800 cm\(^{-1}\) due to CH stretching and bands at 1550-1100 cm\(^{-1}\). The region from 1550 to 1450 cm\(^{-1}\) is thought by Painter\(^8\) to be due to aromatic ring stretching and deformation modes. Assignments in this region can also be made by analogy to aromatic ring compounds such as benzene and naphthalene which exhibit strong absorptions at 1486 cm\(^{-1}\) and 1514 cm\(^{-1}\) respectively, due to ring stretch and deformation modes. Comparing this region of the matrix-isolated tar spectra for the four coals in Figure 2, one observes a strong broad absorbance (1530-1430 cm\(^{-1}\)) for higher ranked coals indicative of greater aromaticity. Absorbances in the C=O stretching region (1700-1800 cm\(^{-1}\)) are most intense for the lower ranked coals and are due in part to esters which are found predominately in lower ranked coals.\(^9\)

The hydroxyl stretching region of the matrix-isolated tar spectra also contains information concerning the hydroxyl functional groups present in the tar molecules; however, we have found that the presence of water OH stretching modes and absorptions due to water-tar complexes in this region complicate the reliable identification of tar hydroxyl functional groups. In order to eliminate this possible source of confusion we have studied the effect of adding water. Co-deposition of water (0.5 H\(_2\)O/100 N\(_2\)) with tar molecules resulted in noticeable increases in absorptions due to water-tar complexes. Figure 3 compares the matrix-isolated FTIR spectra of Illinois #6 tar molecules with the results obtained from tar-water co-deposition experiments. As can be seen, two distinct broad absorptions at 3626.5 and 3580.9 cm\(^{-1}\) remained unaffected by the addition of water molecules. These have been assigned to hydroxyl functional groups present in the tar. The hydroxyl stretching frequencies for all four of the coal tar molecules studied are shown in Figure 4. Considerable amounts of these hydroxyl functional groups were found in the tars of the two higher rank coals, Pittsburgh bituminous and Illinois #6, with Illinois #6
Figure 2. MI-FTIR Spectra of Four Coals Below 1900 cm\(^{-1}\)
Figure 4. MI-FTIR Spectra of Four Coal Tars
possessing the greater amount. Considerably less hydroxyl absorption was observed for the two lower rank coal tars, Rawhide subbituminous and Texas lignite. This observation suggests that these hydroxyls are phenolic in character since lower rank coals possess less aromatic character than higher rank coals but are known to contain significant hydroxyl group concentrations prior to vaporization. Another explanation for why the low ranked coals have fewer tar hydroxyls is evidenced through depolymerization studies of Solomon and Squire. They observed that lower rank and subbituminous coals undergo more crosslinking than do the higher ranking coals and so release a lower molecular weight tar fraction. Aliphatic and carboxylic hydroxyls are thought to play a major role in crosslinking mechanisms via water elimination reactions. These reactions reduce the number of hydroxyl functionalities present in coal tars by formation of new ether crosslinkages. As low rank coals are thought to contain many of these hydroxyl groups the tars for Texas lignite and Rawhide subbituminous would thus contain less hydroxyl groups in vaporized tars as has been observed.

The C-O stretching region at 1100-1200 cm\(^{-1}\) shows absorbances due to the complementary C-O stretching of the phenolic hydroxyl groups discussed above. Indeed comparing the C-O stretching regions in Figure 2, Illinois #6 is seen to have the largest absorbance followed by Pittsburgh with Rawhide and Texas lignite showing very low absorbance in this region.

Comparison of hydroxyl stretching frequencies of phenol, 2-naphthol, cyclohexanol and benzoic acid in a nitrogen matrix with those of matrix-isolated tar is shown in Figure 5. The broad tar hydroxyl absorption at 3626.5 cm\(^{-1}\) compares favourably with the hydroxyl stretching frequencies of phenol and 2-naphthol but not with cyclohexanol or benzoic acid. In general, the less acidic alcoholic hydroxyls have O-H absorptions at frequencies higher than 3630
Figure 5. Comparison of Hydroxyl Stretching Frequencies in N\textsubscript{2} Matrix
cm$^{-1}$. For example the hydroxyl stretching frequency of nitrogen matrix-isolated methanol is 3664 cm$^{-1}$. The peak at 3626.5 cm$^{-1}$ observed for the matrix-isolated tar is thus assigned to a phenolic hydroxyl. No alcoholic hydroxyls are detected in matrix-isolated tar molecules, although others of this group could be masked underneath the H$_2$O absorptions themselves.

The less intense tar hydroxyl absorption at 3580.9 cm$^{-1}$ is clearly less acidic than benzoic acid (3560-3540 cm$^{-1}$); therefore, its acidity is between that of phenol and benzoic acid. At this point further statements concerning the environment of this hydroxyl functionality cannot be made other than its being phenol related.

2.4 Conclusion

Two distinct hydroxyl functional groups in the tar molecules free of hydrogen bonding were identified for the first time without interference from H$_2$O absorptions. Some are thermally stable and they survive the vaporization process. The absorptions at 3626.5 and 3580.9 cm$^{-1}$ have been assigned to phenolic hydroxyls but the specific manner of bonding in this latter type of hydroxyl can only be approximated at this time. Tars from Illinois #6 were found to contain the largest amount of phenolic hydroxyl; Pittsburgh #8 tar contained approximately half of that for Illinois #6; while Rawhide and Texas lignite contained much less phenolic than either of the other coals. This study suggests that carboxylic and aliphatic hydroxyl groups do not survive the vaporization process; however, the possibility that other hydroxyl groups go undetected due to overlap with H$_2$O absorbances cannot be ignored.
REFERENCES


3.1 Introduction

This chapter describes an investigation of the types of hydroxyl groups present in coal and the roles that they play in tar evolution mechanisms. The study was carried out by comparing the results of pyrolysis studies of O-methylated coals with those of the original coal. Methylation replaces all of the hydrogens in phenolic, alcoholic and carboxylic hydroxyl groups in coal with methyl groups,\(^1\)-\(^3\) thus eliminating all hydrogen bonding through these hydroxyl functional groups.

The role of hydroxyl functional groups in the mechanism of tar evolution is of great interest. Hydrogen bonding through the hydroxyl functional groups has been thought of as an important intermolecular bond in the coal structure.\(^3\) If hydrogen bonding through the hydroxyl functional groups is a predominant factor in determining the volatilities of coals (as determined by the ease of tar evolution and percent weight loss), then it is expected that replacing the hydroxyl hydrogens with methyl groups will make the coals more volatile. Hydroxyl functional groups may also play another role in reducing the coal volatility since adjacent hydroxyl groups can also undergo water elimination reactions to form new ether (C-O-C) cross linkages during pyrolysis. Methylation of the coal hydroxyl functional groups may prevent the formation of these new cross linkages, causing an increase in the volatility of the coal. If the evolution of tar during thermal decomposition of the coal occurs primarily through the cleavage of weak linkages such as methylene linkages, then methylation would be expected to have little effect on the volatility of the coal or the amount of tars and oils which are volatilized.

3.2 Experimental

From previous studies of coal pyrolysis processes, tar evolution was observed to occur within the temperature range of 150-600°C for the four coals
studied. Therefore, in order to determine the effect of O-methylation on the pyrolysis process, the experimental temperature was kept in the same range as that of the reference unmethylated coal, i.e., from room temperature to approximately 620°C. One matrix surface was used for every 40-100°C increase in temperature over a 10 min. trapping period, corresponding to a heating rate of 5-10°C min⁻¹. All other experimental procedures for the pyrolysis of the methylated coals were identical to those of the original coal in order to determine the effect of methylation on the original coal.

