CHARACTERIZATION OF PYROLYZED LIGNIN CHARS
FOR USE IN A NOVEL FOUNDRY FUEL SOURCE

A Thesis in
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by
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ABSTRACT

Briquettes containing 86-92% anthracite fines, 2.3-8.6% lignin, 4.5% silicon metal powder, and 0.9% hydrolyzed collagen (gelatin) by mass have been investigated as a promising coke replacement in the foundry industry. The inclusion of lignin is important; we hypothesize it thermally fuses, providing the necessary strength for the briquettes to maintain their structural integrity throughout the extremely harsh pyrolitic conditions of the foundry’s cupola furnace. In order to mimic the cupola environment, eucalyptus hardwood lignin has been pyrolyzed at a series of temperatures ranging from 300°C to 800°C for either 5, 10, or 20 minutes. Following pyrolysis the lignin samples were subjected to nuclear magnetic resonance spectroscopy (NMR), pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS), X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDS), and Raman spectroscopy to gain insight into either the reaction mechanism or the structure of the resultant lignin char. The results of these techniques indicate that the content of aromatic carbon within the lignin increases from 54.1% to 95.6% between the control (un-pyrolyzed) lignin and the lignin pyrolyzed at 500°C for 20 minutes. The average distance between aromatic carbons and their nearest hydrogen atom also increased, indicating the size of aromatic domains is increasing. The XRD data indicate that while the lignin has not become ordered and aromatic enough to be considered “graphitic”, the order and crystallinity is increasing and was trending in the direction of graphite. The diffraction pattern of the 800°C sample roughly resembled the patterns of soots and glassy carbon. Similarly, the Raman spectra of samples pyrolyzed from 400°C to 800°C indicate that the lignin was becoming more ordered; the disordered (D) and graphitic (G) peaks became more defined within samples pyrolyzed at high temperature. The samples did not reach a high level of graphitization but contained ordered aromatic regimes.
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PREFACE

This thesis begins with a brief project overview (Ch. 1) followed by a literature review (Ch. 2). Chapters 3 and 4 will be slightly revised, updated, and submitted as journal papers. Chapter 5 summarizes the results of recent foundry demonstrations. It will also likely be published. Finally, Chapter 6 summarizes key findings and suggests avenues for further work. References are compiled at the end of the document.
ACKNOWLEDGMENTS

I would like to thank Dr. Fred Cannon and Dr. Nicole Brown for their insight, assistance, and the opportunity to work on this research endeavor alongside them. They have both been fantastic advisors and I have cherished the opportunity to work in their labs for the past two years. I would also like to thank those who have trained me and helped me acquire data. This includes but is probably not limited to Drs. Alan Benesi, Wenbin Luo, Emmanuel Hatzakis for assisting with NMR, Nichole Wonderling and Julie Anderson for their help with XRD and EDS, Nicole Labbé and Priyanka Bhattacharya for their assistance with Py-GC-MS, and Joe Stitt for his assistance collecting Raman spectroscopy data. Their assistance throughout this project has been critical to its success. Finally, I would like to thank my family, friends, and labmates for their constant support.

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Chapter 1: Project Overview

1.1 Executive Summary

This study aims to characterize the transformation of lignin under pyrolysis conditions, simulating a cupola furnace environment, to help explain lignin’s ability to serve as a foundry fuel binder. The lignin is hypothesized to be effective as a fusing binder in a foundry coke replacement, but a deeper understanding of the chemical transformation of lignin in the cupola environment (after exposure to steep temperature ramps in pyrolitic environments) is desired.

1.2 Background

Lignin (Figure 1.1) is a complex polymer found in terrestrial plants, constituting 30 percent of all non-fossil organic carbon (1). The function of lignin within the plant is to provide a rigid structure particularly as a reinforcement to conductive vascular tissues, and allowing the trees to maintain their form. Lignin has many attributes that have limited its utility. It is a very heterogeneous polymer, and common extraction methods further degrade the polymer into fragments. Lignin has high potential in many fields, but especially in the realm of renewable energy. However, part of the reason lignin hasn’t been more widely utilized is because its structure, properties, and capabilities are not completely understood.

Figure 1.1: A representative hardwood lignin structure (2); the precise structure in planta is not known. This figure is a model of an extracted lignin fragment.
Figure 1.2: Diagram of a cupola furnace used in some foundries (3).

One specific application for lignin is being studied here - foundries. Specifically, we are trying to replace the coked bituminous coal fuel source used in cupola furnaces (Figure 1.2) with a briquetted anthracite source, using lignin extracted from Kraft black liquor as a fusing binder to adequately increase the strength properties (4). Substitutes for foundry coke have been investigated in the past, but never with the inclusion of lignin. Coke provides a high mechanical strength, a porous structure to provide even burning, and a low volatile content. The motivation for this replacement with anthracite is multi-faceted. The briquetted anthracite does not need to go through the coking process, thus saving 15-20% efficiency for the overall process (5). Utilization of the proposed lignin-bindered anthracite fuel would be a cleaner process, as the coking procedure is very highly emissive (6). Coke providers have been limited by strict regulations in America, due to the pollution inherent with the coking process. There is also a cost factor; obtaining anthracite fines (which have little worth on their own) is a much cheaper acquisition than purchasing coked bituminous coal, which has greatly increased in price over the past several years (5). This cost increase has been driving the search for a cheaper and cleaner cupola fuel source. Lignin is able to serve as a fusing binder, but also as a fuel source, providing 9,100 BTU, as compared to 11,000-15000 BTU provided by anthracite (7).
Preliminary trials have indicated that the lignin-bindered anthracite briquettes have been effective as a fuel source. The next step is to understand, on a molecular level, what is occurring during pyrolysis within the cupola. It is important to study the transitions experienced by the lignin within the pyrolysis conditions within the cupola, to understand its ability to perform the critical role as anthracite binder. To do this, it is necessary to perform an extensive characterization of lignin, within a simulated cupola environment, where a temperature gradient ranging from non-pyrolyzed conditions to 1600°C (in the absence of oxygen) would be experienced. Particularly of interest is the range of 300-500°C, as this is where primary thermal transformation occurs. These transitions are being studied on pure extracted lignin via a variety of analytical techniques including solid-state NMR, pyrolysis-GC-MS, XPS, Raman spectroscopy, and EDS in an attempt to fully characterize the transitions undertaken by the lignin and the gaseous, tar, and char products of these transitions.

Figure 1.3: Effect of pyrolysis temperature and time on the strength of post pyrolysis eucalyptus hardwood lignin. Briquette used 69 MPa precrushed anthracite, contained 0.23% gelatin, 4.5% eucalyptus hardwood lignin, 4.5% silicon metal powder, and was compacted at 69 MPa (4).
1.3 Research Objectives

1. Observe the changing carbon functionalities (methoxyl, Ar-O, Ar-C,H, propyl side chain, carbonyl) semi-quantitatively within the lignin as it is pyrolyzed at a series of temperatures and times.

2. Determine the density of carbon and the degrees of poly-aromaticity and order within the post-pyrolysis lignin char.

3. Study the molecular mechanism of lignin pyrolysis by determining what gases and tars are evolved throughout pyrolysis at various temperatures for both softwood and hardwood lignin.

