

The Pennsylvania State University

The Graduate School

College of Engineering

**LIGNIN AS BOTH FUEL AND FUSING BINDER IN BRIQUETTED  
ANTHRACITE FINES FOR FOUNDRY COKE SUBSTITUTE**

A Thesis in

Environmental Engineering

by

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## ABSTRACT

Lignin that had been extracted from Kraft black liquor was investigated as a fusing binder in briquetted anthracite fines for a foundry coke substitute. Cupola “heat zone” pyrolytic temperatures of 300-1550°C were appraised, with the focus on 900°C. Briquettes with favorable strength were made with 86-92% anthracite fines, 2.3-8.6% lignin, 4.5% silicon metal powder, and 0.9% hydrolyzed collagen (gelatin) by mass. Briquettes were pyrolyzed under a nitrogen atmosphere or a starved air condition to simulate a cupola pyrolytic heat zone, and then crushed after this pyrolysis so as to discern their unconfined compressive (UC) strength. These tests mimicked key features of the crushing load that coke endures in a cupola. After 30 minutes of 900°C pyrolysis, UC strength reached 2,200-3,000 kPa (320 to 440 psi), when these briquettes contained 4.5% softwood lignin or 2.3% hardwood lignin. With  $\geq 6.5\%$  hardwood lignin, the UC strength after 900°C pyrolysis reached 6,000-6,500 kPa. When no lignin was incorporated to the briquette, the UC strength after 900°C pyrolysis was 200 kPa. Gelatin quantity affected lignin heat zone strength, despite by itself losing strength around 300°C: 1.8% gelatin doubled the strength of 0.45% gelatin briquettes. Lignin provided strength up to 1400°C. Moreover above 1100°C, silicon carbide nanowires greatly enhanced UC strength relative to lignin alone. Briquettes gained strength from lignin fusing reactions that increased in rate with increasing temperature. For example, at 900°C, maximum UC strength occurred within 2-3 minutes of pyrolysis. From the UC strength vs. pyrolysis temperature/time, an Arrhenius plot was constructed, which exhibited activation energies of 26-28 kJ/mol. Both the softwood and hardwood lignin briquettes exhibited the same activation energy, with the hardwood Arrhenius plot higher but parallel to that for

softwood. A manufacturing rationale for using bindered anthracite fines rather than large chunks of anthracite is to obtain a fast burning rate. The results herein showed that the bindered briquettes burned at an equal rate as did coke when these were burned at 1100°C in air. The briquettes also contained an energy density that was 38% higher by volume than that of coke. FTIR characterizations of pyrolyzed lignin showed that as temperature increased, oxygen-containing functionality decreased. Further, Raman spectra of 900°C lignin and ambient coke (commercially pyrolyzed bituminous coal) showed almost identical responses to one another, with each exhibiting both the graphitic, G, and first disorder, D, bands. Harnessing these high temperature pyrolytic lignin fusing reactions creates a valuable foundry coke substitute for the future, as well as large scale applications for otherwise underutilized industrial streams of lignin.

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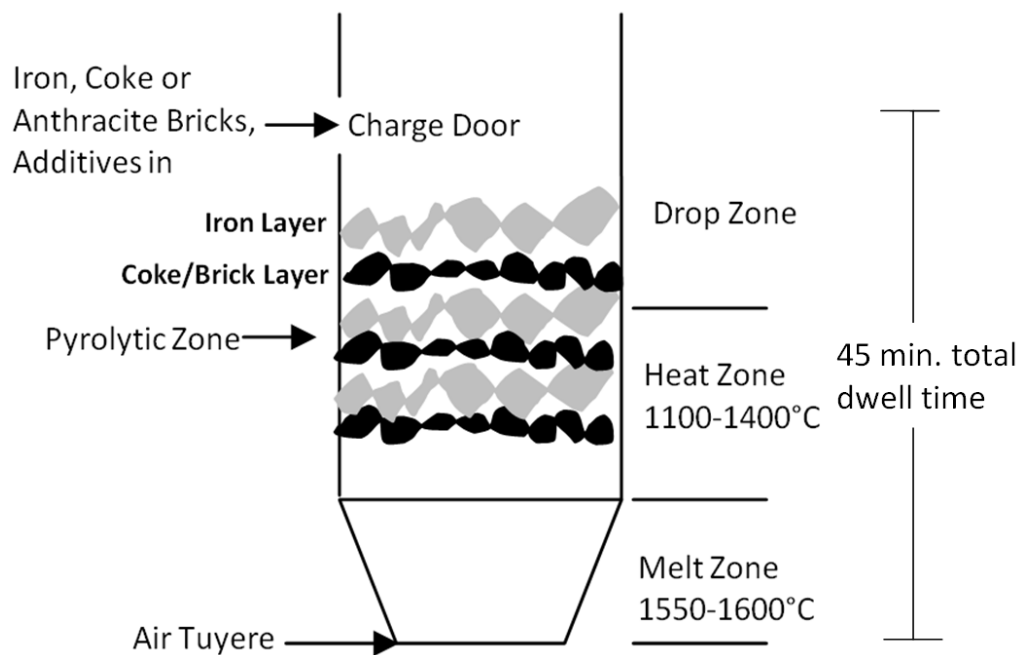
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## Chapter 1 Introduction

Foundry grade coke has long been the traditional fuel source for cupola furnaces in the foundry industry. Coke hosts high mechanical strength, a porous-matrix structure, low volatile content, and low sulfur content which make it ideal for the cupola setting. However, in producing coke, about 15-20% of coke's energy value is inherently wasted in the coking process, which requires a specific grade of fusing bituminous coal to be pyrolyzed at 1000°C for 16-36 hours (1, 2). Strict environmental regulations have limited the coke suppliers in America due to the highly polluting process of transforming coal into coke (3). Also, coke prices have dramatically risen in the past decade (2). These two factors have put pressure on the foundry industry, as they race to find a more sustainable replacement for the cupola coke fuel.



**Figure 1. Iron foundry cupola**

The coke or alternative solid carbon source must maintain structural integrity in all regions of the cupola, namely during its 45-90 minute dwell time as it proceeds through the drop zone, the heat zone, and the melt zone. Figure 1 illustrates the cupola setup. In the drop zone, coke is roughly handled, as it is dropped several meters, along with scrap iron, when charged into the cupola. This creates layers of iron and coke that compress the coke below. In the heat zone, coke is subjected to pyrolytic conditions in temperatures of up to 1,400°C, and it must not be crushed by the weight of layers of coke and metal that are dropped on top of it from above. In the melt zone, coke undergoes temperatures that can reach up to 1,550-1,600°C while still enduring compressive loads from layers above. It is important that the carbon source remain intact through all these zones, so that carbon fines are not blown out the top of the cupola by the air tuyeres and thus unburned. In the upper melt zone, the exterior of coke (or bricks) burns under oxygen enriched air, while the interior remains in a low redox state.

As an alternative to coke, the authors have engineered a bindered anthracite brick that maintains mechanical strength in all three cupola regions, and provides foundries with an alternative to conventional coke. In these bricks, gelatin (derived from animal collagen) provides drop zone strength, lignin that becomes fused in-situ provides lower drop zone and heat zone strength, and silicon carbide nanowires that grow in-situ provide lower heat zone and upper melt zone strength (2, 4). Anthracite fines have little economic worth, but when bindered into bricks, they create a valuable cupola fuel source. Lignin is a by-product of the pulping industry and may become an important byproduct of lignocellulosic bioenergy plants.

It is conventionally used as a low grade fuel source within the recovery boiler of the pulp mill, although it is gaining attention for various other applications (5). For these bricks, lignin serves as both a fuel source and also as a thermally-fusing binder that imparts strength to the bricks in the high temperature pyrolytic heat zone of the cupola.

The main objective of this work is to maximize lab scale briquette post pyrolysis heat zone strength (300-1400°C) by varying binder ingredients, ingredient amounts, and briquette properties. Various pyrolysis temperatures and times are assessed to understand the briquette strength-imparting lignin pyrolytic reactions. Briquette burn rates are also compared to conventional coke. Finally, characterization of the ambient lignin and lignin chars are performed to correlate briquette strength to characterization data.

