SOLID STATE $^{13}$C AND $^1$H NMR STUDIES OF THE EVOLUTION OF THE CHEMICAL STRUCTURE OF COAL CHAR AND TAR DURING DEVOLATILIZATION

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Solid-state $^{13}$C and $^1$H nuclear magnetic resonance (NMR) spectroscopy techniques are used to investigate the chemical structure of char particles and condensed tar vapors produced as pyrolysis products from an Illinois #6 coal at rapid heating conditions ($\sim 10^4$ K/s) at two gas conditions (maximum gas temperatures of 1250 K and 1050 K). The temperature history of particles in the flow reactor is determined using a unique infrared sizing-pyrometry system. The $^{13}$C NMR analyses of the coal chars indicate that significant amounts of aliphatic material are released from the coal during devolatilization, with little change to the aromatic cluster size or number of attachments per cluster. At longer residence times, and at higher temperatures, small increases in the cluster size in the char are observed. The $^1$H NMR analyses indicate that thermal decomposition of tar vapor occurs at the 1250 K gas condition, as evidenced by increases in the aromaticity and decreases in the peripheral aliphatic groups, such as methyl groups and aliphatic bridge material.

Introduction

Recent devolatilization research$^{1-5}$ has identified the rates and the temperature regimes of pulverized coal devolatilization as a function of heating rate, final temperature, and coal type. Particle temperature measurements during devolatilization at rapid heating conditions$^{1,2}$ have eliminated many uncertainties caused by estimations of particle temperatures in early studies. Models of devolatilization have advanced beyond one-step Arrhenius kinetics to descriptions of the bonding structure in the coal, metaplast, and tar.$^5,^6$ Other models include detailed empirical correlations to estimate yields of tar products from elemental compositions of the parent coal,$^1$ as well as mechanisms to describe the evolution of the physical structure of char particles.$^1$ Tar is commonly defined as pyrolysis products that condense at room temperature and pressure. Light gas release is generally modeled independently from solid-phase reactions,$^7$ although a recent mechanism was proposed where light gas release is partially coupled to the char formation rate.$^8$ It is clear that quantitative experimental investigations of the evolution of the chemical structure of solid and condensible pyrolysis products (char and tar) are critical to the understanding of coal devolatilization mechanisms.

Solid-state $^{13}$C nuclear magnetic resonance (NMR) spectroscopy is a convenient, nondestructive tool for the analysis of chemical structure of solid fossil fuels. Cross-polarization$^{12,13}$ (CP), magic angle spinning$^{14-16}$ (MAS) and dipolar decoupling techniques permit direct measurement of the relative number of aromatic and non-aromatic carbons present in the sample. The carbon aromaticity, $f_{ar}$, has
been reported for coals, macerals, soil, and other fossil-related materials. 17,18 Dipolar-dephasing (DD) techniques 19-21 along with normal CP/MAS integrations over selected chemical shift ranges have been used to subdivide $f_{ax}$ values into the amount of protonated and non-protonated carbon. 22 These techniques have recently been used to estimate the average aromatic cluster size of the eight coals in the Argonne Premium Coal Sample Bank. 22

In this paper, we present $^{13}$C and $^1$H NMR data for the chars derived from an Illinois #6 hvb bituminous coal (PSOC-1493), and high resolution $^1$H and $^{13}$C NMR data on the tars produced in each pyrolysis experiment. These data, together with information on the total mass release and elemental analysis for each tar/char pair, are used to evaluate the evolution of the tar and char structures as a function of residence time and temperature.

**Experimental Facility**

Experimental details regarding the particle temperature measurement and sample collection system were previously published, 1,12 and hence only a brief discussion will be given here. The pyrolysis studies were performed in 100% nitrogen in a laminar flow reactor. Transparent flow reactor walls allow radiant emission from the coal particles to be monitored at any axial location. Two gas temperature conditions were used in this study, with maximum centerline gas temperatures of 1250 and 1050 K.

An infrared sizing pyrometer system was used to measure the size, temperature, and velocity of individual particles in the flow reactor at different axial locations. The effective wavelengths of the two pyrometer channels are 1.36 and 2.2 µm. Typical standard deviations in measured particle temperatures are 5 K for pure carbon spheres (Spherocarb) and 30 K for the coal particles. Particle temperature histories and centerline gas temperatures determined for the Illinois #6 coal are presented in Fig. 1 for the two gas temperature conditions.