Methylations of the coal samples were performed according to the procedures of R. Liotta et al.³ Usually sample weights of approximately 0.2g were used in the preparation. The reaction was carried out under nitrogen at room temperature (RT) and ambient pressures. To a 100 mL flask containing the coal, a 3-fold excess (based on moles of organic oxygen calculated from the coal's elemental analysis) of tetra-butylammonium hydroxide was added. Then 10 mL of tetrahydrofuran dried over sodium benzophenone was syringed into the flask and this mixture stirred under nitrogen for two hours. The reaction is shown below:

\[ \text{coal-OH} + R_4\text{NOH} \rightarrow \text{coal-ONR}_4 + \text{HOH} \]

At this time a 5-fold excess (determined by amount of base added) of methyl iodide was introduced and the reaction was left stirring overnight.

\[ \text{coal-ONR}_4 + \text{CH}_3\text{I} \rightarrow \text{coal-OCH}_3 + R_4\text{NI} \]

If the solution was found to be slightly basic, 0.1M HCL was added until the pH was 7. Next a 3-fold excess of sodium nitrate was added to increase the solubility of tetrabutylammonium salts.

\[ R_4\text{NI} + \text{NaNO}_3 \rightarrow R_4\text{NNO}_3 + \text{NaI} \]

THF and other volatiles left over after reaction were removed from the solution by rotary evaporation at 70°C for 30 minutes. The coal was then transferred to
a Büchner funnel using five 20 mL washings of deionized water (100°C) and then transferred to a Soxhlet extractor. Water was used to extract the salts from the desired methylated product. Silver nitrate was used as a test indicator for complete removal of these water soluble salts. Generally no precipitate was found after 5 to 6 days of washing at a rate of about 9 extractions per hour. To prevent loss of low temperature volatiles, the samples were vacuum dried for 5-7 days at room temperature without heating in order to remove excess water. FTIR spectra of each methylated coal were obtained as KBr pellets. For Rawhide and Illinois #6 the spectra compared well to those reported by Liotta, confirming that methylation was complete. KBr spectra of Texas Lignite and methylated Texas Lignite are shown in Figure 1. Water absorption bands have been greatly reduced and growth of the 1700cm⁻¹ peak indicates methylation. Although care was taken to keep KBr pellets dry during their preparation, it is possible that some of this residual H₂O absorption in the methylated coal is due to this type of contamination. Isotopically labeled methyl iodides such as CD₃I and ¹³CH₃I as well as unlabelled CH₃I have been used in the methylation reactions to facilitate FTIR interpretation of the results. Only the -500 mesh coal particles were used in the methylation reactions.

Room temperature quartz crystal microbalance studies were carried out on all coal samples before and after methylation in an attempt to measure the effect of methylation on the condensable tar yield. The coal was pyrolyzed in the same manner as previously stated except that condensable volatiles were collected on the room temperature (RT) crystal rather than on discrete matrix surfaces. The only condensable products at RT were the high molecular weight tar molecules and other gaseous products were pumped away. The conversion factor, 5.4 mg/KÅ, is used as the standard for calibration of geometric factors.
Figure 1. FTIR Spectra of Methylated Texas Lignite (Top) and Texas Lignite (Bottom) in KBr
3.3 Results and Discussion

**Determination of Tar Evolution Mechanism**

Slow pyrolysis studies of methylated coals were performed to determine if O-methylation in any way altered the pyrolysis behavior of the original coal. Figure 2 shows the matrix-isolated FTIR spectra of the pyrolysis products of methylated Pittsburgh bituminous from RT to 612°C and similar spectra for the other coals can be found in the Appendix. Comparison of pyrolysis results of the methylated coal with those of the original coal showed several differences indicative of coal structural changes after methylation. Phenolic hydroxyl absorptions at 3627 cm⁻¹ and 3581 cm⁻¹ were essentially absent in the matrix-isolated tar spectra for the methylated coal. Significant increases in evolution of a low temperature fraction at 150-300°C were evident for the methylated coals other than Pittsburgh Bituminous. Increases in total coal weight loss after methylation can be found in Table I. These values for each coal were obtained by taking the difference in weight before and after pyrolysis divided by the weight before pyrolysis and multiplied by 100. All of the coals showed an increase in weight loss after methylation. This effect was greater for the higher ranked coals. We attribute the major portion of this weight loss to the methylation process which is removing the inorganic components of the coal.

The total amounts of tar deposited from RT-624 °C for each coal are given in Table II. A graph showing total tar evolution for Texas Lignite and methylated Texas Lignite can be seen in Figure 3 and similar plots for the other coals are located in the Appendix. The values in column 3 of Table II for Illinois #6 and Rawhide correspond to an upper limit contribution to tar weight for the added CH₃ groups which replaced the hydrogen in each hydroxyl group. This assumes all types of hydroxyl groups survived the volatilization process. These values represent an upper limit since our results show that not all hydroxyls
Figure 2. MI-FTIR Spectra of Methylated Pittsburgh Bituminous Coal
<table>
<thead>
<tr>
<th></th>
<th>Texas Lignite</th>
<th>Rawhide Sub-bituminous</th>
<th>Illinois #6 Bituminous</th>
<th>Pittsburgh Bituminous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylated Coal</td>
<td>58.9</td>
<td>51.8</td>
<td>56.0</td>
<td>55.9</td>
</tr>
<tr>
<td>Original Coal</td>
<td>47.2</td>
<td>37.9</td>
<td>37.5</td>
<td>37.1</td>
</tr>
<tr>
<td>Difference</td>
<td>11.7</td>
<td>13.9</td>
<td>18.5</td>
<td>18.8</td>
</tr>
<tr>
<td>Sample Type</td>
<td>Tar (mg)</td>
<td>Calculated Wt % Increase in Tar Yield</td>
<td>Calculated Maximum Expected Wt % Increase from Added Wt of CH₃ Group</td>
<td></td>
</tr>
<tr>
<td>-----------------------------</td>
<td>---------</td>
<td>--------------------------------------</td>
<td>---------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Methylated Pittsburgh</td>
<td>5.401</td>
<td>0.0</td>
<td>5.4 (3)</td>
<td></td>
</tr>
<tr>
<td>Pittsburgh Bituminous</td>
<td>5.634</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methylated Illinois #6</td>
<td>4.067</td>
<td>0.5</td>
<td>5.4 (3)</td>
<td></td>
</tr>
<tr>
<td>Illinois #6 Bituminous</td>
<td>4.045</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methylated Rawhide</td>
<td>2.781</td>
<td>62.1</td>
<td>8.4 (3)</td>
<td></td>
</tr>
<tr>
<td>Rawhide Sub-bituminous</td>
<td>1.716</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methylated Texas Lignite</td>
<td>3.539</td>
<td>31.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Texas Lignite</td>
<td>2.691</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 3. Tar Evolution Measured as a Function of Temperature
survive pyrolysis. Clearly Pittsburgh and Illinois #6 can be seen to have undergone essentially no increased yields of high molecular weight tar. Thus for these high rank coals while the overall coal is more volatile after methylation the percent increase in tar yield after methylation is not appreciable. This same observation is noted by Rose et al. for their pyrolysis work with Illinois #6 O-alkylated, O-benzylated, and C-benzylated samples\textsuperscript{6}. However, for both low rank coals, Texas lignite and Rawhide Sub-bituminous, the increase in tar yield is found to be well above that calculated for added weight of methyl groups, thus for the low ranked coals the tars were indeed more volatile after methylation.

Comparisons of the tar evolution behavior of the unmethylated coal with the respective methylated coals are shown in Figures 4-7 for the four coals. The figures show the C-H stretching region of the matrix-isolated tars from room temperature to approximately 600°C and that of the matrix-isolated methylated (CD\textsubscript{3}) tars in the same temperature range. Results of isotopically labeled -OCD\textsubscript{3} methylated coals were used for comparison with those of the original coal rather than the results of the regular -OCH\textsubscript{3} methylated coals. Since C-D stretching absorptions occur at much lower frequencies (~2200 cm\textsuperscript{-1}) than the C-H stretching absorptions, the use of -OCD\textsubscript{3} methylated coal will prevent CH\textsubscript{3} groups present in the tar as a result of methylation from interfering in the interpretation of the spectra. Thus any variations in the C-H stretching absorptions observed in Figures 4-7 can be attributed directly to changes in the tar evolution behavior as a result of methylation.

Noticeable differences in the matrix-isolated tar spectra between the methylated and unmethylated coals were observed for all coals except Pittsburgh (Figure 4). For the unmethylated coals, a low temperature fraction was observed from ~150-300°C; however, these absorptions were very weak.
Figure 4. Comparison of Matrix-Isolated FTIR Spectra of Tars
Figure 5. Comparison of Matrix-Isolated FTIR Spectra of Tars
Figure 6. Comparison of Matrix-Isolated FTIR Spectra of Tars
Figure 7. Comparison of Matrix-Isolated FTIR Spectra of Tars
After methylation, this fraction exhibited a marked increase in absorption for Illinois #6, Rawhide, and Texas Lignite. For the original unmethylated coal, the tar was evolved at higher temperatures from ~350-500°C.