4. Evaluate lignin-bound anthracite briquettes as a foundry fuel source via full-scale industrial demonstrations.
Chapter 2: Literature Review

The reason for the inclusion of lignin is to use its capabilities as a binder to provide the required briquette strength and add to the reducing nature of the cupola. The anthracite coal briquettes need to provide the proper mechanical strength to maintain structure throughout the cupola furnace, under the immense weight of layered metal and fuel, until burning is to take place. The dwell time in the cupola is 45-90 minutes, depending on its dimensions. Throughout loading into the cupola and dwell time, the briquettes are subjected to harsh treatment. In the “drop zone”, the fuel source is dropped into the cupola from several meters up, and in the heat zone, the carbon source is subjected to temperatures up to 1400-1500°C. The lignin-bindered briquettes have been proven to provide strength in the cupola’s “heat zone” from about 300-900°C, as shown in Figure 1.3 via unconfined compressive strength tests after pyrolysis at high temperatures (4). Outside that zone, strength is provided by other additives. Above 900°C, the ~4.5% silicon metal powder in the briquettes leads to the formation of silicon carbide nanowires.

![Figure 2.1: A and B) Images of products formed during pyrolysis of a compact of anthracites, lignin, silicon metal powder (2.8 weight percent) and collagen compressed at 5,000 psi at regions of low density deposition (A) and high density deposition (B) (Courtesy of Allura Jiles).](image-url)
which provide the necessary strength, and below 300°C the addition of 0.9% denatured collagen does such (5, 8). As the briquettes, containing between 2.3% and 8.6% lignin, are being heated to high temperatures in the absence of oxygen, thermal transitions are taking place, allowing the lignin to provide this strength. This thermal degradation results in a number of gases and volatile aromatic products (often in the form of tar, or bio-oil), while leaving behind a char comprised of fused aromatic rings. In addition to providing mechanical strength, the lignin would also help provide the reduction capacity required within the furnace. This is a very critical function of the cupola furnace as the ore must be reduced. Likewise, the added silica must also be reduced to silicon carbide, which, as previously mentioned, is necessary to provide strength above 900°C. Without a reducing environment within the cupola, proper operation would be impossible, due to the product not meeting required specifications.

Lignin itself is comprised of three monolignols; primarily coniferyl alcohol in softwood lignin and a mixture of coniferyl alcohol and sinapyl alcohol in hardwood lignin (9). Each of these monolignols contains an aromatic ring, but throughout pyrolysis certain functionalities are being broken off the lignin backbone, and aromatic rings are fusing together, eventually forming a poly-aromatic carbonaceous char (11). Direct analysis of the char is difficult, due to its insolubility in virtually any solvent.

The mechanism of lignin pyrolysis has been shown to occur in a series of three steps (12, 13). Throughout these three steps, three products will be mentioned; the gaseous product, the tar product, and the carbonaceous char. The weight loss of Kraft lignin prior to 150°C has been almost entirely

![Figure 2.2: The monolignols that form lignin (10).](image-url)
attributed to the evaporation of water, and loss of water via dehydration reactions (12, 13). The TG-FTIR study completed by Shen et al. states that following this preliminary stage, alkyl groups are readily released from the lignin polymer, beginning at about 200°C and reaching a maximum at 270°C (12). The release of alkyl groups characterizes the second step of lignin pyrolysis. This shows

Figure 2.3: TG (a) and DTG (b) curves of lignin at heating rates of 20 K/min and 40 K/min (12).

that most volatile aromatic products (guaiacol or syringol derivatives, alkyl-substituted phenols) evolved throughout pyrolysis are lost in this stage (12). The evolution of methanol is still relatively low in this secondary step. What methanol is released originates from cleavage of the side-chain gamma carbon, when attached to a terminal hydroxyl group; it does not come from the aromatic methoxy constituents (14). The aromatic methoxyl bonds remain strong enough to withstand these temperatures. They are not cleaved until the third stage of lignin pyrolysis with a maximum at 380°C (12). These groups also lead to the evolution of methane. Methane is first observed at 340°C, with maxima at 430°C and 535°C. Coupled to this evolution, methanol formation reduces after 390°C. This indicates that methanol formation is closely related to, and
likely a precursor to, methane evolution (12). The second methane maximum occurs at 535°C and might be generated from the cracking of primary compounds (12). Though the mechanism of cleavage is not well characterized, it is important to note that CO₂ is also being evolved at temperatures of 220-570°C (12).

At temperatures exceeding ~650°C, the tar yield declines, while the yield of gaseous product increases. This is likely due to the secondary cracking of aromatic compounds in the tar (12). Due to the cracking of active substituent groups (primarily methoxy), yield of guaiacol, syringol, and other substituted aromatic rings decreases throughout this high temperature range, while phenol-type, cresol-type, and catechol-type derivatives increase. Shen et al. describe these specific mechanisms in detail (12). The char fraction remains relatively constant, at approximately 36% yield, after this temperature (12).

![Figure 2.4: Yield of gas, bio-oil, and char products from pyrolysis of lignin at increasing temperatures (12).](image)

It is vital to not only determine what chemicals are evolved from the lignin, but also the mechanism of volatile evolution and char formation. It has been shown that the methoxyl constituents of the lignin are critical for the formation of char (15). A series of monomers was pyrolyzed by Hosoya et al. and it was discovered via GC-MS analysis that the compounds without methoxy groups did not form char while those with methoxy content all formed char. It is likely that homolysis within the methoxy (forming methoxyl radicals) constituents within the secondary stage of lignin pyrolysis serves as the initiation of this pathway (11). This homolysis then leads to free radical recombinations (11). In Figure 2.5, a proposed degradation pathway of guaiacol (coniferyl alcohol without the propyl side chain) is shown (15). The yield of char via this pathway for pyrolyzed guaiacol is ~17%. Asmadi et al. has shown that the additional methoxy constituents in syringol (sinapyl alcohol without the propyl side chain), which is present in hardwood lignin, lead to increased char formation (11).

Many authors have taken a deeper look at the effect of methoxy substituents in lignin

![Figure 2.5: Proposed pyrolysis pathway of guaiacol and syringol (15).](image-url)
model compounds (12, 16-18). In addition to characterizing the radical-induced pyrolysis mechanism of phenethyl phenyl ether (PPE), a lignin model compound, a study conducted by Britt et al. also showed that the substitution of a methoxy constituent to the para- or ortho-position of PPE increased the rate of conversion to various pyrolyzed products by a factor of 4.7 (16). Adding methoxy constituents to both ortho-positions on the phenyl ring has a multiplicative effect: Rather than a factor of 4.7, the rate of reaction increased by a factor of 25. The reason for this increase in reactivity of PPE is due to the oxygenated, aromatic constituents weakening the bond of the ether linkage, the homolysis of which is the initiation step for pyrolytic transformation (16). The addition of a hydroxyl group to the opposite ring of PPE increased the rate of transition by a factor of 7.8. This is also important, as this is a realistic substitution when considering the structure of the complete lignin polymer (16). This study suggests that aromatic substituents within the structure of lignin vastly increase the pyrolytic reaction rates as compared with the basic PPE molecule. The results of this study are summarized in Table 2.1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Rate (% h⁻¹)</th>
<th>Rel rate</th>
<th>Selectivity (α/β)</th>
<th>Rel Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.7 ± 0.2</td>
<td>1.0</td>
<td>3.8 ± 0.3</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>8.0 ± 0.2</td>
<td>4.7</td>
<td>4.6 ± 0.1</td>
<td>1.2</td>
</tr>
<tr>
<td>3</td>
<td>10.7 ± 1.0</td>
<td>6.3</td>
<td>3.0 ± 0.03</td>
<td>0.8</td>
</tr>
<tr>
<td>4</td>
<td>42.1 ± 3.1</td>
<td>25</td>
<td>7.3 ± 0.4</td>
<td>1.9</td>
</tr>
<tr>
<td>5</td>
<td>13.1 ± 2.8</td>
<td>7.8</td>
<td>5.1 ± 0.1</td>
<td>1.3</td>
</tr>
<tr>
<td>6</td>
<td>3.2 ± 0.1</td>
<td>1.9</td>
<td>7.4 ± 0.3</td>
<td>1.9</td>
</tr>
<tr>
<td>7</td>
<td>41.9 ± 8.2</td>
<td>25</td>
<td>6.6 ± 0.6</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table 2.1: Pyrolysis rates and selectivities at 345 °C for substituted phenethyl phenyl ether (PPE) (16).
Most relevant to our project is the characterization of what is left behind: the char. There has been a variety of research done on model compounds to characterize how this char is able to form, and how it rearranges and condenses at extremely high temperatures (19-24).