## Chapter 2 Literature Review

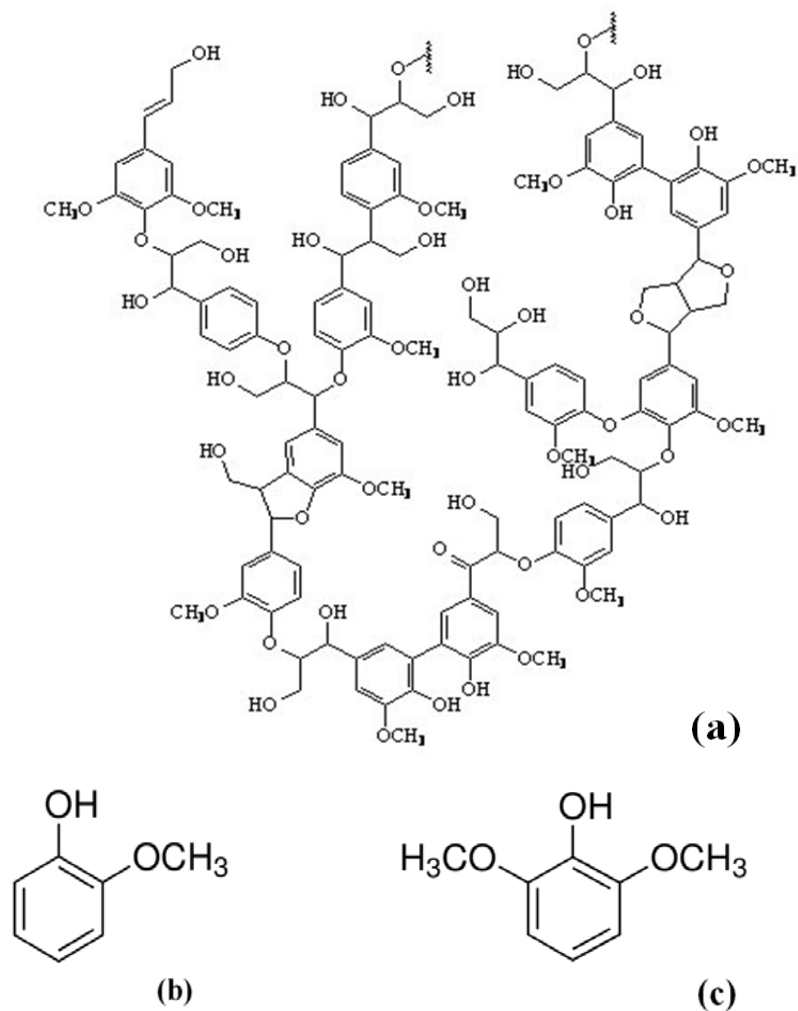
Substitutes for foundry coke have been investigated in the past, however incorporating lignin as a high temperature binder for coal fines has not been performed. There has been much research on lignin pyrolysis, however identifying its strong high temperature char fusing capability with anthracite has also not been discovered. Thus, linking this lignin feature with the cupola high temperature pyrolytic setting has produced a new coke substitute as well as provided insight into carbon chemistry.

Anthracite fuel briquettes have previously been developed using coke breeze (fines) and coal tar acid resin, however those were not produced for a foundry cupola and did not provide adequate strength (6). Adygezalov et al. developed a briquet made of coke, anthracite, and coal carbon siftings and an organic binder (7). They found that the briquettes had high thermal stability and structural strength; however details of the experimental methods or strength capacity were not given. Similarly, coke briquettes comprised of 80% coke fines, 10% cement, and 10% fly ash have been developed, but these briquettes contained higher amounts of inorganics and ash than our current anthracite briquettes (8).

Lignin has been identified as a promising carbon reducing agent in the cupola, giving it the reducing function in addition to the high temperature binding function (9). Adjusting the redox conditions in the cupola is very important, so that the iron ore and prospective silica from rice hull ash can be reduced. The high valence ore needs to be reduced to zero valence iron and the silica ( $\text{SiO}_2$  Si +4 valence) needs to be reduced to zero valence Si in silicon carbide (SiC). Anthracite has also been proposed as a carbon

reducing agent for ferroalloy production, due to its low ash content, low volatile yield, and high electrical resistivity (10).

Lignin is a heterogeneous biopolymer that is highly aromatic in nature. Softwood lignin is primarily derived from coniferyl alcohol units whereas hardwood lignin originates from both coniferyl and sinapyl alcohol units (11). Guaiacol, 2-methoxyphenol, which contains one methoxy group on the aromatic ring, is more predominant in softwood lignins. Syringol, 2,6-dimethoxyphenol, which contains two methoxys on the aromatic ring, occurs more in hardwood lignin. A model of the chemical structure of lignin (12), and the structures of guaiacol, and syringol are below.



**Figure 2. Lignin (a), guaiacol (b), and syringol (c) chemical structures**

The authors have found that the methoxy content difference between hardwood and softwood lignin may possibly play a role in the lignin binder behavior under high temperature pyrolytic conditions. Hosoya et al. found that the methoxy group was important in the pyrolytic coking process of lignin char formation (13). This char formation may be a key indicator in the bindering, fusing reaction that the lignin char provides to the anthracite. Asmadi et al. investigated high temperature ( $\leq 600^{\circ}\text{C}$ ) pyrolysis of guaiacol and syringol to elucidate lignin pyrolysis mechanisms (14). Methoxy bond homolysis was observed for both guaiacol and syringol above  $400^{\circ}\text{C}$ . By  $450^{\circ}\text{C}$ , coke formed from both compounds, but more extensively for syringol due to the extra  $\text{O-CH}_3$  group (14). Similarly, Asmadi et al. also found that hardwood lignin produced more coke than softwood lignin did under  $600^{\circ}\text{C}$  pyrolysis (15). The radicals formed from methoxy homolysis may offer an additional bonding location on the aromatic ring for hardwood lignin relative to softwood lignin.

Pyrolysis of lignin results in a variety of volatilized products, leaving behind a fused char. Much work has been done on the evolution of these volatilized products. Brodin et al. pyrolyzed Kraft lignin stepwise from  $200\text{-}900^{\circ}\text{C}$  to better understand pyrolysis products. Only small amounts of material were released at  $200\text{-}300^{\circ}\text{C}$ , which were mainly guaiacol (softwood and hardwood) and syringol (hardwood only). At  $400^{\circ}\text{C}$  hardwood lignins released large amounts of phenols, as well as maximum products released at  $500^{\circ}\text{C}$ , but nothing above  $700^{\circ}\text{C}$ . Softwood lignins released most material at  $500\text{-}600^{\circ}\text{C}$  whereas h hardwood released most at  $400^{\circ}\text{C}$  (16). Schlotzauer et al. reported similar results with the highest volatile release at  $500^{\circ}\text{C}$  consisting of guaiacol, phenol, and cresols (17). At about  $500^{\circ}\text{C}$  hydrogen gas,  $\text{H}_2$ , begins to be released due to the



rearrangement and condensation of the aromatic rings, indicating an important transformation that will be discussed later (18). Many water-soluble products are also formed from lignin pyrolysis due to the large amount of dehydration that occurs when forming water (19). This dehydration produces pyrolysis products with unsaturated side chains such as styrene derivatives and vanillin. Ultimately, the cleavage of the aromatic C-O bond leads to one oxygen atom products and the methyl C-O bond leads to two oxygen atom products. Slow heating rates favor the formation of oxygenated compounds whereas fast rates favor more hydrocarbons and alkyl-phenol compounds (20). The cupola setting offers a fast heating rate from ambient to about 700°C in seconds.

The mechanisms of these volatilizations under pyrolysis have been well researched, over a wide temperature range with the aid of lignin model compounds. Britt et al. investigated the importance of ionic reactions versus free radical reactions in the thermal degradation of lignin. Acid catalysts were used for comparison, and it was found that degradation primarily occurs by a free radical reaction pathway (21). Similarly, aryl-ether linkages cleave to form highly reactive free radicals that can form very stable products (22). Wittkowski et al. found that the propanoid side chains degraded in the 230-260°C range, subsequently forming various guaiacol compounds and vanillin (23). Ferulic acid, a lignin model compound, showed similar results with the propanoid side degradation at 240-260°C (24). The  $\beta$ - $\beta$  and C-C linkages connecting the monomeric units cleave at 275-350°C, leaving radicals that recombine to form guaiacols and syringols as intermediate products as described (25). Secondary decomposition of the guaiacols can form catechol, a compound not typically found in lignin (26).

Little work has been performed on the pyrolyzed lignin char. Sharma et al. characterized alkali lignin char based on pyrolysis temperature and found that the lignin melted and fused together starting at 250°C (27). They performed FTIR, <sup>13</sup>C CPMAS NMR, and SEM. They found that as temperature increased, the char began to form networks of fused aromatic rings at 400°C, accompanied by oxygenated functional groups diminishing, which are the beginning stages of graphitization. Precursors that form graphitizing carbons usually melt on heating to temperatures around 400-500°C, but non-graphitizing carbons generally form solid chars without melting (28). This graphitization attribute based on melting may be a key indicator of lignin pyrolytic bonding behavior. Wang and Low pyrolyzed kraft pine softwood lignin in vacuo to 700°C and discerned two pyrolysis stages (29). Up to 450°C, aliphatics and small fragments fused with single aromatics to form polyaromatic structures; and above 450°C, these structures fused together to form even larger fused ring systems.

Although the cited authors observed the thermal fusion and coking of lignin, they did not monitor the strength that this fused lignin imparted. In contrast, the authors herein have discerned that this lignin fusing reaction offers a bindering system for anthracite fines so that the lignin may fuse these fines together in very short pyrolytic times of minutes. The high temperature pyrolytic conditions of a cupola offer the ideal setting for this.