In Figure 3 the quartz crystal data for evolution of tar from RT-624°C for Texas Lignite and methylated Texas Lignite are shown. It is interesting to note that although FTIR data indicated an increase in light oils in the 150-300°C range after methylation, the crystal data showed no significant difference in tar evolution until after this temperature range. One assumes that this low temperature fraction was too volatile and could not be condensed at room temperature. Thus, while there were clearly increased low temperature yields of lighter oils after methylation, their weight percent has not been determined.

The increased yields of a low temperature fraction for O-methylated coals suggested that something was inhibiting their evolution in coal. A likely mechanism which would lead to fixation of volatiles in the coal char is as follows. If favorable geometry exists for a water elimination reaction, i.e., if two hydroxyl groups are adjacent, then new ether cross linkages can be formed which inhibit low temperature tar evolution by the following mechanism:

```
Coal — O
\ H
\ O—Coal —> H2O + coal-O-coal
\ H
```

The methylation process has apparently eliminated this trapping mechanism since no evolution of methyl ether (the water analogue) was observed.

From the above discussion one sees that water evolution plays a major role
in cross linking mechanisms. Water evolution for original and methylated coals are compared in Table III in order to see if any relationship between the two can be determined. One expects a decrease in water evolution upon methylation which is the case for all coals except Pittsburgh; however, this difference in evolution is not likely to be due to reduced cross linkage alone. Water evolution should also decrease after methylation due to new species such as methanol which would be evolved in place of water. Methanol evolution was indeed found to be significant. Methanol evolution was highest for Texas Lignite followed by Rawhide, Illinois, and Pittsburgh in that order, and so water evolution was not found to be a reliable indicator of the extent of cross linking.

Tar evolution at higher temperatures remained unaffected by methylation for Pittsburgh and Illinois #6. It is reasonable to assume that cleavage of weak linkages such as bridging methylenes would be involved in the high temperature tar evolution mechanism and their behavior would not be affected by methylation. This has also been suggested by Solomon.7 Pyrolysis of a coal model compound8 which consists of naphthalenes with bridging methylene linkages showed evolution of tar molecules in the same temperature range as observed for the high temperature tar evolution of coal. However, for Texas Lignite and Rawhide a cross-linking mechanism was probably responsible for reduced yields of high molecular weight tars since methylation increased these yields for the two low-ranked coals.

Identification of Hydroxyl Functional Groups through Isotopically Labeled (CD$_3$)$_2$ Methylation Studies

Studies of organic oxygen functional groups in coal have shown the existence of three different types of hydroxyl functional groups,9 i.e., phenolic, carboxylic and alcoholic. Determinations of the phenolic, carboxylic and
### Table III

Total Water Evolution Calculated from Peak Integration of the 1615-1585 cm\(^{-1}\) Region

<table>
<thead>
<tr>
<th></th>
<th>Texas Lignite</th>
<th>Rawhide Sub-bituminous</th>
<th>Illinois #6 Bituminous</th>
<th>Pittsburgh Bituminous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylated Coal</td>
<td>25.11</td>
<td>18.88</td>
<td>14.52</td>
<td>17.20</td>
</tr>
<tr>
<td>Original Coal</td>
<td>32.65</td>
<td>24.95</td>
<td>16.68</td>
<td>13.39</td>
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</table>
alcoholic functional group contents in coal have been undertaken by various researchers either through spectroscopic or chemical means.\textsuperscript{9-11} We have been able to isolate and identify spectroscopically the three different types of hydroxyls in coal, by using isotopically labeled CD\textsubscript{3}I as the methylating reagent in our coal methylation studies. Figure 8 shows the KBr spectra of the four methylated coals using isotopically labeled CD\textsubscript{3}I as the methylating agent. Distinct C-D stretching absorptions were observed for the methylated coal in the 2300-2100 cm\textsuperscript{-1} region. C-D deformation modes as well as C-O stretching modes of the methylated coal were also observed in the 1150-1000 cm\textsuperscript{-1} region. Detailed plots of these regions for the four methylated coals are shown in Figure 9.

Study of the C-D degenerate stretching absorptions in Figure 9 showed a group of three overlapping absorptions, labeled (a), (b), and (c), with respective frequencies at 2251, 2217, and 2188 cm\textsuperscript{-1}. The high-ranked coals Pittsburgh bituminous and Illinois #6 exhibited more intense absorptions for peak (b) at 2217 cm\textsuperscript{-1} while peak (c) at 2188 cm\textsuperscript{-1} is almost non-existent. Since high-ranked coals are more aromatic in character, it is expected that they should contain more phenolic hydroxyls. Comparison of C-D frequencies with those of anisole-d\textsubscript{3} leads to the assignment of peak (b) at 2217 cm\textsuperscript{-1} to a methylated phenolic group, i.e., an aromatic-OCD\textsubscript{3} group in the methylated coal (ph-OCD\textsubscript{3}) (Table IV). This assignment also agrees with the thermal behavior of peak (b) which was shown to be more thermally stable than peaks (a) and (c) (Figure 10).

Information helpful in the identification of peaks (a), (b), and (c) was obtained through thermal decomposition studies of the methylated coal. KBr studies of thermally treated CD\textsubscript{3}-methylated Rawhide sub-bituminous coal from room temperature to 405°C were carried out. Rawhide sub-bituminous was chosen
Figure 8. Comparison of FTIR Spectra of Methylated (CD$_3$I) Coals in KBr
Figure 9. Comparison of the C-D Stretch and Deformation Region of the FTIR Spectra of Methylated (CD$_3$I) Coals in KBr:
(a) Coal-COO-CD$_3$; (b) Coal-Ø - OCD$_3$; (c) Coal-R-OCD$_3$
### Table IV
Comparison of C-D Absorption Frequencies (cm\(^{-1}\))

<table>
<thead>
<tr>
<th></th>
<th>(CH(_3)COOCD(_3))(^a)</th>
<th>(CH(_3)OCD(_3))(^a)</th>
<th>(C(_6)H(_5)OCD(_3))(^b)</th>
<th>Methylated Coal</th>
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</thead>
<tbody>
<tr>
<td><strong>CD(_3) d-stretch</strong></td>
<td>2288 M</td>
<td>2244 S</td>
<td>2255 M</td>
<td>2251 M -a</td>
</tr>
<tr>
<td></td>
<td>2263 M</td>
<td>2189 S</td>
<td>2217 S</td>
<td>2217 M -b</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2205</td>
<td>2188 M -c</td>
</tr>
<tr>
<td><strong>CD(_3) s-stretch</strong></td>
<td>2104 M</td>
<td>2058 S</td>
<td>2071 S</td>
<td>2125 M -a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2071 S</td>
<td>2071 S -b,c</td>
</tr>
<tr>
<td><strong>CD(_3) d-deformation</strong></td>
<td>1050 W</td>
<td>1061 M</td>
<td>1050 Sh</td>
<td>1087 S -a,c</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1062 W</td>
<td></td>
</tr>
<tr>
<td><strong>CD(_3) s-deformation</strong></td>
<td>1106 S</td>
<td>1111 S</td>
<td>1114 S</td>
<td>1104 S -b</td>
</tr>
<tr>
<td><strong>O-CD(_3) stretch</strong></td>
<td>1043 M</td>
<td>1156 VS</td>
<td>1004 M</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Coal-COO-CD\(_3\) ; \(^b\) Coal-Ø-OCDOCD\(_3\) ; \(^c\) Coal-R-OCD\(_3\)

\(^a\) Shimanouchi, Takehiko, 'Tables of Molecular Vibrational Frequencies Consolidated Volume I', p. 114.