A water-cooled, helium-quench probe was used to collect solid samples iso-kinetically. The inner wall of the probe is made from porous tubing, allowing helium to transpire through the wall to reduce tar deposition. A virtual impactor and three-stage Andersen cyclone system were used to aerodynamically separate char particles from condensed tar vapors and aerosols. Tars were collected on polycarbonate filters following the separation system.

Both the organic elemental composition and the inorganic elemental composition of the char particles were measured using standard techniques. The elements Ti, Si, and Al were used as tracers, in addition to the total ash content, to determine the extent of mass release from the char particles. The tars collected in this experiment are assumed to be representative; mass balances show that approximately 50% of the tar expected (based on model predictions) was collected and analyzed. Chars and tars were stored at temperatures less than 0° C until final preparation for NMR analysis. The 106–125 µm size fraction of the Illinois #6 bituminous coal used in these experiments exhibited the following ASTM proximate and ultimate analyses: 38.0% volatile matter and 11.3% ash (wt.% moisture free), with 74.1% C, 5.0% H, 13.2% O, 1.4% N, and 6.3% S on a dry ash-free (daf) basis.

**NMR Analysis**

The $^{13}$C NMR data on the coal and char particles were obtained by a variation of the method described by Solum, et al. 24 The total magnetization was obtained by a variable contact time experiment in which the data were fit to a model employing a Gaussian distribution, including Lorentzian terms in the T$_{CH}$ parameter and a single value for T$_{1p}$. 25 Dipolar dephasing data were employed to separate the aromatic Gaussian (C-H) component from the Lorentzian (non-protonated) component of the carbon magnetization. Segmental motion in the aliphatic region of the $^{13}$C CP/MAS spectrum of coals creates some uncertainty in the relative contributions of CH$_3$ and CH$_2$/CH groups 25 and hence, the methyl contribution was approximated from the integrated intensities of the 0–22 (alkyl and aryl
methyl groups) and 50–60 (methoxy group) ppm regions of the spectrum. All other structural parameters were obtained using a Bruker CXP-100 spectrometer as described by Solum, et al. 22

The 1H and 13C NMR data for each tar sample were obtained with a Varian VXR-500 spectrometer. Tars were manually removed from the tar filter and dissolved in 1 ml samples of deuterated (98%) dimethyl sulfoxide (DMSO). The 13C NMR data on tars were obtained by using a 30° carbon pulse with an acquisition time of 1.2 s and a 0.5 s pulse delay. These conditions provide semi-quantitative data that slightly underestimate the carbon aromaticity. Small amounts of particulate matter were observed in the solutions following dissolution, but no serious degradation of spectral resolution was observed due to the presence of the colloidal material.

In the analysis of the 13C NMR data, the amount of bridgehead carbon $f_a^B$, present is an important structural parameter. The fraction of aromatic bridgehead carbons, $x_B$, is defined as $x_B = f_a^B / f_a'$, where $f_a'$ is the fraction of aromatic carbons present in the sample. The empirical relationship between $x_B$ and the number of aromatic carbons per cluster is discussed in detail by Solum, et al. 23 The total number of attachments per cluster, $\sigma + 1$, is also called the coordination number, and has been used directly to describe the initial state of the coal lattice in a recent devolatilization model. 6

Results and Discussion

Evolution of Char Structure:

The carbon skeletal parameters determined from the 13C NMR analyses of the coal and chars obtained at the 1250 K gas condition are given in Table I, together with the total mass release determined for each sample. The ultimate volatiles yield measured at the 1250 K gas condition for this coal is 51% (daf), as shown in Fig. 2. Approximately 40% of the volatiles are released by 43 ms, and 75% of the total mass release occurs by 65 ms. The tar release zone is approximately 50–65 ms, based on model predictions 9 and comparison with similar data. 5 During this period, the carbon aromaticity (percentage of carbon in aromatic groups) for the chars increases by less than 5%. The number of aromatic carbons per cluster in the char reaches a final value of 15 (a 40% increase) at 225 ms, which is viewed as only a modest increase compared to graphitization, where the number of carbons per cluster may be in the range of 50 to 100. Recent data of Solum, et al. 25 indicate that the number of carbons per cluster for a high volatile bituminous coal and a lignite increases at higher temperatures and residence times. The percentage of aliphatic carbon in the collected char remains constant until the late stages of devolatilization, and then rapidly

| TABLE I |
| Carbon structural parameters determined from 13C NMR spectroscopy for PSOC-1493D Illinois #6 Char Samples |