Previously published studies have shown characterized products of, and explained mechanisms for, pyrolysis of model compounds representative of solid fuel moieties such as catechol (21-25). These studies have shown that a variety of polycyclic aromatic hydrocarbon (PAH) products is evolved from the model compound when pyrolyzed at high temperatures. This process is thought to occur via a heat-induced carbonization process where the organic char undergoes a rearrangement, condensing its aromatic moieties and releasing PAHs (23). PAH evolution is reported to occur in temperature ranges of 450°C to 550°C and also at higher

![Figure 2.6: Evolution profiles for 4-5 ring polycyclic aromatic hydrocarbons: fluoranthene, pyrene, chrysene, benzo[a]anthracene, and benzo[a]pyrene over the temperature range of 300-650°C (22).](image-url)
temperatures of 700-900°C (19, 22, 23, 25, 26). Either there exist two steps in PAH formation, in different temperature ranges, or the methods reported in various studies (residence time, etc.) were different such that the activation energy of rearrangement and PAH formation was achieved at varying temperatures. As expected, the activation energy values for formation of PAHs are directly proportional to the size (number of rings) of the molecules (25).

It has been proven that the char from organic compounds such as cellulose and lignin is densely aromatic after ~400°C (22, 27). It is also evident that the aromatic regimes are changing orientation throughout higher temperatures. Knowledge of this carbonization mechanism is very valuable to this study.

Catechol is representative of structures of monolignols present in lignin. Wornat et al. reported that pyrolysis of catechol at 1000°C resulted in the evolution of 59 individual PAH
species, ranging in size from one to eight fused aromatic rings (24). The mechanism of catechol pyrolysis has been widely studied. It is well documented that ring-growth reactions involving catechol species are commonly initiated by H-abstraction and addition of C$_2$H$_2$, acetylene (21, 25). Acetylene is a common product of catechol pyrolysis, so it is likely that catechol would be prone to forming PAHs. Subsequent acetylene additions result in the continued growth of the ring structure, likely by initiating the addition of single-ring aromatics (28).

Due to its heterogeneous and complex structure, pyrolysis of lignin leads to a wider variety of products, including many small hydrocarbon species like methane, ethane, ethylene, propylene, and acetylene (among others) (25). In cellulose, and likely lignin, an increase in

Figure 2.8: Reversed-phase HPLC chromatogram of the products of catechol pyrolyzed at 1000 °C in a high temperature laminar flow reactor (24).
pyrolysis temperature leads to an increase in reactive small molecules and radical ultimately

leading to recombination of aromatic radicals and bridging between aromatic moieties by cross-linking via –CH₂-, -C-C-, and C-O-C groups (22). The cleavage of these cross-links at higher temperatures leads to the release of PAHs (22). It is logical that the smaller PAHs would be released at a lower temperature, and as the cluster sizes within the lignin increase at higher temperatures, so would the evolved PAHs (22). It also makes sense that the evolution of PAHs occurs simultaneously with the third stage of lignin pyrolysis outlined earlier. The reactive molecules released during that time are necessary to build PAHs (23). Eventually the physical size of the aromatic moieties would prevent their evolution from the solid char, allowing further carbonization and densification at temperatures upwards of 700°C. There is some evidence that larger PAHs are formed at temperatures of 900-950°C through secondary reactions (26). These studies were conducted with very low pyrolysis times though, whereas our study discusses residence times practical for a cupola furnace, which is on the order of minutes rather than

Figure 2.9: Yields of CO and acetylene as a function of pyrolysis temperature (21).
seconds, or microseconds. The same reaction rate constant necessary to cause these high temperature transitions might be achieved at lower temperatures.

This mechanism and knowledge of evolved PAH species is important, but what is of greater interest is knowledge of the residual carbonized material after extreme temperature pyrolysis. There has been limited work done in this field, as characterization of these chars is difficult. While the evolved PAHs of model compounds (e.g. catechol) were soluble and able to be analyzed by techniques such as HPLC and GC-MS, the lignin char is insoluble. This is consistent with extensive aromatic systems, which are difficult to solubilize. It is an understanding of the properties of this extensive polyaromatic structure that has thus far escaped us.

Aside from using analytical techniques to confirm that it consists almost entirely of aromatic carbon, a large portion of the characterization done on pyrolitic chars has been done using SEM imaging (13, 27). Sharma et al. studied char pyrolyzed at 250°C and explained that the polygonal lignin particles had softened, melted and fused into a mass of matrix and vesicles (27). Vesicles are caused from the release of gaseous products; when discussing the low-temperature samples, probably a large portion of these are from water vapor (27). Vesicle formation increased with an increase in pyrolysis temperature. Chars formed at temperatures of over 550°C exhibited a brittle nature and conchoidal and planar fractures (common with amorphous solids) (27). Vesicle formation and deformation occurred up to temperatures of 950°C (the maximum temperature in the SEM studies), indicating that chemical transformation is indeed occurring at such temperatures (13, 27). The 850°C char exhibited visible carbon
Figure 2.10. SEM micrographs of lignin (a) and its pyrolysis chars at various temperatures (b, c, d, e) (27).

Figure 2.11. SEM micrographs of lignin and its chars pyrolyzed at various temperatures (a, b – control; c – 550 C; d – 650 C; e – 750 C; f – 850 C; g – 950 C) (13).
structure ordering on its surface (13). The 950°C sample indicated that further ordering had taken place (13). This is an important discovery, as this order among the char likely helps to provide the strength within the anthracite foundry fuel.

As stated previously, it has been shown that the formation of char is directly dependent upon the methoxy functionalities in the lignin (15). That being said, there should be differences in the mechanism and product yields of softwood lignin vs. hardwood lignin, as their monolignol content and therefore methoxy content differs. Hardwood lignin has been proven to be the stronger binder for the foundry application (4). Pyrolysis at a series of temperatures has shown that softwood lignin actually yields a slightly higher char yield for samples pyrolyzed at and exceeding 400°C (29). This makes sense, because (as stated previously) hardwood lignin has a greater mass percentage of methoxy groups, due to the presence of syringol, which would be cleaved around this temperature. This would lead to a lower char mass. It is still a mystery as to the difference in binder strength between hardwood and softwood lignin, but it likely corresponds with the difference in methoxy content. In the presence of anthracite coal fines, it is also possible that the lignin is able to fuse to the anthracite grains during thermally induced rearrangement and carbon ordering. This would certainly help to provide an explanation for the increased strength.
Chapter 3: Study of the pyrolytic reactions of lignin for foundry fuel application

3.1 Introduction

Lignin is an amorphous, propylphenol-based polymer that provides structural support to woody plants. Lignin, which constitutes about 1/3 of the plant, allows plants to grow tall, by imparting the necessary strength and rigidity to reinforce vascular tissues, facilitating water conduction (1). Softwood lignin is primarily derived from coniferyl alcohol units whereas hardwood lignin contains both coniferyl alcohol and sinapyl alcohol units (9). Due to a lack of complete characterization of lignin’s structure in plants and its heterogeneous nature when extracted, lignin has become an under-utilized and widely available resource. Lignin is a major

byproduct of the paper milling industry, and is primarily burned for its moderate heating value. Increasing the value of lignin will help drive the economic feasibility of all lignocellulosic processing operations. Lignin has potential in many fields, but especially in the realm of renewable energy.