Figure 10. FTIR Spectra of Methylated (CD₃) Rawhide in KBr

(a) Coal-COO-CD₃ ; (b) Coal-Ø - OCD₃ ; (c) Coal-R-OC₃₃
because it exhibited the most distinct group of peaks \((a), (b), \text{ and } (c)\) in the C-D degenerate stretching region. Figure 10 shows KBr subtraction spectra of the original Rawhide from thermally treated CD$_3$-methylated Rawhide sub-bituminous coal at various temperatures for the C-D stretching region of 2300-2000 cm$^{-1}$ and the C-D deformation and C-O stretching region of 1150-1000 cm$^{-1}$. Peaks (a) and (c) were observed to decompose first at temperatures as low as 254°C and thus can be assigned to the less stable methylated carboxylic and alcoholic groups. The more thermally stable form of methylated hydroxyl is observed to decompose at slightly higher temperatures from 327- 405°C and has been assigned to the methylated phenolic hydroxyl. Assignment of peaks (a) and (c) to the carboxylic and the aliphatic OH has also been made by comparing their C-D frequencies with analogous isotopically labeled compounds (Table IV). The C-D degenerate stretching frequency of CH$_3$COOCD$_3$ occurred at a higher frequency (2288 cm$^{-1}$) than the corresponding frequency for CH$_3$OCD$_3$ (2244 cm$^{-1}$) thus suggesting that the higher frequency of the methylated coal at 2251 cm$^{-1}$ can be assigned to methylated carboxylic groups while the lower frequency of 2188 cm$^{-1}$ was assigned to methylated alcoholic groups. Comparison of the KBr spectra of the four coals (Figure 9) showed that the low-ranked coals contain similar amounts of the three oxygen functional groups while the high-ranked coals contained mainly the phenolic functional group with some carboxylic but very little of the alcoholic functional group. Figure 8 shows a carbonyl absorption in the C=O stretching region of $\sim$1700 cm$^{-1}$ for the high-ranked coals. Its growth after methylation indicated formation of an ester group from a carboxylic group in the original coal. A possible explanation for this peak's absence in the original coal is that the carboxylic groups are chelated to ions such as calcium which were present in original coal but removed during methylation. A chelated carboxylic
group would not exhibit a C=O absorption but when converted to the ester would then show this group in the infrared.

Other assignments were made through similar methods of analyzing the thermal decomposition behavior of the C-D stretching region and comparing the C-D frequencies with analogous CD$_3$ compounds (Table IV) as follows. The weak symmetric C-D stretching absorption at 2125 cm$^{-1}$ has been assigned to the methylated carboxyl group. The strong symmetric stretching absorption at 2071 cm$^{-1}$ has been attributed jointly to the methylated phenolic and alcoholic groups. Assignments in the C-O stretching frequency region of 1150-1000 cm$^{-1}$ were complicated by strong C-D deformation modes in the same region. However, it is clear from our studies that the absorption at 1104 cm$^{-1}$ can be assigned to the methylated phenolic groups. This peak was shown to be more intense for the high-ranked coals and its thermal decomposition behavior also followed that of the corresponding C-D degenerate stretching frequency of 2217 cm$^{-1}$, i.e., absorptions at 1104 and 2217 cm$^{-1}$ decrease simultaneously starting from 327°C (Figure 10).

**Pyrolysis Mechanisms of the Methylated Hydroxyl Functional Groups**

The decomposition behavior of the phenolic, the carboxylic and the aliphatic hydroxyl functional groups during slow coal pyrolysis has been discussed. Methylation of the coal hydroxyl functional groups which replaces all of the hydroxyl hydrogens with methyl groups was expected to change the thermal decomposition behavior of the coals. The tar evolution behavior has already been observed to be quite different after methylation. Other changes in the pyrolysis behavior of the methylated coals have also been noted and can be attributed directly to methylation. One of the major products evolved from the pyrolysis of O-methylated coals was methanol. Figure 11 shows the total methanol peak area obtained from the pyrolysis of each of the four methylated
Figure 11. Comparison of Methanol Produced from Slow Pyrolysis of Methylated Coals: □ - Texas Lignite; Δ - Rawhide Sub-bituminous; O - Illinois #6 Bituminous; V - Pittsburgh Bituminous
coals. A direct correlation is found between the amount of methanol evolution and the coal rank. The low-ranked coals were found to have the greatest methanol evolution. This points to methylated carboxylic and aliphatic hydroxyl groups as the source of methanol evolution.

From pyrolysis of isotopically labeled $^{13}$CH$_3$-methylated Rawhide sub-bituminous coal, other products directly related to methylation were clearly discernable e.g. there was evolution of $^{13}$CO, $^{13}$CH$_2$O, and $^{13}$CH$_4$. However, no evidence for ph-CH$_3$ group (the phenolic hydroxyl analogue) was observed in the volatilized tar suggesting that this methoxy form is less stable than the hydroxyl form. Plots illustrating the temperature dependent evolution of these $^{13}$C labeled pyrolysis products are shown in Figures 12 and 13. The evolution of methanol and formaldehyde was found to be closely related. Figure 12 shows that the evolution of $^{13}$CH$_3$OH and $^{13}$CH$_2$O occurred simultaneously starting at the relatively low temperature of 163$^\circ$C, reaching a maximum evolution rate at 288-340$^\circ$C and disappearing at 428$^\circ$C. It thus appears that the same source was contributing to the evolution of methanol and formaldehyde. From KBr studies of isotopically labeled CD$_3$-methylated Rawhide, it has already been shown that peaks attributed to methylated carboxylic and aliphatic functional groups decomposed first at temperatures as low as 254$^\circ$C. This correlated well with the low temperature evolution of methanol and formaldehyde. Therefore methylated carboxylic and aliphatic groups have been assigned as the major source of methanol and formaldehyde whose evolution mechanism can be envisioned as dependent on the availability of labile hydrogens near the methylated sites.
Figure 12. MI-FTIR Spectra Showing Evolution of Carbon-13 Species for Methylated (13CH3) Rawhide Sub-bituminous
Figure 13. MI-FTIR Spectra Showing Evolution of Carbon-13 Species for Methylated ($^{13}$CH$_3$I) Rawhide Sub-bituminous
Proposed mechanisms are as follows:

1. *Methylated Carboxylic*

   A. Labile H available
      \[(\text{coal})-\text{COO} \cdot ^{13}\text{CH}_3 \rightarrow ^{13}\text{CH}_3\text{OH} + \text{CO} + \text{coal}\]

   B. No labile H available
      \[(\text{coal})-\text{COO} \cdot ^{13}\text{CH}_3 \rightarrow \text{H}_2 \cdot ^{13}\text{CO} + \text{CO} + \text{coal}\]

2. *Methylated Aliphatic Hydroxyl*

   A. Labile H available
      \[(\text{coal})-\text{R-O} \cdot ^{13}\text{CH}_3 \rightarrow ^{13}\text{CH}_3\text{OH} + \text{coal}\]

   B. No labile H available
      \[(\text{coal})-\text{R-O} \cdot ^{13}\text{CH}_3 \rightarrow \text{H}_2 \cdot ^{13}\text{CO} + (\text{coal})-\text{R-H}\]

Formation of methanol is favored if labile hydrogen is available and formation of formaldehyde is favored if no labile hydrogen is available. It is, however, possible when evolution temperatures for methylated products (Figures 12 and 13) are closely compared to the dissappearance of carboxylic and aliphatic groups (Figure 10, peaks (a) and (c)), to suggest that these groups also contribute slightly to the production of methane and carbon monoxide.

Another mechanism for the decomposition of methylated carboxylic groups should also be considered. An increase in carbon dioxide evolution was noted in the pyrolysis products of the methylated coals. This increase could be a result of coal oxidation during the methylation process; however, considerable care was taken to prevent oxidation. It appears that methylation has promoted the formation of carbon dioxide. Since this must occur from the ester one is lead to suggest that the esters favor formation of CO$_2$ relative to the carboxylic or possibly the chelated carboxylic group in the original coal.