<table>
<thead>
<tr>
<th>Residence Time (ms)</th>
<th>0</th>
<th>43</th>
<th>65</th>
<th>89</th>
<th>128</th>
<th>224</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass Release (% daf)</td>
<td>0</td>
<td>22</td>
<td>38</td>
<td>47</td>
<td>51</td>
<td>51</td>
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<tr>
<td>Aromatic carbon, $f_a = f_a^C + f_a^H$</td>
<td>.71</td>
<td>.72</td>
<td>.74</td>
<td>.79</td>
<td>.81</td>
<td>.86</td>
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<tr>
<td>Carboxyl, $f_a^C$</td>
<td>.04</td>
<td>.05</td>
<td>.04</td>
<td>.05</td>
<td>.03</td>
<td>.02</td>
</tr>
<tr>
<td>Aromatic carbon, carboxyl subtracted, $f_a'$</td>
<td>.67</td>
<td>.67</td>
<td>.70</td>
<td>.74</td>
<td>.78</td>
<td>.84</td>
</tr>
<tr>
<td>Protonated aromatic carbon, $f_a^H$</td>
<td>.27</td>
<td>.29</td>
<td>.27</td>
<td>.34</td>
<td>.33</td>
<td>.32</td>
</tr>
<tr>
<td>Non-protonated aromatic carbon, $f_a^N = f_a^C + f_a^S + f_a^P$</td>
<td>.40</td>
<td>.38</td>
<td>.43</td>
<td>.40</td>
<td>.45</td>
<td>.52</td>
</tr>
<tr>
<td>Aromatic carbon with oxygen attachment, $f_a^O$</td>
<td>.08</td>
<td>.09</td>
<td>.07</td>
<td>.07</td>
<td>.05</td>
<td>.05</td>
</tr>
<tr>
<td>Aromatic carbon with alkyl attachment, $f_a^A$</td>
<td>.17</td>
<td>.19</td>
<td>.16</td>
<td>.19</td>
<td>.18</td>
<td>.22</td>
</tr>
<tr>
<td>Aromatic bridgehead and inner carbon, $f_a^B$</td>
<td>.15</td>
<td>.10</td>
<td>.20</td>
<td>.14</td>
<td>.22</td>
<td>.25</td>
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<tr>
<td>Aliphatic carbon, $f_a^A$</td>
<td>.29</td>
<td>.28</td>
<td>.26</td>
<td>.21</td>
<td>.19</td>
<td>.14</td>
</tr>
<tr>
<td>Aliphatic CH and CH$_2$, $f_a^H$</td>
<td>.18</td>
<td>.19</td>
<td>.17</td>
<td>.15</td>
<td>.14</td>
<td>.10</td>
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<tr>
<td>Aliphatic CH$_3$ and non-protonated carbon, $f_a^*$</td>
<td>.11</td>
<td>.09</td>
<td>.09</td>
<td>.06</td>
<td>.05</td>
<td>.04</td>
</tr>
<tr>
<td>Aliphatics with oxygen attachment, $f_a^O$</td>
<td>.07</td>
<td>.07</td>
<td>.06</td>
<td>.08</td>
<td>.07</td>
<td>.07</td>
</tr>
<tr>
<td>Number of carbons per cluster, $C$</td>
<td>$11 \pm 2$</td>
<td>$9 \pm 2$</td>
<td>$14 \pm 3$</td>
<td>$10 \pm 2$</td>
<td>$14 \pm 2$</td>
<td>$15 \pm 2$</td>
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<tr>
<td>Total attachments per cluster, $\sigma + 1$</td>
<td>4.1</td>
<td>4.2</td>
<td>4.6</td>
<td>3.5</td>
<td>4.1</td>
<td>4.8</td>
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<tr>
<td>Bridges and loops per cluster, $B_c$</td>
<td>2.3</td>
<td>2.9</td>
<td>2.8</td>
<td>2.7</td>
<td>3.2</td>
<td>4.1</td>
</tr>
<tr>
<td>Fraction of intact bridges per cluster, $p$</td>
<td>.56</td>
<td>.68</td>
<td>.61</td>
<td>.77</td>
<td>.78</td>
<td>.85</td>
</tr>
</tbody>
</table>
Fig. 2. Carbon skeletal parameters for chars collected at different residence times in the 1250 K gas temperature environment, as measured by $^{13}$C NMR spectroscopy, including % aromatic carbon, % aliphatic carbon, number of carbons per cluster, and ring attachments per 100 carbons. Mass released as volatiles is also shown.