Figure 3.1: The three monolignols that comprise the lignin polymer (a) and a representative structure of lignin (b) (2, 10).
A prior study has shown that, when combined with anthracite fines in a cylindrical briquetted form, a small quantity of lignin (2.3-8.6%) can be an effective binder, allowing the anthracite to be used as an alternative fuel source in the cupola furnace of a foundry (4). The lignin is not just a binder, however; it is also able to serve as a fuel source, providing 9,100 BTU, as compared to 11,000-15,000 BTU provided by anthracite (7). These anthracite-based briquettes also employ a number of ‘waste’ materials, including both the lignin and anthracite, making these ingredients cheap and readily available. In comparison, the current cupola fuel source is a coked bituminous coal. The necessary transformation of bituminous coal to coke is an expensive and highly polluting process which involves pyrolysis of the coal at 1000°C for 16-36 hours (5). This coking pre-treatment reduces the energy efficiency of the overall process by 15-20%, and environmental regulations are limiting the highly polluting coke production process (6, 30). This has led to a great increase in the cost of coke over the past decade, whereas the anthracite and lignin-based briquettes use very low-value waste materials (5).

In anthracite briquettes, the coking is not needed, as the briquettes exhibit an adequately porous nature without pre-treatment. The briquettes are able to retain their structural integrity, withstanding increasing pressure and temperature throughout the 45-90 minute dwell time in the cupola, and will be described later in the discussion of the full-scale foundry demonstrations. This was proven via unconfined compressive strength studies (4). In the “drop zone” of a cupola furnace, the fuel source is dropped into the cupola from several meters up, and

Figure 3.2 An iron foundry cupola (37).
in the heat zone, the carbon source is subjected to temperatures up to 1400°C. The briquettes need to maintain form and avoid ‘blowout’ throughout the drop zone and the heat zone, until the melt zone, where the temperature rapidly increases to 1600°C. This is where oxygen enters the cupola through tuyeres and the burning of the fuel and melting of scrap metal takes place. We hypothesize the lignin provides strength from about 300°C-1000°C, while other components provide strength in other temperature regions. Within the cupola, the briquettes are in a starved oxygen atmosphere, and undergo pyrolysis as the temperatures increase. This pyrolysis process forces the lignin to undergo a thermal transition. The pyrolysis of lignin has been studied via thermogravimetry, and most mass is lost in the 350-400°C range (31).

It appears that the lignin is evolving into a system of fused aromatic rings, creating a much denser, carbonaceous char structure (32). Cao has shown that pyrolysis occurs between 200 and 500°C, and between 500 and 900°C C-C and C-H bonds begin to break to form an amorphous carbon structure (33). Above 900°C, the structure becomes even more graphitic. This was proven showing a massive reduction in electrical resistivity of the lignin char throughout pyrolysis (33). This char-creating transformation occurring between 200°C and 500°C is likely propagated by the loss of certain functionalities from the lignin during the rapid temperature ramp of the pyrolysis process (11). Recently, it’s been shown that the presence of methoxy constituents within the lignin allows the formation of char upon pyrolysis (15). It is likely that homolysis of the C-O bonds between the methoxyl oxygen atoms and the aromatic carbon at approximately 400°C serves as the initiation of this pathway (11). This homolysis then leads to free radical recombinations, ultimately, leading to char formation (11, 15). It is important to fully understand this transition, and to characterize the resulting structure of the lignin under the pyrolitic conditions we are employing. This can be done using a variety of
analytical techniques, including $^{13}$C CP-MAS NMR spectroscopy, Raman spectroscopy, and pyrolysis-GC-MS. It is important to note that the studies were done using pure lignin, in an effort to characterize how the lignin itself is changing throughout a steep temperature ramp. It would be difficult or impossible to determine how the lignin (only 2.3-8.6%) is transforming when analyzing the briquetted combination (which contains ~90% anthracite fines).

3.2 Materials and Methods

3.2.1 Lignin Purification

Eucalyptus hardwood Kraft lignin was acquired from Innventia (Stockholm, Sweden). Lignin obtained from Innventia was comprised of less than one percent carbohydrates, and was approximately 40 percent water by weight. The lignin had been extracted via the LignoBoost™ process (by Innventia) and following arrival at The Pennsylvania State University, it was dried for 24-48 hours at 55°C and sieved to pass a US mesh #40 (< 425 μm) filter.

3.2.2 Pyrolysis

In order to simulate the cupola’s physical environment, the lignin samples were pyrolyzed in an Applied Test Systems, Inc. series 3210 fluidized bed furnace. Samples were pyrolyzed for either 5, 10 or 20 minutes at each of 300°C, 400°C and 500°C, resulting in a total of nine samples. Lignin samples of 0.3 g were individually placed in a glass vessel and positioned in the furnace glass tube. The furnace was preheated to the set temperature before the glass tube and lignin vessel were inserted. The samples, under steady nitrogen flow, were then pyrolyzed for either 5, 10 or 20 minutes, and following this, the furnace was cooled down with a
fan to 100°C at a declining rate of 15-50°C/min, based on hold temperature. Samples were stored individually in glass containers at room temperature.

3.2.3 $^{13}$C CP-MAS NMR spectroscopy

The solid-state $^{13}$C CP-MAS NMR spectra were acquired on a Bruker UltraShield 300 MHz spectrometer at a carbon resonance frequency of 75.5 MHz. This was done using a Bruker double resonance MAS (magic angle spinning) probe. The MAS spinning speed was 5000 Hz. A zirconium dioxide rotor was packed with 55 mg of pyrolyzed lignin and 15 mg of tetrakis(trimethylsilyl)silane (TKS) (Sigma-Aldrich) which was utilized as an internal standard. Ten lignin samples pyrolyzed at different times and temperatures were analyzed. The specified parameters allowed the instrument to achieve total suppression of side bands (TOSS). The cross-polarization contact time was 1000 µs, while a relaxation time of 5 seconds was used. The number of scans was 16,384 for each sample, and each sample required ~24 hours to run. Spectral peaks were identified according to the literature (34). Using known peak assignments, curve fitting analyses were performed in Spinworks in order to compare amounts of carbon functionalities, relative to the TKS standard.

3.2.4 Raman Spectroscopy

Raman spectra were acquired using a WITec CRM 200 confocal Raman microscope equipped with a 40X (NA = 0.6) objective. A 488 nm argon ion laser was used for excitation. The spectra were recorded by an AndOr DV401-BV CCD camera attached to an Acton Research Corporation SpectraPro-2300i spectrometer using the 600 g/mm diffraction grating. The integration time for each spectrum was 30 seconds. Each sample was pressed onto a strip of
double-sided tape for attachment to a glass slide. Each sample was observed at 4 locations, and
the average of those 4 spectra is reported here.