## Chapter 3 Materials and Methods

### 3.1 Materials

Two lignin sources originated from Innventia (Stockholm, Sweden), which had been isolated from Kraft black liquor via the Lignoboost™ process. These were derived from pine softwood and eucalyptus hardwood and are designated herein as “softwood lignin” and “eucalyptus hardwood lignin”. When received, these contained about 40% water content by weight. At Penn State, the lignins were partially dried (to about 6.5% moisture) for 24-48 hours at about 55°C and then sieved to pass a US #40 mesh (< 425 µm). Several experiments employed oak hardwood lignin that the Penn State team extracted from the Kraft black liquor of a Pennsylvania pulp mill via a sulfuric acid precipitation protocol as per Gonzalez et al. (30). This has been identified as “oak hardwood lignin” herein. Also, alkali lignin was purchased from Sigma-Aldrich (St. Louis, Missouri). The inorganic compositions of these lignins are presented in Table 1, per inductively coupled plasma atomic emission spectroscopy (ICP) analysis at Penn State.

**Table 1. Inorganic and metal composition of lignins, % by mass**

Lignin source	Al	Ca	Fe	K	Mg	Na	Si	S ICP	S LECO
Oak hardwood	0.01	0.27	0.05	0.53	0.05	1.29	0.04	1.37	1.99
Eucalyptus hardwood	0.01	0.29	0.01	0.09	0.02	1.09	0.03	1.04	1.74
Pine softwood	0.02	0.07	0.01	0.12	0.01	0.43	0.01	0.40	0.99
Alkali	0.01	0.02	0.01	0.10	0.02	0.38	0.01	0.78	-

\*Ba, Mn, P, Sr, Zn all less than 0.01% for all lignins

Anthracite fines, of coal-designation #4 (1.19 x 2.38 mm) or #5 (0.152 x 1.19 mm) sizes, were obtained from Jeddo Coal Company (Hazelton, Pennsylvania). Sieve analysis for the #4, #5, and #4 precrushed anthracites are listed in Table 2. Unless otherwise identified, the #4 anthracite was precrushed at 69 MPa (10,000 psi), and then blended with binder ingredients in making briquettes. In some cases, #5 anthracite was used without precrushing. Hydrolyzed collagen (gelatin) was provided in granular form by Entelechy Company, which represented Hormel Foods Company (Austin, Minnesota). Silicon metal was purchased from Sigma-Aldrich (St. Louis, Missouri) as 98.5% silicon lumps. The silicon lumps were crushed into powders by a SPEX 8000 mixer/mill from A.O. Smith Corp. (Milwaukee, WI) with 8 steel balls for 2 minutes and then sieved to pass a US mesh #100 (< 150  $\mu\text{m}$ ).

**Table 2. Anthracite sieve analysis**

Grain size (mm)	69 MPa #4 precrushed	#4 “as received”	#5 “as received”
	% passing	% passing	% passing
1.7	97	91	99
0.85	60	11	76
0.60	44	2	45
0.425	30	0	18
0.15	14	0	4

### 3.2 Anthracite briquette preparation

Anthracite fines were dried overnight at 110°C to remove moisture so that they could be mixed with dry lignin and silicon metal powder. If anthracite fines were not precrushed, then they were used as per Table 2. If precrushed, the #4 anthracite fines were loaded into a cylindrical briquette die and compacted in a Carver #3912 unit hydraulic press at 69 MPa (unless otherwise specified) and then removed from the die and used. Next, 100 g anthracite fines were mixed with 0-10 g lignin and 0 or 5 g silicon

metal powder. Also, 0.25-2.0 g hydrolyzed collagen (gelatin) was dissolved and denatured in 10-15 mL water using a water bath at 70°C. The mixed anthracite was added to the gelatin/water and mixed together with a metal stick by hand. The mixture was pressed into the same cylindrical briquette die and compacted to the designated pressure. The briquette was then carefully removed from the die and allowed to sit at ambient temperatures in 40-65% humidity overnight so as to gain ambient strength. Briquette dimensions were 2.46 cm (0.97 in.) diameter by 4.70 cm (1.85 in.) in height.

### **3.3 Pyrolysis procedure**

Unless otherwise specified, for temperatures  $\leq 900^{\circ}\text{C}$ , pyrolysis was achieved by placing briquettes in a vertical Applied Test Systems, Inc. series 3210 vertical tube furnace with 105 cubic cm/min. nitrogen flow. The briquette sat on a frit in a 3.18 cm (1.25 in.) dia. quartz glass tube, directly at the thermocouple location. For the pyrolysis protocol in Section 3.1, briquettes were subjected to a three step pyrolysis, all under nitrogen atmosphere. First, the furnace was heated at a rate of 20°C/min from ambient to the set temperature. Next, the temperature was held for 30 minutes at the set temperature, and then the furnace was cooled down with a fan to about 100°C at a declining rate of 15-50°C/min. As another alternative pyrolysis protocol for Section 3.2, briquettes were subjected to the set temperature directly from ambient condition without heat-up time due to the furnace already being at the set temperature, without the glass tube and briquette in the furnace during heat-up. Cool-down time was minimized to a few minutes by removing the tube from the furnace and cooling down with a fan, still under nitrogen atmosphere.

When pyrolysis temperature exceeded 900°C, pyrolysis occurred in a sealed horizontal alumina tube furnace that was 40 cm long and 5 cm in diameter with no gas flow, creating a starved-air condition. Briquettes were subjected to a three step pyrolysis. The furnace was heated up at a gradual rate of 3°C/min to the set temperature, held at the set temperature for 10-120 minutes, and then cooled down at a gradual declining rate of 3°C/min.

### **3.4 Unconfined compressive strength**

The unconfined compressive strength (UC strength) after pyrolysis was used to simulate key features of the crushing strength in a cupola. The UC strength was obtained by a Simpson-Gerosa electronic universal sand strength machine (Model 42104). A horizontal moving arm applied pressure on the unconfined briquette until failure. The final UC strength was calculated based on the initial cross sectional area of the briquette. The machine could deliver a maximum pressure of 6320 kPa (916 psi) for this briquette size of 2.46 cm diameter.

### **3.5 Burning rate**

Briquette and coke samples were burned in air at 1100°C in a Thermolyne 1400 box furnace for varying times. This furnace was open to air via a 1 cm vent, but air was not forced through this vent. Burning rate is given as percent mass loss of original based on gravimetric analysis. Some briquettes were first pyrolyzed to 900°C for 5 minutes, (plus heat up and cool down), as to mimic passing through the cupola heat zone. Each data point represents a different briquette sample.

## **3.6 Lignin characterization**

### **3.6.1 Fourier transform infrared spectroscopy**

FTIR samples were prepared by pressing thermally treated neat lignins (without anthracite fines) into thin films using a diamond compression cell. FTIR measurements were made in transmission mode on a Bruker Hyperion 3000 microscope coupled to an IFS 66/s spectrometer. Spectra were acquired by averaging 400 scans at  $6\text{ cm}^{-1}$  and all spectra were referenced to the bare diamond cell. To prepare for these analyses, 1.5 grams of softwood lignin was pyrolyzed for five minutes--to  $300^{\circ}\text{C}$ ,  $400^{\circ}\text{C}$ ,  $500^{\circ}\text{C}$ ,  $600^{\circ}\text{C}$ , and  $900^{\circ}\text{C}$  - prior to the FTIR analyses; and these were compared to ambient lignin that had not been pyrolyzed.

### **3.6.2 Raman spectroscopy**

Raman spectroscopy was performed on a WITec CRM200 confocal Raman microscope (Wissenschaftliche Instrumente und Technologie, Ulm, Germany) using a 488 nm wavelength and 40X objective. Integration time was 10 seconds, and grating was 600 lines/mm. Eucalyptus hardwood and softwood lignin samples were pyrolyzed to  $900^{\circ}\text{C}$  for 30 minutes, and coke samples were used as received (i.e. commercially pyrolyzed) for analysis.

### **3.6.3 Sulfur and minerals analysis**

Inorganic content of the lignin was performed by inductively coupled plasma atomic emission spectroscopy, ICP-AES. Six grams of lignin was ashed at  $550^{\circ}\text{C}$  for 4 hrs, then dissolved in 100 mL 37.5% hydrochloric acid (Sigma-Aldrich, St. Louis, Missouri) and 100 mL distilled water, and finally filtered through a  $0.45\mu\text{m}$  filter. Samples were run on a Perkin-Elmer Optima 5300 ICP.