Evolution of methane and carbon monoxide was found to be closely related. Figure 13 illustrates the evolution of these two $^{13}$C labeled pyrolysis products,
$^{13}\text{CH}_4$ and $^{13}\text{CO}$. Evolution was shown to start at temperatures higher than that of methanol and formaldehyde. This raises the question as to whether methane and carbon monoxide could be derived from the secondary pyrolysis of methanol. Studies of Rawhide sub-bituminous coal pyrolysis with an added external source of $^{13}\text{CH}_3\text{OH}$ have shown that methanol slightly reacted with the coal to form traces of methane and carbon monoxide above 480°C. This is above the temperature range where the majority of the methane and carbon monoxide was evolved for the methylated coal. Therefore, the $^{13}\text{CH}_4$ and $^{13}\text{CO}$ observed from the pyrolysis of methylated Rawhide sub-bituminous coal were due to a primary decomposition mechanism and not from secondary reactions of methanol with the coal.

Methane and carbon monoxide evolution began at 288°C, reaching maximum rates at 388-428°C and gradually leveled off between 428-600°C (Figure 13). The temperatures of initial and maximum rates of evolution correlate with the temperature range where decreases in the methylated phenolic absorptions (peak b in Figure 11) of CD$_3$-methylated Rawhide coal were observed from 327-405°C. Therefore, it appears likely that the more thermally stable methylated phenolic group was the primary source of methane and carbon monoxide evolution. However, it is possible that the methylated phenolic group was also producing methanol and formaldehyde. Schlosberg et al.\textsuperscript{12} have reported on the pyrolysis of anisole whose structure is analogous to that of the methylated phenolic groups in coal. Methane and carbon monoxide were reported as part of the low molecular weight products of anisole. A free radical mechanism was proposed by Schlosberg as the mechanism by which methane and carbon monoxide were evolved. Rose et al. have also proposed free radical mechanisms for evolution of these higher temperature methylated species from their studies of O-methylated, O-benzylated, and C-benzylated
Illinois #6 derivatives. The ease of cleavage of C-O and C-C bonds in modified coals is suggested to lead to an increased concentration of radicals which promote other secondary radical reactions favoring decarbonylation and demethylation reaction sequences. Due to the increased number of hydrogen donors after methylation, abstraction reactions represent another possible route to methane formation. This work suggests that methyl esters and alkyl ethers may not participate in a free radical mechanism leading to methane to the degree that the methylated phenol is involved.

Since evolution of $^{13}$C-labeled species is directly related to methylated hydroxyl functional groups, a measurement of evolved $^{13}$C-labeled species should give an indication of the relative amounts of hydroxyl functional groups present in coal. Figure 14 shows plots of $^{13}$C-labeled methanol, carbon monoxide and methane evolution (in moles) for methylated Rawhide sub-bituminous coal from room temperature to 600°C. An approximate molar ratio of 13:10 was found for methanol to methane and carbon monoxide evolution. In the limit of complete separation of reaction types as discussed above this can be interpreted as due to the presence of 10 phenolic functional groups for every 13 carboxylic and/or aliphatic OH functional groups in Rawhide sub-bituminous coal.

3.4 Conclusions

It is clear from these studies that methylation of the hydroxyl functional groups in coal has a noticeable effect on the pyrolysis behavior of the original coal. Significant increases in volatile hydrocarbons were noted after methylation for the low rank coals. A pronounced increase occurred in the evolution of a low temperature hydrocarbon fraction from 150-300°C. It is apparent that elimination of adjacent hydroxyl groups prevented the formation of new ether cross linkages through water elimination reactions, the net result of
Figure 14. Evolution of Carbon-13 Species for Rawhide Sub-bituminous
which was an increase in the yields of lighter oils and tars. From quartz crystal studies the high temperature tar fraction from 300-500°C was shown to be more volatile for methylated low rank coals, Rawhide and Texas Lignite, while the higher ranked coals underwent no appreciable change.

Studies of the pyrolysis behavior of the O-methylated coals have provided insight into the decomposition mechanisms of different methylated hydroxyl functional groups and by inference suggested loss mechanisms for the respective hydroxyl group during pyrolysis. Depending on the availability of labile hydrogens near the methylated sites, either methanol or formaldehyde is thought to originate predominantly from the pyrolysis of methylated carboxylic and aliphatic hydroxyls. Decomposition of methylated phenolic groups appeared to favor methane and carbon monoxide formation presumably through a free radical mechanism.

KBr studies of methylated coals using CD₃I as the methylating agent have revealed distinct infrared absorptions in the C-D stretching region which can be attributed to different methylated hydroxyl functional groups. Three peaks in this C-D stretching region have been identified and have been assigned to methylated phenolic, methylated carboxylic and methylated aliphatic hydroxyl groups. It appears possible to obtain good relative measurements through peak deconvolution methods of the three hydroxyl functional groups present in the original coal.
REFERENCES


4.1 Introduction

It has been noted that thermal decomposition of most of the oxygen containing functional groups in coals proceeds by free radical mechanisms.\(^1\) Tar is thought to be evolved from cleavage of weak methylene-type bridges. Retcofsky et. al. have observed greater spin concentrations in coals after heating to 450°C.\(^2\) One concludes that the formation of free radicals is involved in the initial steps of coal pyrolysis or gasification. It would therefore be of interest to analyze by use of electron spin resonance any possible radicals surviving the vaporization process. Experimental designs similar to those of the matrix-isolation FTIR work were utilized for this study. The presence of free radicals in evolved tars was observed upon slow pyrolysis of four coals. The observed powder spectra are strikingly similar to those reported for peroxo-type radicals in various polymers.\(^3\)–\(^8\) Much of this work involved temperature dependent studies of these radical types and dependence of the spectra on motion of the O-O bond about the chain axis. The values cited for the spectroscopic splitting factor, g, agreed closely with those determined for the coals studied here. Tar formation temperatures corresponded to the temperature range during which the radicals were observed. From this kind of comparison the ESR spectrum of each coal was interpreted as being due to evolved peroxo radicals associated with the vaporized tar molecules in an unknown mechanism. Some effort was made to relate the signal produced to the amount of coal pyrolyzed. It was found that the concentration of the radicals produced varied with the amount of coal pyrolyzed. Finally various additives such as CaO, MgO, SiO\(_2\), CaCO\(_3\), and K\(_2\)CO\(_3\) were added to a Pittsburgh #8 coal (1:1 by weight) and changes in the observed spectra were noted.

4.2 Experimental

Coals were analyzed by ESR using the apparatus shown in Figure I. This
Figure 1. Matrix-Isolation ESR Apparatus
apparatus was made of stainless steel and located between the magnets of the ESR spectrometer. Vacuum was obtained by a mechanical pump coupled to a 4" diffusion pump and typical pressures before experiments were \( \sim 5 \times 10^{-6} \text{ torr} \). Experimental designs were similar to the matrix-isolation FTIR experiments in that the same pyrolysis reactor design, furnace, and cell were used. The furnace and cell were directed at the deposition surface which consisted of a sapphire rod attached to a vertically translatable hollow tube. This tube was filled with liquid nitrogen to cool the sapphire rod to approximately 77K. Coals were pyrolyzed at a heating rate of 4-10°C/min; a tungsten-5% rhenium vs. tungsten-26% rhenium thermocouple was used to measure the temperature of the sample cell. In experiments for calculation of the g values, each coal was heated from room temperature to approximately 700°C and spectra were taken afterwards. Spectra were obtained by lowering the sapphire rod into a 1" outer diameter thin wall quartz tube situated in the microwave cavity. Products were analyzed with a Varian E-9 ESR spectrometer at the X band (9.1 GHz) with 100kHz magnetic field modulation, 7 mW microwave power, 0.1sec time constant, 4 min scan and a field set of 3176 G. Carbon dioxide was used as a matrix diluent in all experiments and the pressure of this carrier gas was usually 200-250 microns. The weight of coal with additive used was about 80mg yielding a coal weight of 40mg. Amounts of coal for calculation of g values were 70-80mg - 500 mesh particle size. Diphenyl picryl hydrazyl, DPPH\((g=2.0037)\), was used to calibrate spectral g values and a Hewlett Packard microwave frequency counter was used to measure the exact frequency. To calculate the g- values the following equation was used:

\[
g = \frac{h \nu}{\beta H}
\]

were \( g \) is the spectroscopic splitting factor, \( h \) is Planck's constant\((6.626 \times 10^{-27} \text{ erg/sec})\), \( \nu \) is the frequency of radiation measured by the counter, \( \beta \) is
the Bohr magneton (9.2741 x 10^-21 erg/G), and H is the field strength in gauss (G) established by calibration with DPPH.