3.2.5 GC-MS

Samples were pyrolysed at both 450°C and 600°C for 12 seconds using a Frontier
single shot pyrolyser system. Gas evolved during pyrolysis was analysed with a Perkin Elmer
Clarus 680 gas chromatograph coupled with a Clarus SQ 8C mass spectrometer. The GC initial
oven temperature was 50°C. It was held at that temperature for 2 minutes and was then heated at
a 6°C/min rate to 270°C. An Elite 17 MS column (30 x 0.25 x 0.25) was used for the analysis.

3.3 Results and Discussion

3.3.1 $^{13}$C CP-MAS NMR

A solid-state $^{13}$C CP-MAS NMR spectrum was acquired for each of nine pyrolyzed
hardwood lignin chars, in addition to the control lignin sample as a control. The spectrum for the

![Figure 3.3: $^{13}$C CP-MAS NMR spectrum of the control hardwood lignin with TKS
standard, showing functional group peak assignments.](image-url)
control is shown in Figure 3.3. Spectral assignments were made on a functional group basis, rather than by assigning peaks to certain bonds (34); in the solid-state NMR, peaks are too broad for this type of characterization. For this study of lignin, the change in carbon functionality over a range of pyrolysis times and temperatures can provide valuable information about the progressive changes in the lignin sample. Figure 3.4 shows the series of ten spectra staggered, with the control appearing in the background and the lignin samples pyrolyzed under more extreme conditions in the foreground.

The signal integration for each carbon type was calculated using the Spinworks curve-

![Image showing 13C CP-MAS NMR spectra representing each of the pyrolyzed lignin samples.](image)

**Figure 3.4:** 13C CP-MAS NMR spectra representing each of the pyrolyzed lignin samples.

fitting analysis software, and this peak area was divided by the integration value for the TKS standard. The calculated number for each carbon type was then divided by the total integration
to obtain a percentage of the total amount of carbon comprised of each functionality.

Based on the peak assignments in Figure 3.3, it is clear that by the time the sample is pyrolyzed at 500°C, most non-aromatic carbons (signals below 100 ppm) have been evolved from the lignin as low molecular weight products. Primary decomposition of the lignin occurs between 300°C and 400°C, first evidenced in the 400°C samples, as is consistent with published data (11). The methoxyl carbon (55-56 ppm) and aliphatic carbon (1-54 ppm and 57-100 ppm) peaks rapidly decrease as pyrolysis progresses. The samples are rapidly becoming more aromatic as certain groups are volatilized in the 300-400°C range; however, the amount of aromatic carbon signal (101-140 ppm) doesn’t increase, coupled with the decrease in oxygenated functionalities, as was expected. Due to the same mass of sample being used for all NMR experiments, a similar amount of signal quantity should be evidenced with respect to the TKS.

![Figure 3.5: Peak integration for each functional group and each sample with respect to the TKS standard.](image-url)
Aromatic Me-O Aliphatic C=O Total Adjusted Aromatic Content
Control w/TKS 39.4 16.9 12.2 4.4 72.8 54.1%
HW 300C 5 min 40.3 15.0 12.9 1.2 69.4 58.1%
HW 300C 10 min 44.7 17.5 15.1 0.8 78.1 57.2%
HW 300C 20 min 41.5 15.8 12.0 0.4 69.8 59.5%
HW 400C 5 min 44.4 12.6 13.8 0 70.8 62.7%
HW 400C 10 min 40.7 12.4 8.5 0 61.6 70.1%
HW 400C 20 min 32.3 7.0 3.6 0 42.9 84.9%
HW 500C 5 min 16.5 2.2 1.5 0 20.2 94.7%
HW 500C 10 min 15.6 0.6 2.5 0 18.7 95.6%
HW 500C 20 min 23.8 0 3.4 0.2 27.4 94.9%

Table 3.1 The unitless contribution of each functionality with respect to the TKS standard is tabulated. The adjusted aromatic content is also shown.

standard, even though the pyrolysis mass loss is greater for the higher temperature samples. The total signal quantity should slightly increase following increasing pyrolysis temperature, as oxygenated moieties are being lost and the 70 mg of sample is becoming increasingly

Figure 3.6: Carbon functionality contribution for each sample, including adjusted aromatic content.
carbonaceous with harsher pyrolysis conditions (higher carbon content leading to a greater amount of \textsuperscript{13}C NMR signal). As mentioned, the aromatic signal actually begins to decrease with respect to the standard. It has been shown for \textsuperscript{13}C CP-MAS NMR on coal samples, approximately 50\% of the aromatic signal is not observed, due to problems with the spin dynamics and the presence of paramagnetic centers which results in \textsuperscript{1}H spins relaxing quickly, before polarization can be properly transferred to the \textsuperscript{13}C atoms (42, 43). Therefore, it can be assumed that the missing signal quantity in this experiment can be attributed only to aromatic carbon. Table 3.1 shows the quantity of signal that is present in each sample. The aforementioned assumption of aromaticity indicates that the 500°C, 20 minute pyrolysis sample would contain up to 95.6\% aromatic carbon, and only 4.4\% other carbon types (mostly propyl side chain aliphatics). This suggests that the lignin is indeed becoming highly aromatic, via the departure of side chain and oxygenated carbon atoms. It is likely that these aromatics have become fused into poly-aromatic domains, indicated by the elevated-temperature pyrolysis data. The size and density of these aromatics is under further investigation.

3.3.2 Pyrolysis-GC-MS

The results of the pyrolysis-GC-MS following pyrolysis at 450 and 600°C analysis offer an interesting look into the mechanism of pyrolysis and the transformation to fused polycyclic hydrocarbons. At a retention time of 1.49 min, carbon dioxide was eluted from the column; at 1.63 min methanol was eluted from the column; and at 1.83 min 1,2-ethanediol was eluted from the column. Note that compounds with an m/z ratio lower than 30 could not be observed by this

<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention Time</th>
<th>Area % at 450°C</th>
<th>Area % at 600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO\textsubscript{2}</td>
<td>1.49 min</td>
<td>4.68</td>
<td>7.58</td>
</tr>
<tr>
<td>CH\textsubscript{3}OH</td>
<td>1.63 min</td>
<td>2.31</td>
<td>4.26</td>
</tr>
<tr>
<td>CH\textsubscript{2}OHCH\textsubscript{2}OH</td>
<td>1.83 min</td>
<td>0.92</td>
<td>0.66</td>
</tr>
</tbody>
</table>

Table 3.2: Peak integration at a series of retention times.
system. Despite this limitation, useful data can be obtained by evaluating the change in percent for carbon dioxide, methanol, and 1,2-ethanediol according to the pyrolysis exposure. It should also be noted that the remaining 88-92% mass can be attributed to other higher molecular weight aromatics, such as o-cresol, phenol, ethylphenol, and benzofuran, being evolved from the lignin.

It is interesting to note that even though the ratios of carbon dioxide to methanol stayed approximately the same with increased temperature, the total percentages of each increased. This is consistent with the solid-state NMR data and also indicates that Brodin et al. were correct in assuming that a greater amount of volatiles evolved in the 500-600°C range (35).