Fig. 3. Average number of attachments per cluster, and the number of bridges and loops per cluster versus the extent of mass release due to devolatilization for chars collected at different residence times in the 1250 K gas temperature environment. Continuous curves represent correlation of the data.

declines. The percentage of aliphatic carbon in the char at 224 ms is a factor of two lower than in the parent coal, but has changed by less than 10% at the point where 75% of the volatiles have been released (65 ms).

The aliphatic attachments to aromatic clusters consist of alkyl groups and oxygen functional groups (i.e., phenols and/or alkyl and aryl ethers). These attachments include bridges and loops between aromatic clusters, as well as bridge fragments that are eventually released as light gas. The bridge fragments are distinguished from intact bridges by the presence of methyl groups. Even though the percentage of aliphatic carbon decreases by a factor of two at 225 ms, the total number of aromatic ring attachment sites per 100 carbon atoms is essentially constant. The number of bridges and loops (i.e., bridges between aromatic rings and aliphatic loops on aromatic rings, such as tetralin) per cluster does not change significantly until the end of the mass release period, as shown in Fig. 3. The increase in the number of bridges and loops per cluster represents the extent of crosslinking that occurs between neighboring aromatic clusters. The total number of attachments per aromatic cluster, however, does not change significantly, meaning that the bridge fragments are released at a rate proportional to the formation of crosslinking bridges. These bridges may be formed at the site of the original bridge fragment or at new aromatic sites. These data at rapid heating conditions clearly indicate that the average molecular structure of the coal does not undergo major changes in functional group distribution until after most of the tar is released, at which time reactions occur in the char/metaplast that are associated with gas release.

Analysis of the elemental composition of the char, in conjunction with the determination of the extent of mass release, permits determination of the percentage of each element (C, H, N, O, and S) released in pyrolysis products (see Fig. 4). In the early stages of mass release (0 to ~10%), hydrogen and oxygen are released at a higher rate than carbon, corresponding to light hydrocarbons, H$_2$O, and CO$_2$. At intermediate extents of mass release (approximately 10 to 45%), carbon is released in a manner.

Fig. 4. Fractional elemental mass release of C, H, O, N, and S relative to the total mass release measured during devolatilization for the Illinois #6 coal studied at two different gas conditions. Carbon aromaticity is also shown.
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proportional to hydrogen and oxygen, corresponding to the region of tar release. The sulfur and nitrogen release are proportional to the carbon release, although there is some scatter due to the small samples used for ultimate analysis. During the late stages of mass release (~45 to 53%), corresponding to release of bridge fragments as light gases, the loss of carbon reaches a plateau at a value of 40%, while rapid hydrogen and oxygen release continues. The increase in carbon aromaticity, rapid release of hydrogen and oxygen, and plateau in carbon release are indicative of dehydrogenation of aliphatic ring structures. Possible gases evolving from the char during the later stages of devolatilization are \( \text{H}_2 \), \( \text{CH}_4 \), and \( \text{H}_2\text{O} \).\(^{25}\)

Evolution of Tar Structure:

The tar released from the coal undergoes further reaction in high gas temperature environments, with eventual formation of soot at long residence times.\(^{29}\) Analysis of the tars collected in this study at the 1250 K gas condition shows that the chemical structure of these tars changes as a function of residence time, in a region of little or no tar release, indicative of gas-phase chemical reaction of tar vapors. The tars collected at the 1050 K gas condition do not show such changes in chemical structure.