4.3 Results and Discussion

At least two free radicals were observed during the pyrolysis of coal. Spectra for Illinois #6 Bituminous showing radical variation with temperature can be found in Figure 2. The spectra for the remainder of the coals are located in the Appendix. Radicals were first detected at approximately 320°C and increased in intensity to about 600°C. This corresponds to the temperature evolution range for the major tar fraction as noted in the FTIR studies. A low temperature tar fraction, 150-300°C, was seen for the coal and attributed to light oils. However this temperature range showed no radical formation in the ESR spectrum. Experiments were performed on the coals to determine the g tensor values for the observed radical. It is important to note that the entire pyrolysis process was completed before the spectrum was obtained in these experiments. Spectra of the four coals studied with g values marked are shown in Figure 3. Table I contains the g values calculated for each coal, along with a comparison of typical g values found for peroxy radicals in various polymers.3,8 The first radical (g_1, g_5, g_6) exhibits g anisotropy similar to a peroxy radical as illustrated in Figure 4(a).9 From Table I the comparison of typical g values for a peroxy radical agree well with g values for the high ranking coals Pittsburgh Bituminous and Illinois#6 Bituminous. Based on reported studies of peroxy radicals3,5-9 these features are assigned to the formation of a peroxy radical. An interesting observation from comparison of the coal spectra of Pittsburgh and Illinois#6 with that reported by Taarit et. al. in Figure 4(a) is the feature at g^* = 2.025. Taarit reported the presence of a (CO_2 - O_2)^- radical on an MgO surface at 77K with principal g values of 2.040, 2.0072, 2.0015 and g_{avg} of 2.0162, which compares well with the two high rank
Figure 2. Matrix-Isolation ESR Spectra of Illinois #6 Bituminous
Figure 3. ESR Spectra of Pyrolysis Products for (a) Pittsburgh Bituminous, (b) Illinois #6 Bituminous, (c) Rawhide Sub-bituminous and (d) Texas Lignite
Table I
Comparison of Observed g-values

<table>
<thead>
<tr>
<th>$g$ values of P3H2COQ-</th>
<th>Texas Lignite</th>
<th>Rawhide Sub-bituminous</th>
<th>Illinois #6 Bituminous</th>
<th>Pittsburgh Bituminous</th>
<th>$g$ values of typical peroxy radicals</th>
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<tr>
<td>$g_1$</td>
<td>--</td>
<td>--</td>
<td>2.0363</td>
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<td>$g_2$ $2.0320^8$</td>
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<tr>
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<td>--</td>
<td>2.0246</td>
<td>2.0248</td>
<td></td>
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<tr>
<td>$g_4$ $2.0092^8$</td>
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<td>2.0098</td>
<td>2.0093</td>
<td>2.0098</td>
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</tr>
<tr>
<td>$g_5$ $2.0083^*$</td>
<td>2.0077$^*$</td>
<td>2.0073</td>
<td>2.0069</td>
<td>2.008$^3$</td>
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<td>$g_6$ $2.0035^8$</td>
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<td>2.0013</td>
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<td>$g_{avg}$</td>
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<td>$g_{avg}$ $2.0149^8$</td>
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<td>2.0136</td>
<td>2.0137</td>
<td>2.0139</td>
<td></td>
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</tbody>
</table>

* This feature was not a distinct peak but rather a weak shoulder on the 2.0098 feature.
Figure 4. Comparison of (a) ESR Spectrum for a \((\text{CO}_2\cdot\text{O}_2)^-\) Radical on an MgO Surface and (b) Simulated ESR Spectrum Assuming Motion of the Radical on the MgO Surface
coals. When reaction occurred between a mobile CO$_2^-$ and oxygen an added peak with a g value of 2.025 was seen.\textsuperscript{10} These authors had no evidence for assigning this peak to another type radical such as O$^-$ and so its identity was left unknown. Other researchers, however, reported a possible interpretation for the observance of this added feature.\textsuperscript{4} They suggest that the radical, (CO$_2$-O$_2^-$)$^+$, retains some mobility on the MgO surface which gives rise to the observed spectrum. To support this view they employed theoretical calculations to generate ESR spectra characteristic of motion of the radical on the surface. In fact they do obtain a spectrum similar to that reported by Taarit et. al., as shown in Figure 4(b).\textsuperscript{4} Perhaps, then, mobility of the peroxy radical from the coal is the reason for the spectral g-values at 2.0248 and 2.0236 for Pittsburgh and Illinois#6 respectively. Another probable reason to associate this feature with the identified peroxy radical is seen in Figure 3 which shows a comparison of the ESR spectra for all four coals. During pyrolysis of the low ranked coals, Rawhide Sub-bituminous and Texas lignite, formation of the above mentioned radical is not evident and the feature at 2.025 is also absent.

The second radical seen by pyrolysis of all the coals has averaged g tensor values of $g_2=2.0302$, $g_4=2.0098$ and $g_6=2.0014$. These features also show g-anisotropy and are within range of expected values for a peroxy radical. Comparison with work of Schlick and Kevan\textsuperscript{8} on a triphenylmethyl peroxy radical, Ph$_3$COO$^-$, support this view. They report g values of 2.0320, 2.0092 and 2.0035 for the radical at 81K which is in the range of the radical formed during coal devolatilization. On the basis of these comments another peroxy-type radical must be assigned to the spectra with principal values of g as noted in Table I.

It might be surprising that pyrolysis yields a peroxy radical but Lynch et. al.\textsuperscript{11} have reported detection of carbonyl oxygen functional groups at the surfaces of
powdered coals derived from the thermal decomposition of precursor surface peroxides, which they claim as present on the surfaces of all except the most freshly prepared coal samples. The structure of coal is generally thought to be a highly crosslinked amorphous polymer consisting of stable clusters connected by relatively weak bridging groups such as methylene (CH₂-CH₂) linkages. During primary pyrolysis, when swelling and other changes in coal thermal behavior are occurring, these bridging groups are cracked forming radical sites and allowing volatiles to exit the coal matrix. Retcofsky et. al. have noted an increase in spin concentrations in the coal matrix for coal samples heated to temperatures of 450°C (g=2.0028) by as much as 3 times the spin found in bulk coals.² The g value found is in the range of that for π-hydrocarbon radicals. Attar et al have noted that thermal decomposition of most of the oxygen-containing functional groups in a coal proceeds by free radical mechanisms.¹ For radicals to be evolved as gaseous free radical species and observed experimentally by matrix-isolation ESR they must exit the coal matrix without further reaction with other radicals or donor groups. As no carbon-centered radicals were-characterized in the pyrolysis products it seems likely that they are more readily stabilized before exiting the intricate matrix of the coal than are the surface peroxides. In addition, since the peroxides are on the coal surface, they are more able to escape without much contact with stabilizing groups. It seems that the focus in any discussion of radical detection is thus the pathlength through which the radicals must travel and the surface area of the coal. A study of how the signal varied with different sample weights is shown in Figure 5. It shows a roughly linear variation of signal with sample weights less than 3mg. Coal weights greater than 20mg show a leveling of signal at a peak height of approximately 15. It would seem that the amount of coal in the cell to be pyrolyzed affects the amount of radical exiting the coal
Figure 5. Variation of ESR Signal (Peak Height) with Weight of Coal
structure. Smaller weights of coal have a greater surface area and so perhaps this deviation of signal with weight is not surprising, especially as the source of coal peroxy radicals is presumably adsorbed oxygen on the coal surface.

Finally a study of the pyrolysis behavior of Pittsburgh Bituminous in the presence of various additives was performed. The additive samples were obtained from M. R. Khan and were prepared by mixing coal and additive in a 1:1 ratio by weight. None of the additives (CaO, MgO, CaCO₃, K₂CO₃, and SiO₂) had any affect on observed pyrolysis behavior. Temperature studies of all the samples by matrix-isolation ESR can be found in the Appendix. Figure 6 shows the spectrum obtained after pyrolysis to 700°C for each sample. These spectra show the formation of peroxy radicals similar to that observed for Pittsburgh Bituminous (see Appendix). The weak signal may be caused by experimental factors since spectra were taken at each temperature making quantitative analysis difficult. In addition sample weights were ~80mg which corresponds to 40mg of the coal. Radical formation is observed at similar temperatures for coal pyrolyzed with and without additive, 350-600°C. Since no differences were noted in the ESR spectra it is likely that the isolated radicals formed during pyrolysis are derived from peroxides on the coal surface. For a given coal sample these peroxides should pyrolyze in like fashion. Furthermore there seem to be no carbon centered radicals evolved as these are significantly decreased in the coal matrix when Pittsburgh is pyrolyzed in the presence of CaO at 450 and 460°C. Khan attributed this decrease in spin concentration noted from ESR studies to the ability of CaO to catalyze char forming reactions by increasing the extent of cross linking occurring as pyrolysis takes place.