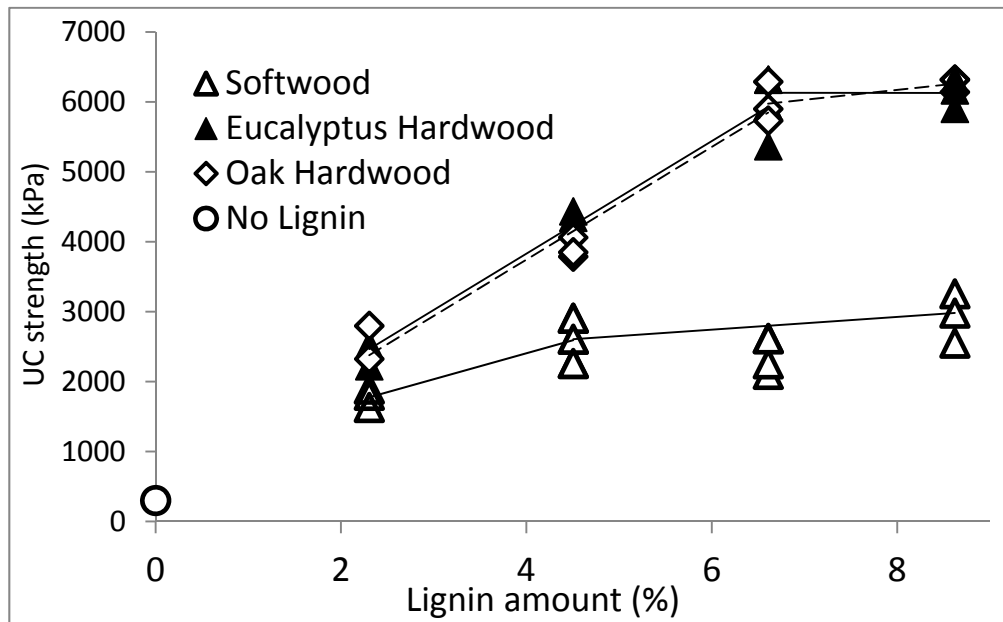
Sulfur analysis was performed on a LECO SC-144DR which adheres to ASTM D4239. Sample sizes ranged from 170-300 mg. Lignin samples were combusted at 1350°C in an oxygen rich environment, and infrared detection measured sulfur as sulfur dioxide, SO<sub>2</sub>. The standard was calibrated with Alpha Resources AR-1708 which contained 2.99±.03% sulfur on a dry weight basis.



## Chapter 4 Results and Discussion

### 4.1 Briquette post pyrolysis strength

Experiments in Figure 3 evaluated a range of hardwood or softwood lignin (2.3-8.6% by mass), while holding constant amounts of hydrolyzed collagen (gelatin- 0.9%), silicon metal powder (4.5%), and the balance of precrushed anthracite fines (86.0-92.3%). These briquettes were pyrolyzed at 900°C for 30 min., cooled, and then monitored for UC strength. The briquettes that contained as little as 2.3% hardwood lignin exhibited 2,400±170 kPa UC strength; and this strength increased linearly with increasing the lignin amount up to 5,900±480 kPa (850±70 psi) at 6.3% lignin; and the UC strength reached a plateau at this strength as lignin increased to 8.3%. The same strength was sustained whether oak or eucalyptus hardwood was employed. In



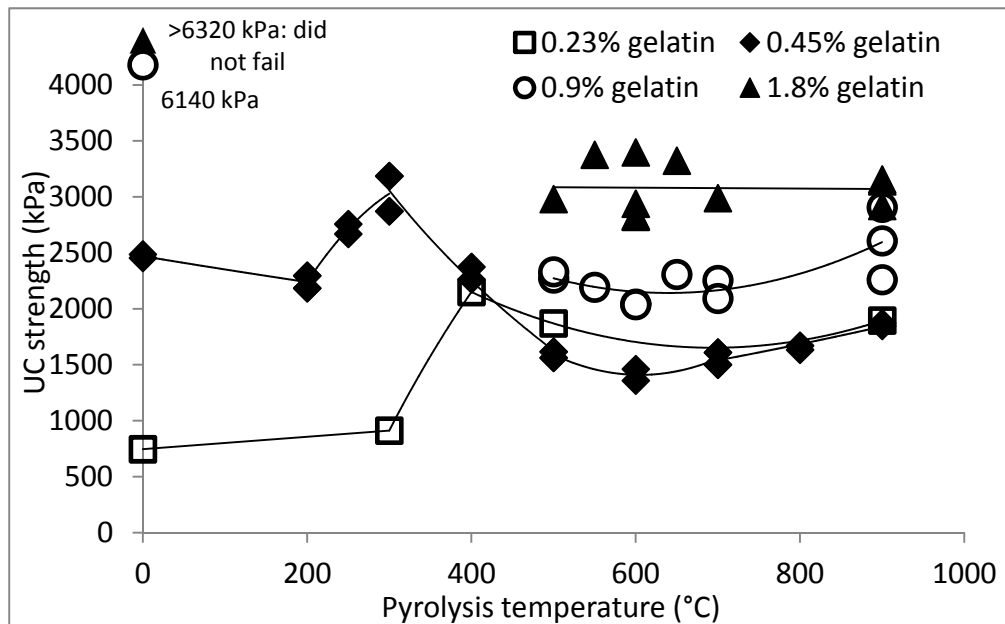
**Figure 3. Effect of lignin amount and source on UC strength after 30 min. 900°C pyrolysis. Briquette contained 2.3-8.6% lignin, 0.9% gelatin, 4.5% silicon metal powder, and the balance (86.0-92.3%) precrushed #4 anthracite by mass. Compaction pressure 69 MPa.**

comparison, when 2.3% softwood lignin was used, the UC strength was  $1,800 \pm 13$  kPa; and this increased to 2,000-3,000 kPa when softwood lignin ranged from 4.5 to 8.3%. Notably, for any given binder recipe, the UC strength varied by no more than 800 kPa. The authors also compared these briquette strengths to those for conventional coke—which is a bituminous coal that was commercially pre-pyrolyzed at  $1000^{\circ}\text{C}$  for a day. At Penn State, coke chunks were hydraulically cut into dimensions equal to the anthracite briquettes: 2.46 cm (0.97 in.) diameter by 4.70 cm (1.85 in.) in height, and then monitored for UC strength. For 14 coke cylinders, UC strength ranged from 2,270 to 5,250 kPa, with an average of 3,870 kPa; and the values at one standard deviation were 2,860 and 4,890 kPa. The broad span in coke UC strength highlights the element of uncertainty in its use. Moreover, as much as 10-15% of purchased coke can abrade as coke breeze (i.e. fines) in conventional foundry operations. In contrast, these anthracite bricks can diminish these losses (4). As a further benchmark comparison, the bricks should withstand a UC strength of about 1000 kPa; per computation that accounts for an 8:1 iron to coke ratio by mass and assuming 3 layers each above the bricks (with a safety factor of 4). This calculation would create 6 m of compressive load on the bricks.

Of note, briquette lignin percentages above 8.6% (10 g per 100 g anthracite plus other binder) were not employed, due to swelling of the briquettes upon pyrolysis from the lignin. Further, the authors note that lignin alone that was compacted to 69 MPa swelled to about 400% of its original volume upon  $900^{\circ}\text{C}$  pyrolysis and thus provided no UC strength. This swelling is due to the release of volatiles from the fast heating rate.

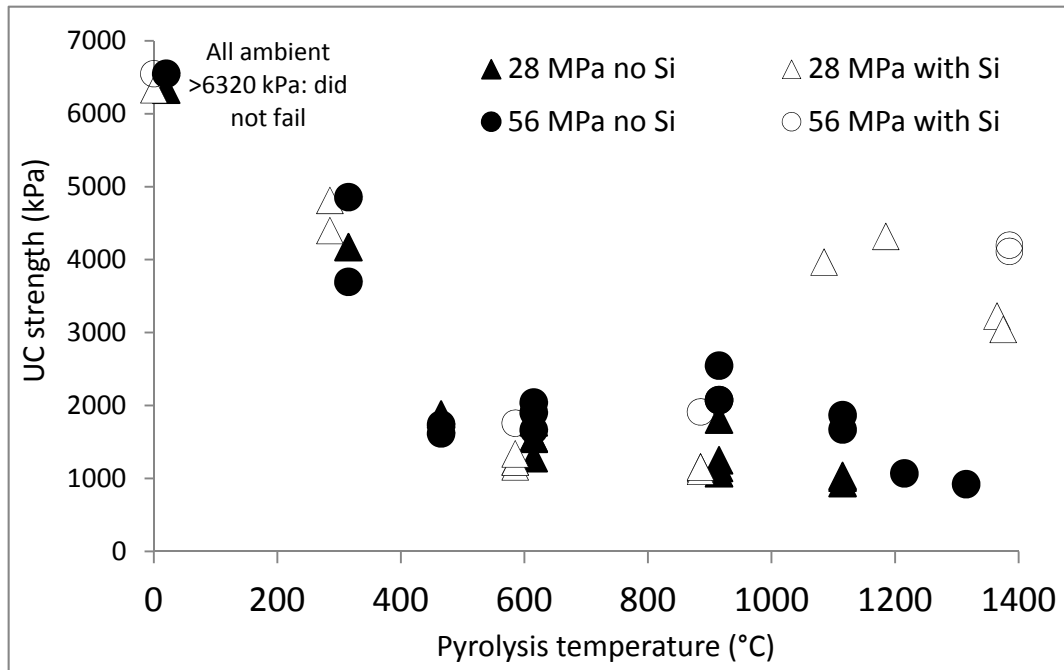
The amount of gelatin also enhanced briquette strength following pyrolysis, as shown in Figure 4. Following pyrolysis at  $500\text{-}900^{\circ}\text{C}$ , the briquettes that included 1.8%