Aromatic Structure: Perhaps the best indication of the extent of pyrolytic transformation of evolved tars is the change in the hydrogen aromaticity (percentage of hydrogen attached to aromatic rings). The hydrogen aromaticities of tars collected at the two gas temperature conditions, measured by standard \(^1\text{H}\) NMR spectroscopy, are shown as a function of residence time in Fig. 5. The fraction of coal released as volatile material is also shown for reference. The hydrogen aromaticity of the tars collected at the 1050 K gas condition remains relatively constant at 35–40%, whereas the hydrogen aromaticity of tars collected at the 1250 K gas condition increases as the temperature increases. The hydrogen aromaticity of the tar collected at 225 ms is twice as high as the hydrogen aromaticity of the initial tar evolved at the 1250 K gas condition. The hydrogen aromaticity of the initial tar evolved seems to be independent of the gas temperature condition studied. The hydrogen aromaticity shown in this figure at 0 ms represents the hydrogen aromaticity computed from the carbon aromaticity, the amount of protonated aromatic carbon, and the elemental composition of the parent coal, and is similar to the hydrogen aromaticity of the initial tars evolved. The similarity of parent coal structure and tars evolved is expected for bituminous coals, whereas tars evolved from lower rank coals should not be similar to the parent coal.\(^{30,31}\)

The carbon aromaticity was determined for the tars from the 1250 K gas conditions from the \(^13\text{C}\) NMR spectroscopy data, and is also shown in Fig. 5. The carbon aromaticity increases from 74% to 96%, indicating the elimination of the majority of aliphatic carbon from the tars. The increase in carbon aromaticity corresponds to the increase in hydrogen aromaticity observed from the \(^1\text{H}\) NMR data. The structure of the tar at long residence times in the 1250 K gas condition is highly aromatic, with the major fraction of the aliphatic carbons comprised of methyl groups attached to aromatic rings. Aryl ether and keto groups are also observed in the final tar structure.

The \(^1\text{H}\) NMR analysis yields the percentage of hydrogen in the tar attached to 1-ring 2-rings, and 3-rings or greater, as shown in Fig 6 for the tars collected at the two different gas temperature conditions. The percentage of hydrogen in aromatic structures with three or more rings increases as a function of residence time at the 1250 K gas condition (Fig. 6a), seemingly at the expense of the hydrogen in 1-ring aromatic structures, which decreased as a function of residence time. Tars collected at a residence time of 225 ms contain twice as much hydrogen in aromatic structures with three or more rings as do the initial tars evolved at 40 to 65 ms. The hydrogen in 2-ring aromatic structures also increases substantially at this temperature condition. In contrast, the data obtained from tars collected at the 1050 K gas condition (Fig. 6b), although somewhat scattered, do not show any such trend.

Aliphatic Structure: The aliphatic hydrogen attached to carbons at the \( \alpha \), \( \beta \), and \( \gamma \) positions (relative to the closest aromatic group), as measured by \(^1\text{H}\) NMR, was resolved into methyl groups (\( \text{CH}_3 \)) and the combination of \( \text{CH} \) and \( \text{CH}_2 \) groups. The

![Fig. 5. Percentage of hydrogen contained in aromatic groups in the tar versus residence time for the two different gas temperature condition are also shown. The hydrogen and carbon aromaticities at 0% mass release are taken from analysis of the parent coal.](image-url)
hydrogen in the β and γ positions decreases from 19% to 4% in the same time period, as shown in Fig. 7. These data indicate preferential release of β- and γ-hydrogen relative to α-hydrogen, and that CH₃ groups are released preferentially to CH and CH₂ groups. The release of aliphatic chain ends is more energetically favored than breakage of fairly stable aliphatic bridges and loops between aromatic structures.

**Conclusion**

Based on the NMR analyses of the tar and char formed during devolatilization of an Illinois #6 coal, the following conclusions are reached:

1. The number of bridges and loops attached to each aromatic cluster in the char remains constant during the period of rapid mass release (i.e., tar release), and gradually increases at longer residence times and at higher temperatures, accompanied by little or no mass release. The average cluster size in the chars also remains relatively constant during the tar release period, followed by modest (40%) increases at longer residence times. This implies that at the rapid heating conditions in this study, the crosslinking between aromatic clusters and associated cluster growth are slow compared with the tar release rate.

2. Tar vapors change chemical structure at 1250 K by releasing aliphatic groups (preferably from the β and γ locations) and by aromatic ring condensation, whereas only small changes in the chemical structure of the tar occur at 1050 K. Gas-phase thermal decomposition of tars at 1250 K is more rapid than changes in chemical structure in corresponding char particles. For example, the carbon-aromaticity of the tar increases from 74% to 96% at 1250 K in approximately 150 ms, while 75% of the mass release occurs in 40 ms. The NMR data help quantify both the temperature regimes and mechanisms associated with tar decomposition and soot formation from coal pyrolysis products in rapid-heating conditions.

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