Hosoya et al. have proven via pyrolysis of guaiacol (one of two primary monolignols present in hardwood lignin) that two common products can be formed (15). 1,2-Ethanediol can be formed via the homolysis of the oxygen-carbon bond within the methoxyl group, or via a radical induced rearrangement, where a highly reactive o-quinone methide would be formed (15). The presence of 1,2-ethanediol in these data indicates that the pathway proposed by Hosoya et al. is likely accurate (15). The quinone methides produced would be unstable and would quickly react with nearby nucleophilic constituents. Due to the nature of its reaction, the quinone methide formation only gives off water as a byproduct and would be nearly impossible to identify using this technique. As stated, the presence of 1,2-ethanediol is a clear indicator that reactive quinone methides are being created during pyrolysis. Though it is only slight, the decrease in area percent of quinone methides from 450°C to 600°C could mean the quinone methide formation has slowed, due to a lesser amount of remaining appropriate reactant. This would again agree with the solid-state NMR data, indicating that the structure is very aromatic by the time pyrolysis reaches the 500°C point.
3.3.3 Raman Spectroscopy

Our interpretation of SS-NMR results suggested increasing aromaticity within the lignin, but to further examine the structure of the pyrolyzed lignin chars, Raman spectroscopy was also employed. The spectra of various chars are shown in Figure 3.7. Due to their inherent auto-fluorescence, the spectra of samples pyrolyzed at below 400°C (including the control lignin) were omitted from the plot. When analyzing Raman data, it is important to understand the presence of both the D (disordered) and G (graphitic) bands (36). The G band typically occurs at ~1580 cm⁻¹ while the D1 band occurs at ~1360 cm⁻¹ (36). It is important to note that the overlap of D and G bands becomes less of an issue in the higher temperature samples. This is likely because of the disappearance of the D3 band, another disorder band, which occurs at ~1500 cm⁻¹ and can be attributed to amorphous carbon fragments, small organic molecules and attached functional groups within the sample. As this content decreases with harsher pyrolysis conditions (as shown previously), the overlap of the D1 and G bands would also decrease. The D3 band,

![Figure 3.7: A stacked Raman spectroscopy plot of hardwood lignin samples pyrolyzed at 400 °C – 900 °C for 5 minutes.](image)
~1500 cm\(^{-1}\) overlaps primarily with the G band; as it decreases, the G band would appear to decrease (36). This is evidenced in Figure 3.7, as the D/G ratio increases at higher temperatures. The lack of an overlapping D3 band would also lead to a sharper G band, which is also shown in the higher-temperature spectra. The lack of a significant increase in the G band indicates that the lignin isn’t becoming “graphitic” per se, but the lack or decrease of a D3 peak would indicate that the lignin is beginning a transition to a more aromatic and ordered compound. The spectra shown here resemble the spectra of other carbonaceous materials such as coke, soots, activated carbons, etc. Similar D/G ratios are also observed in the spectra of these carbonaceous materials.

3.4 Conclusions

After reviewing the analytical data, it is clear that pyrolysis of lignin results in an almost entirely aromatic product. The adjusted functional group analysis indicates the presence of very few oxygenated functionalities and non-aromatic carbon atoms. More work must be done to determine the density of the aromatic regimes within the polymer. It is also evident that the evolution of methanol and methane lead to secondary recombination reactions that are likely to provide a pathway for covalent binding to anthracite coal fines. This needs to be confirmed, but it would explain the vast increase in strength provided to the coal with the addition of lignin.
Chapter 4 Study into the extent of aromaticity of pyrolyzed lignin using X-ray diffraction and NMR

4.1 Introduction

Powder X-ray diffraction (XRD). This has become a popular method of analyzing the crystalline nature of polymer samples. The technique is based on Bragg’s Law and the fact that X-ray beams are reflected by the cleavage faces of crystalline domains at certain angles of incidence. By observing the diffraction pattern of a material, it is possible to measure the spacing between layers of atoms, the size of crystalline domains, the orientation of grains, and overall graphitization of the material (38). When XRD is coupled with an elemental analysis technique, the identification of impurities can also be gleaned.

Here, it is our goal to determine the graphitization of the pyrolyzed lignin.

Figure 4.1: XRD spectra for a variety of carbonaceous compounds, showing their resemblance to graphite (38).
XRD data are plotted as scattering intensity versus 2θ (degrees), the angle through which part of the incoming radiation is deflected. As a material becomes increasingly graphitic, the 2θ angle of the 002 peak (a primary graphite peak) begins to slightly increase from the broad range of amorphous carbon to the location of the sharp, defined peak evident in the diffractogram of graphite. Figure 4.1 shows an overlay of XRD data from various carbonaceous samples, including graphite (38). Using the X-ray wavelength and the 2θ measurement of the 002 peak, a unitless “graphitization” value of a compound can be obtained. The equation for graphitization is as follows in Equation 4.1 (39):

\[ g = \frac{3.440 - d_{002}}{3.550 - 3.354} \]  \hspace{1cm} (4.1)

The \( d_{002} \) value is obtained using Equation 4.2, where \( \lambda \) is the wavelength of X-ray radiation and \( \theta \) is acquired from the resultant diffraction pattern (40).

\[ d_{002} = \frac{\lambda}{2 \sin \theta} \]  \hspace{1cm} (4.2)

The sharpness of peaks within a diffraction pattern is a general indicator of crystalline size. The sharper the peaks are, the larger the crystalline regimes tend to be.

Determining the degree of aromaticity in the pyrolyzed lignin char is a crucial feature of this project. It has already been shown via NMR functional group analysis that the lignin is becoming increasingly aromatic with increased pyrolysis temperatures and times. What the prior data did not shed light upon was the proposed increase in the density of aromatic regimes within the polymer. A relatively new solid-state NMR technique has been proven able to distinguish between various types of aromatic residues by employing a long-range dipolar dephasing element into the NMR parameters. This method has been used by other research groups to
distinguish between various types of aromatic residues such as lignin, peat humic acid, and charcoal (41). It is based upon long-range dipolar dephasing, which is attained via the recoupling of long-range carbon-hydrogen dipolar interactions. The recoupling is achieved using two $^1H$ 180° pulses per rotation period. A single sample can be run at a series of dephasing times, and by calculating how much of the aromatic signal of interest remains in each spectrum, the slope of initial dephasing for the sample can be calculated. From this, the data are ultimately able to yield an average of the distance between all carbon atoms in the sample and their nearest hydrogen atom. This is done by running the method on a 1,8-dihydroxy-3-methylanthraquinone standard, which has various carbon atoms, each with a known C-H distance. The dephasing behavior of each carbon “type” can then be plotted against its distance from the nearest proton to obtain a constant ($k_{CH}$) (Equation 4.3), which is then plotted versus distance factor (F) to create a calibration curve. $F$ is in units of $1/\AA^3$, so the greater the $F$ value, the lower the C-H distance. Other experimental aromatic residues, such as the lignin, can be plotted onto this calibration curve.

$$k_{CH} = \frac{-\ln\left(\frac{I(0.57ms)}{I(0)}\right)}{0.57ms}$$  \hspace{1cm} (4.3)

Using the NMR data for various lignin samples of interest, an average C-H distance value can be calculated for each. The difference in C-H distance for samples of the control and pyrolyzed lignin can then be compared (41).
4.2 Materials and Methods

Acquisition of lignin is consistent with that of prior experiments. For this experiment, the control and lignin pyrolyzed at 800°C for 5 minutes (0.3 grams at a time) were used. The X-ray diffraction data were collected at 45 kV/40 mA on a PANalytical MPD (theta-theta) system using copper K-alpha radiation (wavelength 1.54059 angstroms) from 5-100 deg. 2-theta and a PIXcel detector in scanning mode with a PSD length of 3.35 deg. 2-theta and 255 active channels for a duration time of ~20 minutes. Phase identification was performed with Jade+9 software by MDI of Livermore, CA. by comparison to the ICDD and ICSD databases in conjunction with chemical composition obtained on an SEM/EDS instrument. The SEM used to image the samples was a FEI NanoSEM 630. It has spatial resolution up to 1.6 nm at 1 kV. The data were collected at 10 kV in high vacuum mode. The EDS system uses a silicon drift detector (X-MaxN) from Oxford Instruments. Aztec Analysis software was used to analyze the data.