gelatin exhibited UC strengths of  $3,100 \pm 210$  kPa whereas those containing 0.9% gelatin exhibited  $2,300 \pm 260$  kPa; and those with 0.23 or 0.45% gelatin exhibited  $1,600 \pm 160$  kPa. From the data that employed 0.45% gelatin, one observes that the highest UC strength occurred at  $300^\circ\text{C}$  (3,000 kPa), and then the UC strength dropped dramatically down to a trough of 1,400-1,800 kPa at  $500\text{-}900^\circ\text{C}$ . The authors surmise that the drop in UC strength corresponding to the temperature rising from 300 to  $500^\circ\text{C}$  could be attributed to the thermal decomposition of carboxyls within the gelatin. Thus, below  $300\text{-}400^\circ\text{C}$  the gelatin offers strength via conventional carboxyl-amine linkages, at least in part. However, above  $300^\circ\text{C}$ , these linkages diminish, and the pyrolyzed residues of the gelatin may engage in other bonding with the fused lignin. These pyrolytically-induced bonds are important, as evidenced by the doubling of UC strength when the gelatin amount increased from 0.45-1.8% in Figure 4.



**Figure 4. Effect of gelatin amount on UC strength after 30 min. pyrolysis. Briquette used 69 MPa precrushed anthracite and contained varied gelatin, 4.5% softwood lignin, 4.5% silicon metal powder. Compaction pressure 69 MPa.**

These temperature effects were also evident in the Figure 5 data, which also exhibit the influence of the silicon metal. In these experiments the #5 anthracite grains were not precrushed, but after binder ingredient mixing, the briquettes were compacted to either 28 or 56 MPa (4,070 or 8,140 psi). Chronologically, these represented some of the

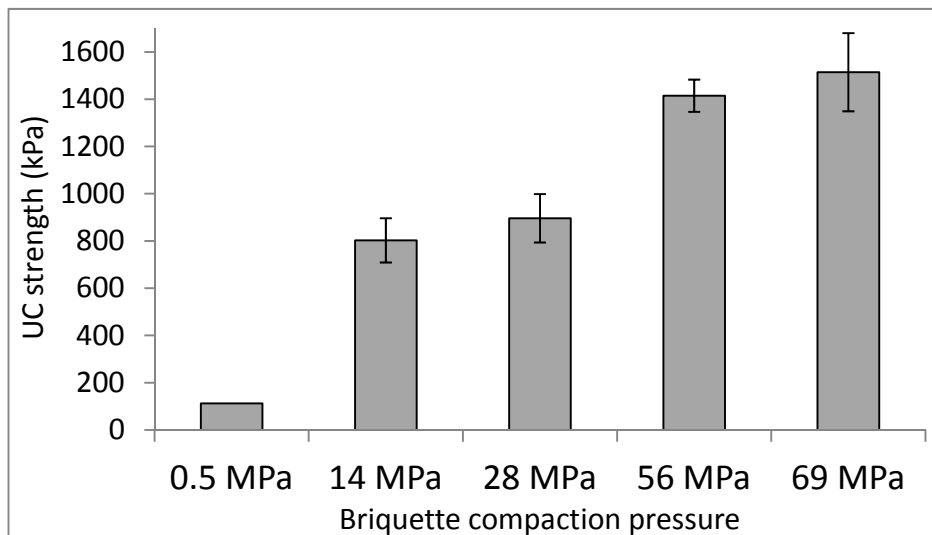


**Figure 5. Effect of pyrolysis temperature on post pyrolysis strength. Briquette contained 2.7% pine softwood lignin, 1.8% gelatin, 4.5% silicon metal powder, and the balance 91% #5 anthracite that was not precrushed. Compaction pressure 28 and 56 MPa.**

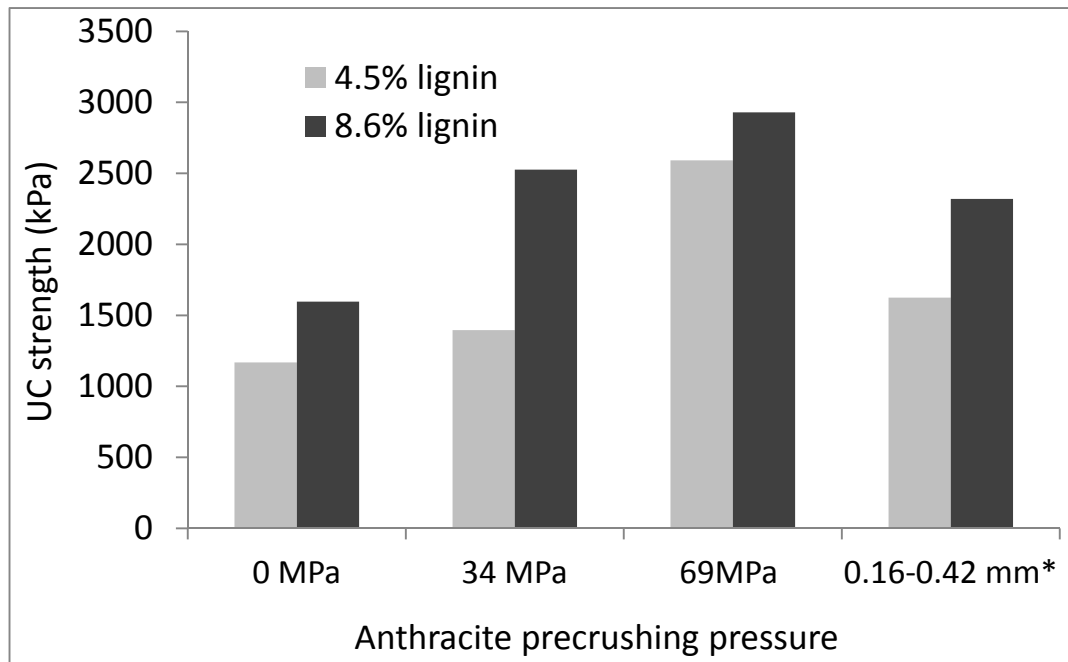
earlier experiments. Subsequent experiments used #4 anthracite that was precrushed to 69 MPa, mixed with binder ingredients, and then compressed into briquettes at 69 MPa. Since the energy involved in this precrushing and briquette compaction was so small compared to the anthracite energy content (<0.5%), all ensuing experiments employed 69 MPa precrushing and compaction pressure. Figure 5 data highlights the importance of silicon metal in the 1,100-1,400°C range. Without any silicon included, UC strength dropped to 1,000 kPa at 1,400°C. However, with 4.5% silicon, the UC strength reached

3,000-4,000 kPa for these non-precruised briquettes. This strength enhancement results from forming an extensive network of silicon carbide nanowires at these high temperatures (2, 4). The formation of SiC at 1,100°C was lower than previously found (2, 4), which may be due to the incorporation of lignin in these briquettes.

Figures 3 and 4 employed 69 MPa precruised anthracite as well as used 69 MPa for the compaction pressure. This value was obtained by varying the briquette compaction pressure (Figure 6), and anthracite precruising pressure (Figure 7), while holding all other variables constant. Figure 6 illustrates the need for a high compaction pressure in order to gain the strength from the lignin inclusion. The minimal 0.5 MPa pressure represents the pressure an individual can exert with his hands, thus these bricks need to be mechanically pressed for large scale application. The maximum 69 MPa value was not the highest the lab press could attain, however above this pressure the UC strengths did not continue to rise, so this 69 MPa was the standard used. The 56 MPa and 69 MPa data set differences were not statistically significant.