The effect of these additives on the pyrolysis products was investigated using MI-FTIR. FTIR spectra for each sample are presented in the Appendix. Figure 7 shows a comparison of tar evolution for each sample, determined by
Figure 6. MI-ESR Spectra of Pittsburgh Bituminous with Additives
Figure 7. Tar Evolution as a Function of Temperature for Pittsburgh with Additives
quartz crystal measurements as described earlier. Table II gives the corresponding tar weights (mg) compared with Pittsburgh Bituminous. CaO caused the greatest deviation in tar production yielding 1/3 that of Pittsburgh heated without additive. Khan and Jenkins\textsuperscript{12} have noted that CaO may provide sites for polymerization of tar molecules before vaporization possibly causing a decrease in volatility and thereby increasing char yield. Indeed, the authors stated that CaO favored char forming reactions implying promotion of cross linking reactions which would inhibit tar evolution. In addition, this additive was seen to catalyze dehydrogenation of the coal, which means that the tar and other hydrocarbon volatiles that compete for hydrogen in order to evolve would be expected to produce smaller yields. MgO displayed a less notable effect on tar production yielding 3/4 that of Pittsburgh heated without additive. The devolatilization of Pittsburgh with the remaining additives showed little variation in tar production as compared to the coal without additive: SiO\textsubscript{2} was next followed by K\textsubscript{2}CO\textsubscript{3} and CaCO\textsubscript{3}.

The other major effect of additive on the pyrolysis behavior of the coal was in reduction of the phenolic or aromatic content of vaporized tar molecules. CaO was seen to have the greatest effect as shown in Figures 8 and 9 which are FTIR plots of the tar regions at 450-500°C. Figure 8 shows the tar-OH region as detailed in Chapter 2. Recall the phenolic groups in tar absorbed at 3626.5 cm\textsuperscript{-1} labeled Tar-OH. Notice the dramatic reduction in this peak for CaO. In Figure 9 the stretching and bending region is depicted. The peak labeled Tar-OH, associated with the C-O stretch for phenol, is seen to decrease in the case of CaO. Khan also noted this same effect\textsuperscript{12} and proposed that the basic CaO was reacting with these acidic compounds (phenols) to produce hydrocarbon salts which decompose. All other additives showed negligible differences in this area.
Table II
Tar Evolution

<table>
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<tr>
<th>Sample</th>
<th>Final Temperature</th>
<th>Tar (mg)</th>
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<tbody>
<tr>
<td>Pittsburgh (PGH)</td>
<td>612°C</td>
<td>4.87</td>
</tr>
<tr>
<td>PGH : CaO</td>
<td>628°C</td>
<td>1.85</td>
</tr>
<tr>
<td>PGH : MgO</td>
<td>595°C</td>
<td>3.60</td>
</tr>
<tr>
<td>PGH : CaCO₃</td>
<td>617°C</td>
<td>5.08</td>
</tr>
<tr>
<td>PGH : K₂CO₃</td>
<td>645°C</td>
<td>5.22</td>
</tr>
<tr>
<td>PGH : SiO₂</td>
<td>650°C</td>
<td>4.33</td>
</tr>
</tbody>
</table>
Figure 8. FTIR Matrix-Isolation Spectra Comparing the O-H Stretching Region
Figure 9. Comparison of FTIR Matrix-Isolation Spectra Below 1900 cm$^{-1}$
4.4 Conclusion

Mild pyrolysis of coal produced a peroxy type radical associated with the tars of all coals studied. The low rank coals, Rawhide and Texas lignite, exhibited predominantly one type of radical with g values of 2.0304, 2.0098 and 2.0014. Two higher ranked coals, Pittsburgh Bituminous and Illinois#6 Bituminous, displayed another peroxy type in addition to that previously mentioned, with g values of 2.0366, 2.0072 and 2.0014. Existence of peroxides on the surface of coals is perhaps the source of the observed signal associated with the tar in a mechanism as yet undetermined. The fact that the two higher ranked coals produce two types of peroxy radicals may indicate the presence of more peroxides on the surface of these coals. As the source of peroxides is thought to be adsorbed oxygen on the coal's surface, it would be expected that the older high ranked coals, which are more weathered, should contain more peroxides. More work is needed to clarify the nature of these peroxy radicals. Any findings should be of interest in that one radical appears rank sensitive.

A weight study on the pyrolysis behavior of the radical with sample variation showed a weight of coal ranging from 21-42mg to give the most intense signal. It is possible that observed leveling of the signal (Figure 5) is an effect of the coal surface area during the devolatilization and the path length the radical travels in order to be detected. A smaller sample size would have a greater surface area and perhaps allow radicals produced further back in the cell an easier escape to the liquid nitrogen cooled matrix surface. A shorter residence time, i.e. smaller path length, for the radical in the cell may mean a greater probability that the radical simply encountered fewer molecules with which to react.

No apparent effect from coal pyrolyzed in the presence of various additives on free radical formation was detected by matrix-isolation ESR analyses. If
surface peroxides are linked to the production of these radicals then possibly they are evolving with the tar in a mechanism yet undetermined. Recall that the tar is evolved in such a way as to be minimally disturbed fragments of the original coal matrix. This idea supports the probable source of radicals being surface peroxides. When tar is vaporized these surface peroxides could evolve with the tar except that during vaporization the peroxide groups have been altered to a peroxy type radical -O-O- detectible in the ESR.

Two major differences were noted from MI-FTIR studies of Pittsburgh Bituminous with and without additives. Both changes were seen to be greatly influenced by the presence of CaO and to a much smaller degree by the other additives: MgO, CaCO₃, K₂CO₃ and SiO₂. The first effect was a significant reduction in tar yield for coal pyrolyzed in the presence of CaO and to a lesser extent MgO. The remaining additives showed little or no difference in tar yield for the coal pyrolyzed with or without additive. A possible explanation is that CaO promotes greater cross-linking reactions inhibiting tar formation and dehydrogenation reactions leaving less hydrogen for tar and other hydrocarbon pyrolysis mechanisms, both of which point to smaller tar yields. The second difference observed in the pyrolysis behavior of the coal with and without the additives was a reduction in the phenolic or aromatic content of the tar produced. The only additive which seemed to have an appreciable effect on this point was CaO. Khan proposed that the reason for this additive effect was that the basic CaO reacts with the acidic phenolic groups to form hydrocarbon salts which decomposed readily. This effect is significant since phenol is soluble in water and has been a problem in contamination of the by products from coal pyrolysis.
REFERENCES


Summary

This work has provided some new and interesting insights into structural aspects of various coals. Pyrolysis to 1500°C allowed quantitative determination of certain functional groups present in the original coal. Devolatilization was noted to begin with evolution of light carbonyls at temperatures below 250°C along with H₂O, CO₂, CO and tar whose evolution continued to higher temperatures. The major fraction of tar was evolved in the 300°-600° temperature range. From quartz crystal microbalance measurements Pittsburgh was found to contain the most tar (13% by weight) followed by Illinois #6 (9.6%), Texas Lignite (7.2%), and Rawhide (4.3%). Thus, higher rank coals were shown to evolve more tar than lower rank coals. Evolved water exhibited two maxima. One of these maxima was observed below 700°C and was attributed to hydroxyl groups which underwent thermal decomposition. The high temperature source of water is not certain, but a likely source is the decomposition of kaolinite (Al₂Si₂O₅(OH)₄) and other inorganic hydroxides.