For the NMR experiment, 1,8-dihydroxy-3-methylantraquinone (Sigma-Aldrich) was used as a calibration standard. Eucalyptus hardwood lignin was obtained from Innventia, and a portion of this lignin was pyrolyzed at 500°C for 5 minutes, as described earlier in this document. The NMR data were collected on a Bruker UltraShield 300 MHz spectrometer. The spinning speed was 7 kHz. Direct polarization was used as it is generally thought to prevent signal loss when analyzing structurally complex and carbonaceous samples, containing carbon atoms that are distant from protons and therefore would not easily cross-polarize (41). NMR pulse lengths were optimized and total suppression of sidebands (TOSS) was utilized. The number of scans was varied, but all samples were standardized for comparison. Dephasing times of 0.04 ms, 0.285 ms, and 0.57 ms were used. The signal intensity for each spectrum was obtained by acquiring the absolute integration of only the aromatic region (100-140 ppm) for
each sample. To obtain the initial rate of dephasing for the aromatic regime, aromatic signal intensity for each spectrum was plotted versus dephasing time. The $k_{CH}$ value was then plotted on the calibration curve that was created with the 1,8-dihydroxy-3-methylanthraquinone standard, to observe the distance factor, F, which is a function of average C-H distance discussed earlier. This plotting technique was carried out with a number of samples, and differences in aromaticity were observed among the samples.

4.3 Results and Discussion

4.3.1 X-ray Diffraction

The important features of the diffraction patterns collected include the position and sharpness of the 002 peak (occurring at ~26.5° for graphite) and the 101 peak (~44.6° for graphite). The data for both the control and 800 °C lignin are shown in Figure 4.3. It is clear from these diffractograms that the lignin is becoming more ordered. Graphitization values for both samples were computed, but were both negative, which indicates a very low level of graphitization. As stated previously, the location and sharpness of the 002 peak are the primary indicators of graphitic organization. While the 002 peak did not shift enough in the 800 °C spectrum to be considered graphitic, it moved closer to the graphite 002 peak at ~26.5°. The peak also became more defined than that of the control. Similarly, while the control pattern
Figure 4.3: An overlay of XRD spectra for both the control and 800 °C, 5 minute pyrolysis hardwood lignin samples.

showed no sign of a 101 peak at ~44°, the pyrolyzed 800°C sample shows a broad peak at the precise angle. Though an accurate graphitization value cannot be computed, it is clear that the lignin is beginning to undergo a transition to a less amorphous and more ordered material.

Zhao et al.’s discussion regarding graphitization of amorphous carbon compounds can help to shed light on these data (40). Zhao et al. discovered that for amorphous carbon compounds treated at high pressures, three regions are evidenced; under 900 °C is considered the non-graphitization zone, 1000-1100 °C is the near-graphitization zone, and 1200 °C is the graphitization zone (40). With the lack of a high pressure, as in the experiments documented here, the temperatures required for graphitization would be even higher than those reported by Zhao.
The impurities in the diffractograms of Figure 4.3 were found to be primarily sodium sulfate (Na₂SO₄), calcium sulfate hydrate Ca(SO₄)(H₂O)₀.₅, gypsum Ca(SO₄)(H₂O)₂, halite (NaCl) and aragonite (CaCO₃). All impurities were observed in relatively low concentration and are logical matches, based on prior elemental analysis.

4.3.2 Recoupled long-range C-H dipolar dephasing solid-state NMR

By using the 1,8-dihydroxy-3-methylanthraquinone standard and the atom assignments shown in Figure 4.3, Figure 4.4 was created. The signal intensity of each atom was plotted versus the dephasing time of each experiment. The initial decay of these curves yielded a \( k_{\text{CH}} \) value for each carbon or group of carbon atoms. The known C-H distances of these atoms was plotted versus their \( k_{\text{CH}} \) value to create a calibration curve. The effort to recreate the 1,8-
dihydroxy-3-methylanthraquinone standardization curve was successful (Figure 4.5). The slope of this curve (45.14 Å³/ms) is different than the slope observed in literature (32 Å³/ms). This variation is due to higher $k_{CH}$ values and can be attributed to instrumental differences.

![Graph showing the calibration curve](image)

**Figure 4.5: The calibration curve created using $k_{CH}$ values acquired via Equation 4.3 and the dephasing behavior of Figure 4.4.**

The data for the lignin experiments are shown in Figure 4.6. As expected, the aromatic region of the pyrolyzed lignin spectrum dephased to a lesser extent than the control. This indicates a greater C-H distance in the aromatic regimes. The $k_{CH}$ value for the control (4.59) is shifted from the literature value by approximately the same percentage as the slope of the calibration curve, indicating consistent results. The $k_{CH}$ value of the pyrolyzed lignin was 3.59. The lower $k_{CH}$ indicates a significantly greater C-H distance within the aromatic regimes of the pyrolyzed lignin. When corrected for comparison to the literature value, the $k_{CH}$ of pyrolyzed lignin exhibited approximately the same dephasing behavior of leonardite, the oxidation...
product of lignite. Calculation of an exact C-H distance is still being investigated.
Chapter 5: Foundry Trials

5.1 Materials

Anthracite fines (1.19 x 2.38 mm) were obtained from Jeddo Coal Company (Hazelton, Pennsylvania). A fraction of the anthracite was crushed to produce smaller particles which promote better packing during the briquetting procedure. Collagen was provided in granular form by Entelechy Company, which represents Hormel Foods Company (Austin, Minnesota). Before use, collagen was denatured into gelatin via water hydrolysis. Silicon metal was purchased from Sigma-Aldrich (St. Louis, Missouri) as 98.5% silicon lumps. Elemental silicon lumps (98.4% purity) from Alfa Aesar (Ward Hill, MA) were crushed into powders (less than #100 mesh).

5.2 Manufacture of Briquettes

Full scale briquettes (5.75 inch diameter x 2.25 inch height) were produced in the Furness-Newburge, Inc. shop (Versailles, KY). The dry components were mixed in 20 pound batches: 16 pounds of as received, non-crushed anthracite, 2 pounds of crushed anthracite, 1 pound of lignin and 1 pound of silicon metal. Collagen (2%, 182 g) was hydrolyzed in boiling water (700 g). The dry components were mixed in an industrial mixer for 1 minute. After that, hydrolyzed collagen (gelatin) was added drop-wise with slow mixing and finally mixed for 1 minute. The mixture was pressed using a hydraulic press at 2,000 psi. The briquettes were removed and introduced to a drying conveyor which includes ultraviolet light and infrared-blower heating. Following this, the briquettes were stored under dry conditions to avoid fungal degradation of the organic components.
A total of 8 tons of anthracite briquettes was created using this procedure. Half of the briquettes were employed in a 1 to 1 replacement (by mass) of coke during the production of malleable iron at Foundry #1. The remaining bricks were used during the production of gray iron in Foundry #2. During these demonstrations, the cupola furnaces started with 100% of metallurgical coke, with an incremental replacement by the anthracite bricks up to 25%. Each demonstration lasted for approximately 7 hours, producing iron continuously throughout this period.