**Figure 6. Compaction pressure effect on post 900°C pyrolysis strength. Briquette used #4 anthracite and contained 4.5% softwood lignin, 1.8% gelatin, and 4.5% silicon metal powder. Four samples per compaction pressure.**

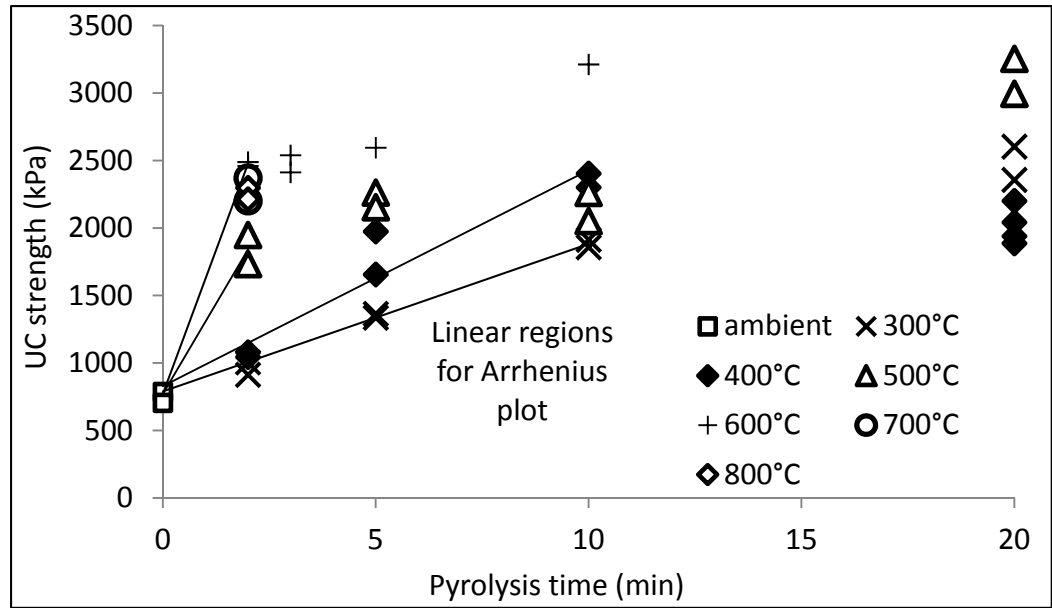


**Figure 7. Anthracite precrushing effect on post 900°C pyrolysis strength. Briquette used #4 pre-crushed anthracite and contained 4.5% softwood lignin, 0.9% gelatin, and 4.5% silicon metal powder. Compaction pressure 69 MPa. \*Anthracite crushed to 69 MPa and only this particle size range used.**

The effect of anthracite gradation and precrushing effect is shown in Figure 7. All briquettes had the same composition and same compaction pressure. It is evident that the anthracite particle size and distribution is important in UC strength, just as compaction pressure. At 8.6% softwood lignin, the strength doubles from using uncrushed to 69 MPa precrushed #4 anthracite. However, when using the 0.16-0.42 mm size anthracite, the UC strength was less than the 69 MPa precrushing pressure. This indicates that the anthracite needs to be graded evenly so that smaller particles can fit into pores that larger particles create, so the lignin has a shorter distance between anthracite surfaces to bond during pyrolysis.

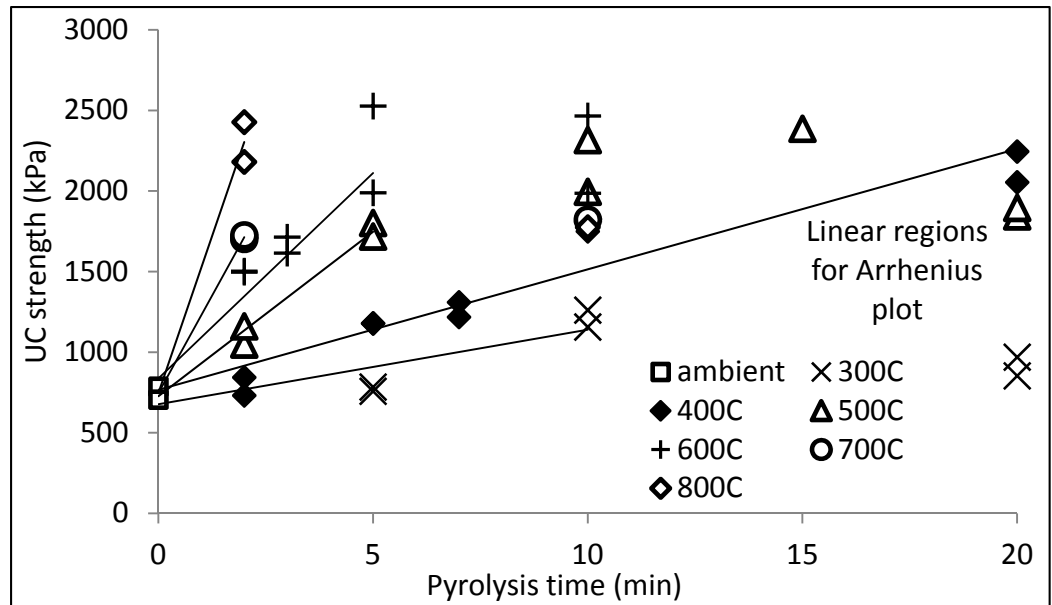
#### 4.2 Effect of pyrolysis temperature and time on briquette strength

The effects of pyrolysis time and temperature on UC strength are presented for eucalyptus hardwood lignin in Figure 8 and for softwood lignin in Figure 9. These timed results following 900°C pyrolysis were compared to those for oak hardwood lignin and alkali lignin in Figure 10. For all these experiments, the briquettes included 4.5%



**Figure 8. Effect of pyrolysis temperature and time on post pyrolysis eucalyptus hardwood lignin strength. Briquette used 69 MPa precrushed anthracite and contained 0.23% gelatin, 4.5% eucalyptus hardwood lignin, 4.5% silicon metal powder. Compaction pressure 69 MPa.**

lignin, 0.23% gelatin, 4.5% silicon, and 90.8% #4 anthracite fines that had been precrushed at 69 MPa; and these briquettes were all compacted to 69 MPa. The general trend was that UC strength increased with time up to a peak value within 2-10 min., then declined slightly during the next 2-10 min., then remained relatively constant

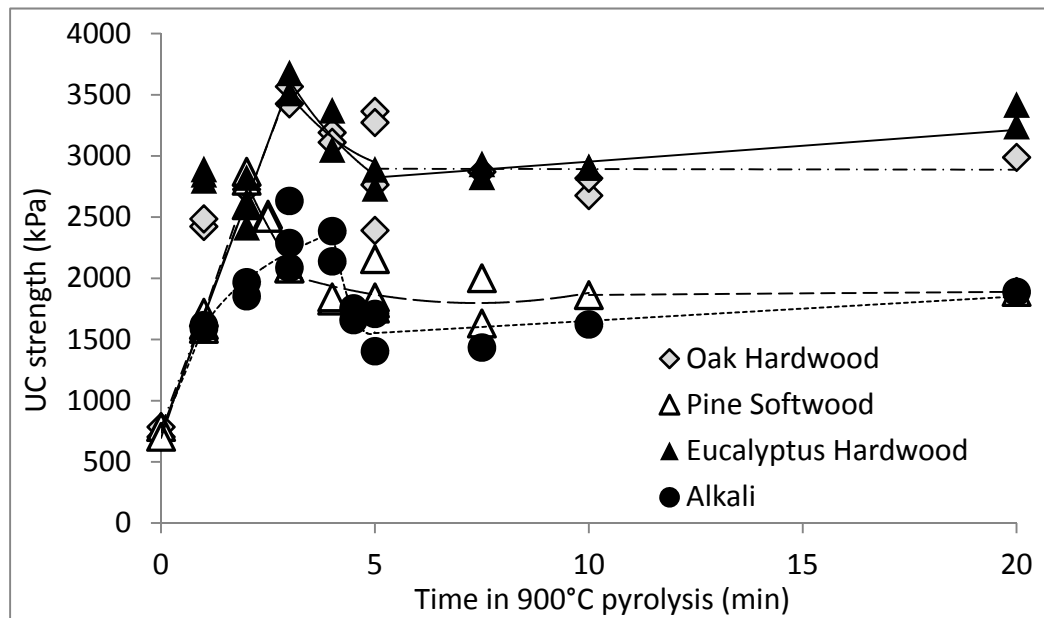


**Figure 9. Effect of pyrolysis temperature and time on post pyrolysis softwood lignin strength. Briquette used 69 MPa precrushed anthracite and contained 0.23% gelatin, 4.5% softwood lignin, 4.5% silicon metal powder. Compaction pressure 69 MPa.**

from 20-60 min. At the lower temperatures of 300-500°C, the UC strengths generally reached a plateau at this peak value for the longer times of 10-60 min. (Figure 8 and 9). However, in contrast for 900°C pyrolysis, the 2-3 min. peak was followed by a decline until 5 min., and then the UC strength was maintained for yet longer times (Figure 10).

During the initial rise in UC strength, the higher pyrolysis temperatures of 700-900°C yielded faster increases in UC strength; which also progressed to higher peak UC strengths than for lower pyrolysis temperatures. This suggests that the lignin was participating in a fusing type reaction that was increasing the UC strength. Notably, at any given time, UC strengths for the hardwood lignin briquettes were greater than for the softwood lignin briquettes.