Carbon dioxide evolution was primarily due to decarboxylation reactions with small amounts possibly evolved from the reduction of inorganic carbonates. From a quantitative study of carbon dioxide evolution, Pittsburgh bituminous was found to contain 0.5 carboxylic (COOH) functional groups per 100 carbon atoms. This agrees well with the value reported by Schlosberg for Illinois #6. Rawhide possessed 2.2 carboxyl groups per 100 carbon atoms and Texas Lignite contained 2.1 carboxyl groups per 100 carbon atoms. These results indicate that the lower rank coals contain greater amounts of carboxylic functional groups. It should also be noted that Rawhide contained 1.0 ester functional group per 100 carbon atoms, but no calculation could be made for Texas Lignite.
Carbon monoxide evolution below 900°C resulted from the thermal decomposition of ether functional groups in coal. Carbon monoxide pyrolysis yields showed Pittsburgh and Texas Lignite to contained 4.28 and 9.13 ether functional groups per 100 carbon atoms respectively. From work produced by Schlosberg et. al. Illinois #6 contained 5.5 ether functional groups per 100 carbon atoms while Rawhide possessed 9.8 ether groups per 100 carbon atoms. Lower rank coals are seen to possess more ether functional groups than the higher ranked coals in the following order: Rawhide Sub-bituminous, Texas Lignite, Illinois #6 Bituminous and Pittsburgh Bituminous.

Hydrocarbon evolution due to dealkylation of coal occurred at a relatively low temperature range, 150°-400°C. Methane was also produced by these reactions although another source of methane is evident from its pyrolysis behavior, i.e., methane production peaks were observed at higher temperatures than those observed for maximum production of other hydrocarbons.

Organic sulfur evolved, predominantly as hydrogen sulfide (H₂S) and carbonyl sulfide (COS), with the tar fraction at 300°-500°C. The source of H₂S is attributed to the presence of thiols in the original coal since they readily decompose and yield hydrogen sulfide at these temperatures. Carbonyl sulfide is thought to evolve from secondary pyrolysis reactions of CO₂ and H₂S. Above 800°C carbon disulfide was produced presumably from degradation of the thiophenic groups in coals. Sulfur dioxide (SO₂) was produced along with the tar fraction but maximized at 550°C. SO₂ evolution is from decomposition of inorganic sulfates in the coals. Weathered coals are known to contain more sulfates due to oxidation of the pyrites in coals. From MI-FTIR spectra the higher rank coals produce more SO₂ and the order follows: Pittsburgh Bituminous, Illinois #6 Bituminous, Rawhide Sub-bituminous and Texas Lignite. Nitrogen in the coal evolved as ammonia (NH₃) at 300°-700°C and as hydrocyanic acid
(HCN) at 350°-800°C. Ammonia was attributed to decomposition of nitrogen-containing side groups such as alkyl amines and amides while HCN resulted from degradation of nitrogen containing rings. For most of the gaseous species evolved a pyrolysis weight in milligrams was calculated (Table II). From the above discussion for COS and SO₂ extinction coefficient work would be useful to supplement this work in the area of sulfur. As for nitrogen containing products (NH₃ and HCN) a similar study of the extinction coefficients could lead to better understanding of how nitrogen is incorporated into coal structure.

At temperatures greater than 900°C major products observed were acetylene along with products of the reduction of kaolinite such as SiO₁, Al₂O₁, and aluminum atoms. As mentioned earlier some water was seen at these temperatures as well as carbon monoxide. One possible source of the CO and H₂O is the gaseous secondary reaction of CO₂ with H₂. Another possibility, in the case of H₂O, would be decomposition of inorganic hydroxides such as kaolinite and, in the case of CO, the reduction of metal oxides in coal.

Matrix-isolation Fourier transform infrared spectroscopy studies indicated the presence of two types of hydroxyl groups in evolved tars. One type was characterized as phenolic hydroxyls which indicates their greater thermal stability; the other aliphatic hydroxyls were less stable. This study of the hydroxyl groups present was facilitated by methylation of the hydroxyl groups: Ø-OH, R-OH, and O=COH. Analysis of the pyrolysis products of the treated coals indicated a difference in the pyrolysis behavior. Analyses of the -CD₃ treated coals as KBr pellets showed three distinct absorbances. Quantitative analysis of these peaks was not possible because no peak deconvolution program was available. However, one could compare relative peak heights and when this was done, it indicated that the two higher ranked coals possess more phenolic than aliphatic hydroxyl functional groups and even fewer
carboxylic functional groups. Decomposition mechanisms were proposed for each hydroxyl group. Aliphatic and carboxylic hydroxyl groups produced methanol and formaldehyde depending on the availability of labile hydrogen. Labile hydrogen induced formation of methanol whereas the absence of labile hydrogen favored production of formaldehyde.

Methylated phenolic groups were noted to yield primarily methane and carbon monoxide. Carbon-13 analyses of one coal, Rawhide sub-bituminous, yielded a rough approximation of the amounts of each type of hydroxyl functional group present in Rawhide. This was found to be 13 aliphatic/carboxylic hydroxyl groups to 10 phenolic groups. Carbon-13 labeled studies on the remainder of the coals could be used to aid characterization of the relative amounts of these groups as rank varies.

Tar evolution was also affected by methylation of the coal. For all coals except Pittsburgh an increase in lighter oils and tars evolved from 150°-300°C was observed. This difference is attributed to the loss of hydrogen bonding resulting from replacement of the hydroxyl group(-OH) with a methoxy(-OCH₃) functional group. This also prohibited water elimination reactions from hydroxyl decomposition and thus formation of new ether cross-linkages. The high temperature (>300°C) evolution of tar remained unchanged for the high ranking coals which implied that the evolution mechanism for these tars involved cleavage of weak methylene bridges. In the case of low ranked coals methylation caused this tar fraction to become more volatile indicating that formation of ether cross-linkages was inhibiting tar production in the original coals.

Electron spin resonance studies of coal pyrolysis products indicated the existence of two peroxyl radicals. One radical with g values typical of alkyl peroxyl radicals was seen predominantly in higher ranked coals with
characteristic averaged g values of 2.0366, 2.0071 and 2.0014. A second peroxy radical with g values comparable to those of a triphenyl methyl peroxy radical was observed for all coals pyrolyzed with averaged g values of 2.0302, 2.0098 and 2.0014. The source of these radicals was presumably surface peroxides which, when the coal was pyrolyzed, evolved with the major tar fraction at approximately 350°-600°C.

Clearly more investigation of the pyrolysis behavior is needed before further statements can be made. Perhaps more coals could be analyzed and compared to the ones already studied. A more sophisticated electron spin resonance apparatus would allow better resolution and greater signal strength for a given weight of sample. Liquid helium temperatures could be incorporated which could aid spectral identification. Studying the spin concentration of chars after pyrolysis could also enhance understanding of the chemistry occurring. Studies of coal samples doped with surface peroxides should clarify this work as well as facilitate development of a model for peroxy radical analysis. Utilization of different matrix diluents might lead to spectral or pyrolysis changes or both. Quantitative ESR analyses would be useful in comparing the various ranks of coal. A possible method to test for the presence of carbon radicals evolving from coal pyrolysis is laser heating or flash pyrolyzing coals and using matrix-isolation ESR for analysis. Clearly, more work in the area of ESR could provide important information about the radicals formed during pyrolysis.

Other areas for future coal investigations would be extended analysis of the thermal behavior of coals in the presence of additives; additional quantitative methylation studies of the coals in order to correlate the water evolution with extent of cross linking and the number of different hydroxyl groups present in the original coal; and more extinction coefficient work with sulfur and nitrogen pyrolysis products. Eventually, the combination of mass spectrometric analysis
of gaseous products, FTIR matrix-isolation studies and ESR studies of radicals should lead to a complete understanding of coal pyrolysis and to a more detailed understanding of coal structure.
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                                         CaCO\(_3\) 153
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                                               SiO\(_2\) 155
Matrix-Isolation FTIR Spectra of Pittsburgh Bituminous Pyrolyzed

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<tr>
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<tr>
<td>SiO₂</td>
<td>160</td>
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\[ y = 0.156 + 0.849x \]

**CO/\text{N}_2**

**Peak Area**

**KA**
$y = 0.138 + 3.306 x$

Water/N$_2$
PCH : CaO \ (1:1)

714°C
614°C
554°C
490°C
450°C
400°C
344°C