5.3 Differences between laboratory-scale and foundry-scale trials

For considerations such as production time and mechanical capabilities, certain aspects of briquette manufacture do not fully translate from the laboratory scale to the larger scale discussed here. On the laboratory scale, it is a trivial task to pre-crush 100% of the received anthracite fines. However, when dealing on a massive scale, it is not rational to pre-crush all of the anthracite. Considering the strength data observed on a laboratory scale, only 20% of the anthracite used in the full-scale briquettes was pre-crushed. There is no reason to believe this would cause a major change in briquette strength or the ability of the briquettes to burn evenly. The compaction of the materials into briquetted form is another variable. On the laboratory scale, compaction pressures of 10,000 psi were used. In the full-scale briquettes, the transverse plane was greatly increased, thus requiring a vast increase in the load necessary to provide the same compaction pressure. Instead, a compaction pressure of 2,000 psi was employed. Prior research proved that 2,000 psi was capable of providing the proper briquette strength (4).
5.4 Results and Discussion

5.4.1 Foundry #1

One major result of interest is the temperature of combustion within the cupola. Historically, attempts to use anthracite as a coke replacement were thwarted by a reduction of temperature within the combustion environment. It was extremely important to maintain the correct cupola temperature by creating a fuel source which contained the appropriate porosity to allow combustion to occur at the proper rate. It was proven in the demonstration at Foundry #1 that coke replacement with anthracite briquettes did not lower the cupola temperature. Figure 5.1 shows the temperature of the cupola for a series of days using only coke and additionally, for the trial with our replacement briquettes. As seen in Figure 5.1, even though the

![Figure 5.1: Iron temperature data shown for the Foundry #1 trial and a series of other trials containing only coked fuel (courtesy of Cesar Nieto Delgado).]
portion of anthracite briquettes was incrementally increased throughout the trial, the temperature of the cupola was not affected. The data points containing both coke and anthracite fuel were within the normal temperature variance of the cupola.

Another indicator of successful replacement would be confirmation of appropriate amounts of gases exiting the cupola stack. Measurements of the amount of CO\textsubscript{2} and CO exiting the stack can help characterize the combustion occurring. Figure 5.2 shows that as the anthracite briquette fraction was increased throughout the trial, the amount of CO\textsubscript{2} gradually increased, while the amount of CO decreased. A higher percentage of CO\textsubscript{2} in gas release is an indicator of efficient combustion and high temperature, but also of a high oxidation rate of desirable elements such as iron and silicon. If the CO\textsubscript{2} composition were too high, it would indicate that these elements could be lost in the slag. A slight over-oxidation is indicated by these data, but it is important to point out that the properties of the 216 tons of malleable iron produced fell within

![Figure 5.2: Percentages of CO and CO\textsubscript{2} in the cupola stack, shown throughout the demonstration (courtesy of Cesar Nieto Delgado).]
specifications.

5.4.2 Foundry #2

Because the iron chemistry and cupola design vary between Foundry #1 and Foundry #2, the results cannot be directly compared. However, similar deductions can be made from both systems. A successful trial at Foundry #2 would indicate the anthracite briquettes were able to serve as a viable replacement at two different foundries with two separate sets of operating conditions.

Introduction of anthracite briquettes began at 6:00 am and continued until the last fuel charge containing anthracite replacement entered the cupola at 1:56 pm. Initially, 440 lbs was the total amount of fuel per charge (including anthracite briquettes and coke), and anthracite was introduced at 10%. At 9:07 am, anthracite was increased to 20%, and the total weight of each fuel charge was increased to 460 lbs. It was discovered during operation that the cupola was being over-charged with metal by up to 10%. To counteract this, the fuel charge was increased by 20 lbs. From 11:40 am to 12:50 pm, the cupola was off blast, due to lack of space for the liquid iron. At 1:26 pm, the anthracite was increased to 25% replacement, while the total fuel charge remained at 460 lbs. By 1:56 pm, there were no remaining anthracite briquettes.

Exact numbers must be withheld, but the results are as follows. The spout temperature and resulting iron chemistry values were slightly different than normal values, but were stable and within an acceptable range throughout the trial. The average carbon reading was 2.6% lower than the normal baseline reading, while the silicon reading was 6.5% higher than average baseline amount. The increased silicon is likely due to the inclusion of silicon metal in the anthracite fuel briquettes, in addition to the ferrosilicon bricks, which are part of the standard
cupola charge. Fuel ratio, the ratio of total fuel (coke and anthracite) to metal produced, was at a normal level, indicating appropriate operation of the cupola. Off-gas analysis indicated that amounts of CO, CO$_2$ and H$_2$ were within standard operating conditions. CO was slightly lower than normal (agreeing with the data collected at Foundry #1), and H$_2$ was slightly higher than baseline. The increased H$_2$ amount was a slight concern, as it increased the volatility of emissions at the cupola charge door. Slag samples were taken every 2 hours during the trial, but the slag data are not yet available. The intact anthracite briquettes could be viewed through the sight lenses at tuyere level of the furnace, visually indicating ample strength properties.

Figure 5.3: Loading of anthracite bricks during full scale demonstration at Foundry #2. A) Anthracite bricks manually loaded without any special care. B) Image of the bucket loaded with coke, limestone, ferrosilicon blocks and the anthracite bricks. C) Anthracite bricks as observed through the tuyere window. The bricks survived all the way through the cupola furnace until the melting zone (Courtesy of Cesar Nieto Delgado)
In conclusion, the second full-scale trial of coke replacement with anthracite briquettes was considered a success by cupola operators. Replacement levels of 10%, 20%, and 25% were achieved, without a drop in the quality of iron poured. Off-gas analysis showed the cupola operating within standard specifications, with slight variations in the amount of CO and H₂. The next task will be to reduce the labor-intensive briquette manufacturing process by automating the system. Once the manufacturing can consistently proceed in an automated fashion, it will become possible to provide large quantities of pressed anthracite briquettes to foundry partners.
Chapter 6: Summary and Future Work

Lignin has been shown to act as an effective binder in a foundry fuel application. In a pyrolytic environment the lignin fuses such that it allows the briquetted fuel the necessary strength to withstand the harsh conditions of a cupola furnace setting. A critical portion of this project has been to characterize the complex, thermally-induced chemical transitions occurring throughout the furnace. The study and characterization of the lignin component has been the focus of this thesis.

$^{13}$C solid-state NMR has indicated that after pyrolysis at 500°C for 20 minutes, lignin has transformed to a product where ~95% of carbon atoms are aromatic; an increase from 54.1% in the control. Furthermore, the average distance between aromatic carbons and their nearest hydrogen atom is significantly increasing. Not only is the lignin polymer becoming more aromatic, but it is evident that there is fusing of aromatic rings (as is consistent with prior studies), leading to denser aromatic regimes. XRD data have also indicated that while “graphitization” is still a term beyond the transition occurring here, a change to a more ordered structure is certainly occurring. Raman spectroscopy data are consistent with this conclusion. Further work must be done involving analysis the recently acquired NMR and XRD spectra to glean the maximum amount of value from that data.

It is important to note that the lignin-bindered fuel research project has not by any means been completed. As the fundamentals and chemistry have been much better understood in the past couple of years, much of the future work lies in the process of creating and distributing the anthracite fuel on a full scale to all foundry partners involved. Currently, the manufacture of briquettes is very labor-intensive and inefficient. While the foundries involved are excited about
the prospect of saving money and energy, they are also anxious to be among the first to install what is clearly a revolutionary fuel technology. That being said, the lignin-bindered anthracite project is very close to fruition and the transition from laboratory-scale to full-scale will soon be under way.
References


[37] Cupola image: http://www.hdowns.co.uk/hdweb_melting_page.htm