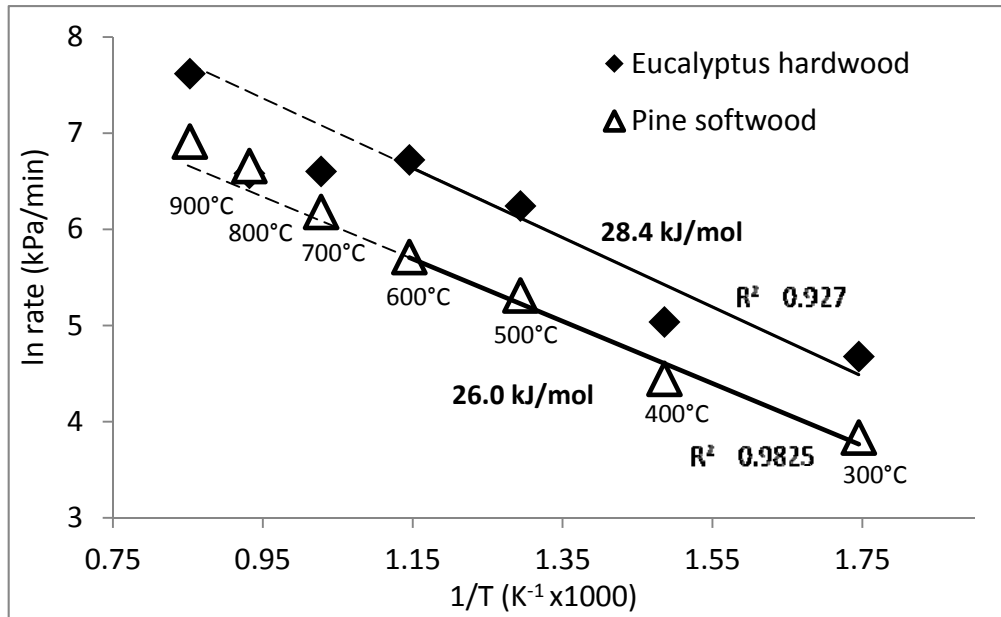


**Figure 10. Effect of 900°C pyrolysis time on lignin strength. Briquette used 69 MPa precrushed anthracite and contained 0.23% gelatin, 4.5% lignin, 4.5% silicon metal powder. Compaction pressure 69 MPa. Linear regions for Arrhenius plot were taken from 0-1 min. for hardwood and 0-2 min. for softwood.**

An Arrhenius plot was developed from Figures 8 and 9 in the initial strength gain region. The Arrhenius plot appears in Figure 11, with apparent activation energies computed as 28.4 kJ/mol for hardwood and 26.0 kJ/mol for softwood lignin. This plot depicts the rate of UC strength gain versus  $1/T$ ; and the slopes are taken to represent the apparent activation energy of the sum of reactions that results in briquette UC strength gain, especially those of lignin pyrolysis. The authors note that in this protocol, the briquettes within the vertical furnace were heating up to target temperature during the first 30-60 sec. Thus, the activation energies were quantitatively computed from a linear regression of the 300-600°C data (solid line), where this ramp up duration was smaller relative to overall pyrolysis time. Nonetheless, the 600-900°C data (dashed line) matches quite well with these Arrhenius lines. As shown in Figure 11, the Arrhenius slopes were about the same for the softwood and hardwood lignins; as depicted by the parallel lines.

Moreover, the hardwood lignin rates were uniformly 2.5 times faster than the softwood lignin rates.

In thermogravimetric studies that monitored mass loss, a number of researchers have observed lignin pyrolysis activation energies in the range of 12 to 63 kJ/mol; and mostly in the range of 23 to 32 kJ/mol (31, 32, 33, 34, 35, 36). These values span around the 26-28 kJ/mol activation energies derived from UC strength data. It is noted that much of the mass loss from pyrolyzed lignin includes the release of oxygen-carbon volatile compounds. Thus this conformance may infer that the UC strength increase corresponds to the cleavage of oxygenated functional groups, coupled with subsequent carbon-carbon bonding at the radical sites in the solid matrix left behind.



**Figure 11. Arrhenius plot of 1/(pyrolysis temperature) vs. briquette unconfined compressive strength gain rate for eucalyptus hardwood and softwood lignin. Activation energies and regression line were computed using 300-600°C data.**

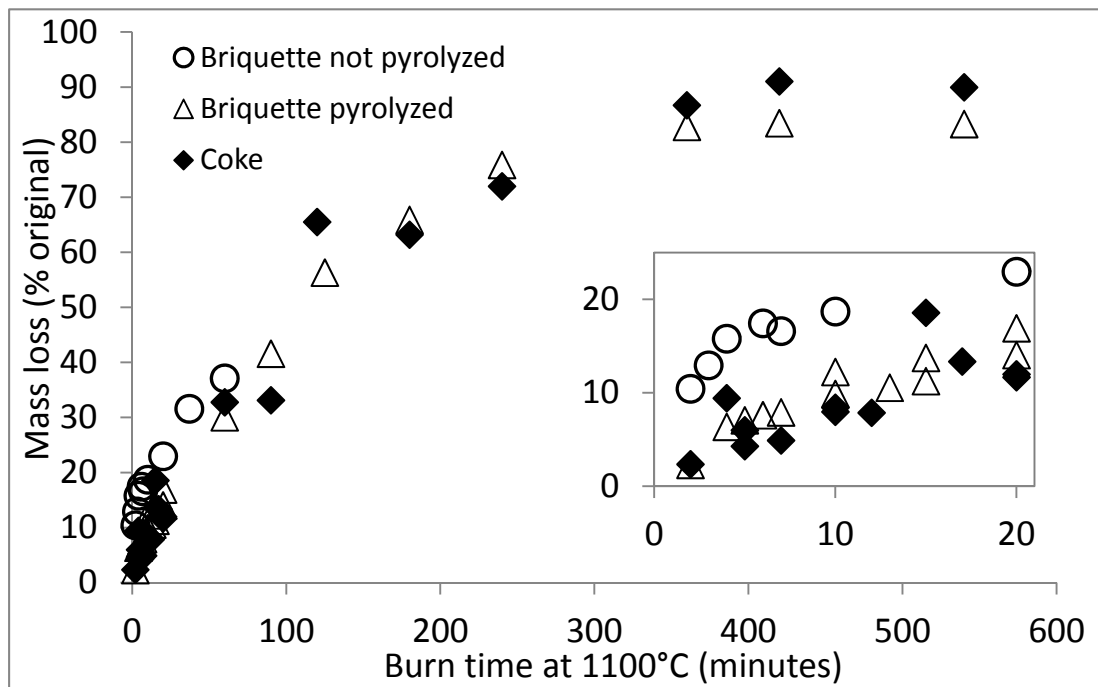
### 4.3 Briquette vs. coke energy content and burn rate

Any solid fuel that substitutes for coke should host an energy content that equals or exceeds coke; and it should also exhibit a burn rate in air that is as fast as or faster than coke. These bindered briquettes host an energy value of  $27,620 \pm 80$  kJ/kg, which is similar to the conventional coke value of  $30,250 \pm 80$  kJ/kg (Table 3). Yet more significantly, on a volumetric basis, the briquettes host a  $3.95 \times 10^7$  kJ/m<sup>3</sup> energy density, which is 38% greater than coke ( $2.87 \times 10^7$  kJ/m<sup>3</sup>). The burn rates in non-forced air at 1100°C were also comparable, per Figure 12. The briquettes burned slightly faster and more uniformly in the first 20 minutes. The coking process creates a labyrinth

**Table 3. Energy content properties**

Parameter	Coke	Anthracite	Bindered briquette <sup>1</sup>	Softwood lignin	Hardwood lignin	Oak Hardwood lignin
Energy content (kJ/kg)	30,250±80	29,370±80	27,620±80	25,710±70	24,210±20	23,770±170
Density (g/cm <sup>3</sup> )	0.95	1.61	1.43	-	-	-
Energy density (kJ/ cm <sup>3</sup> )	28.7	47.3	39.5	-	-	-
Energy density x10 <sup>6</sup> (BTU/ft <sup>3</sup> )	0.77	1.27	1.06	-	-	-
% ash	10	13	17	1.2	2.6	4.0

<sup>1</sup> Briquette containing 4.5% softwood lignin, 0.9% gelatin, 4.5% silicon, 90.1% #4 anthracite precrushed to 69 MPa, and compacted to 69 MPa.



**Figure 12. Burn rate at 1100°C in air for briquette vs. coke. Briquette used 69 MPa precrushed anthracite and contained 4.5% softwood lignin, 0.9% gelatin, 4.5% silicon metal powder. Compaction pressure 69 MPa. Briquettes pyrolyzed to 900°C for 5 min. prior to burning in air. Coke used as received.**

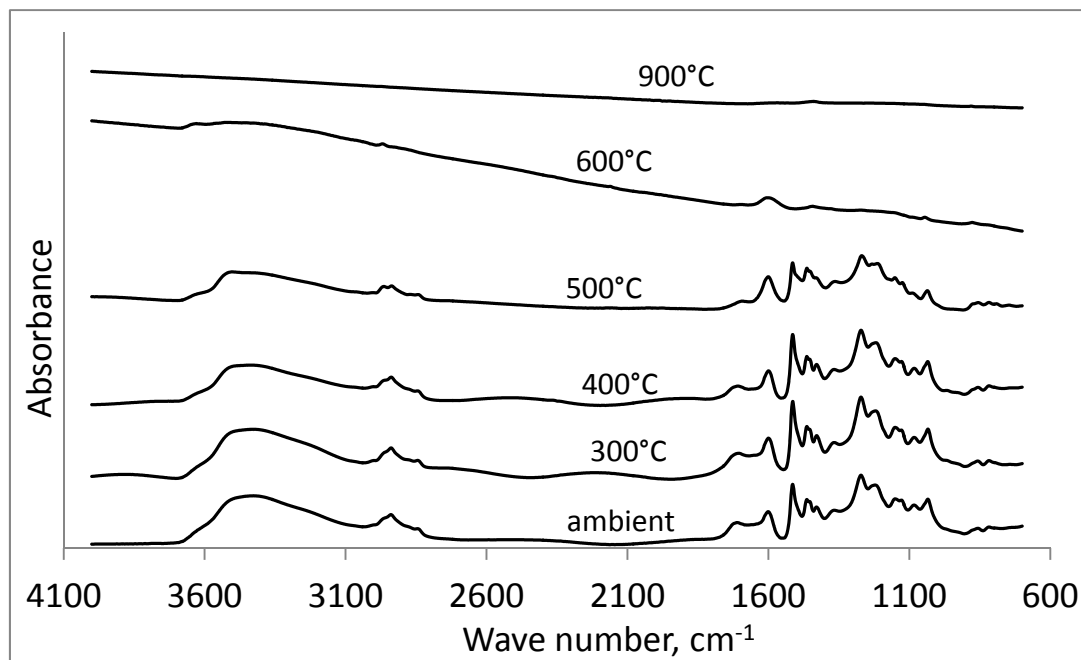
of “worm- holes” through this fused coal network that are created when trapped volatiles force their way out of the fused coke during pyrolysis. These worm holes have widths of 0.1-2 mm, and are visible to the unaided eye. The worm holes have more than adequate widths to facilitate the molecular diffusion of oxygen into the pores, so as to expose a large coke surface area to burning in a shrinking-core type burn (37). The fact that the bindered briquettes burned as fast as coke means that the pore spaces between the anthracite grains and amongst the lignin were also wide enough to facilitate molecular (i.e. fast) diffusion of oxygen into these pores; and this molecular diffusion thus exposed an equally large effective surface area to burning in these briquettes. Thus, the authors surmise from this data that the extent of externally accessed carbon surface is equivalent

for the bindered anthracite briquettes as it is for coke. Yet further, these briquettes held together for all burning times. Moreover, they did not explode even when flash pyrolyzed in the vertical furnace at 900°C (Figure 10). This contrasts with the anthracite chunks that the authors burned in air at 1,100°C: the large chunks broke apart within minutes to hundreds of pieces from a large singular chunk. Likewise, raw bituminous coal chunks have been observed (by others) to explode when abruptly heated; and it is this unfavorable feature of bituminous coals that precludes raw bituminous chunks from being dropped directly into the cupola.

## 4.4 Pyrolyzed lignin characterization

### 4.4.1 Fourier transform infrared spectroscopy

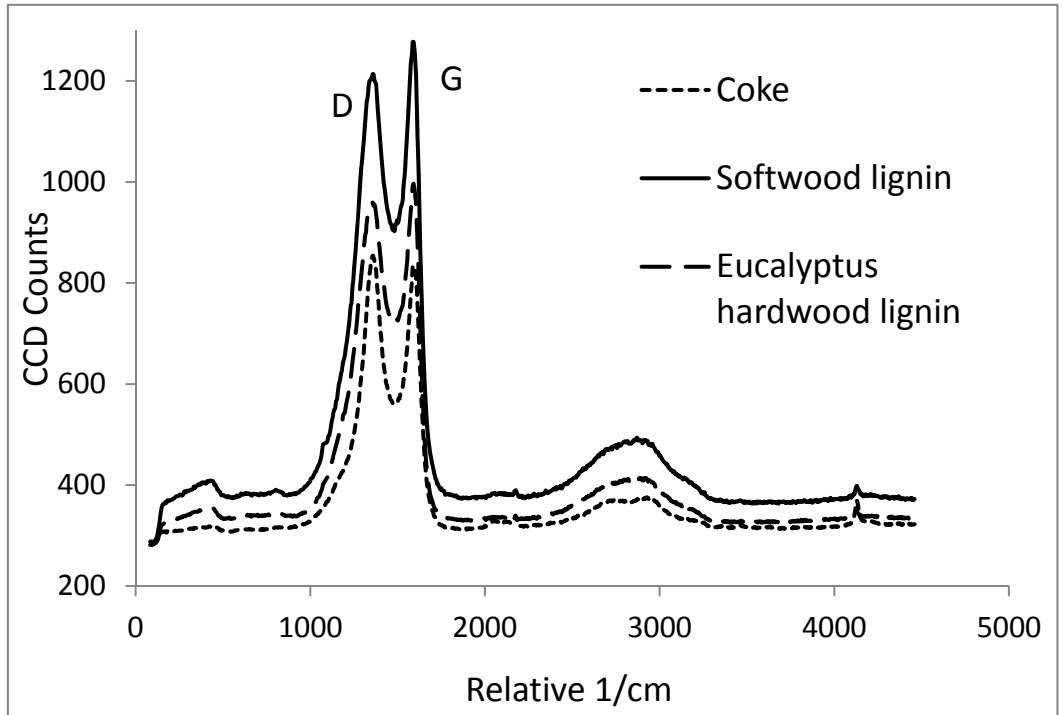
Infrared spectra of softwood lignins that had been pyrolyzed for 5 minutes at 300 to 900°C are shown in Figure 13. Band peaks have been assigned by previous authors (38, 39, 40). As shown in Figure 13, the extent of functionality decreased with increasing pyrolysis temperature, until there was hardly any functionality manifest at 900°C. This concurs with the development of polyaromatic structures as previously discussed. When comparing the FTIR spectra with the UC strength after 5 minutes (Figure 7), one observes consistent patterns. At ambient to 400°C, the FTIR spectra exhibits peaks in the 1,000-1,700 and 2,800-3,700  $\text{cm}^{-1}$  wave number region, and this corresponds to UC strengths of 800-1,200 kPa (Figure 9). By 500, 600, and 900°C, these FTIR peaks have diminished progressively more, while the UC strength has increased progressively to 1,700-2,200 kPa (Figure 9).



**Figure 13. FTIR spectra of pyrolyzed softwood lignin.**

#### 4.4.2 Raman spectroscopy

The Raman spectra of post 900°C pyrolyzed soft and hardwood lignin is compared to conventional coke in Figure 14. The spectra of each were very similar, with lignin bands at 1360  $\text{cm}^{-1}$  and 1590  $\text{cm}^{-1}$  and coke bands at 1360  $\text{cm}^{-1}$  and 1595  $\text{cm}^{-1}$ . The 1590-1595  $\text{cm}^{-1}$  band corresponds to the G graphitic band, and the 1360  $\text{cm}^{-1}$  is the first disorder band D (41). For each lignin sample, the G band was stronger than the D band, and for the coke the bands were very similar. Coke's D band was stronger in intensity and skinnier than the lignin D bands, illustrating that the coke exhibited more disorder. In comparison to these results, Bernard et al. (42) and Ishimaru et al. (43) found that as pyrolysis temperature increased, anthracene coke and carbon D and G bands became narrower. Foundry grade coke is conventionally pyrolyzed at 900-1000°C for 16-36 hours, which is much longer than the 30 minute duration of 900°C that these lignins experienced. The results herein highlight that from lignin, the Penn State team created an industrial coke-like fused binder that could achieve strength within 30 minutes – which is well within the dwell time that these bindered anthracite bricks would endure in a foundry cupola.



**Figure 14. Raman spectra of eucalyptus hardwood and softwood lignin that had been pyrolyzed at 900°C for 30 minutes versus ambient commercially pre-pyrolyzed coke.**



## Chapter 5 Conclusions

Lignin has been shown to act as a fusing binder for briquetted anthracite fines; and these anthracite bricks can serve as a substitute for coke in foundries when 3-8% lignin is included. The lignin fuses in such a manner as to provide the briquette's unconfined compressive strength following 500-1,100°C pyrolysis. Also, hydrolyzed collagen (gelatin) provides UC strength at ambient temperatures; and silicon plus carbon creates silicon carbide nanowires, Si-C, above 1,200-1,400°C, which create UC strength. Thus following pyrolysis at all these temperatures, the bindered briquettes yield consistent UC strengths that are comparable to that for conventional coke. Yet further, the UC strength from fused lignin and Si-C form within ten minutes, which is less time than the dwell-time of carbon materials within an iron cupola. Moreover, the bindered briquettes burned as fast as or faster than coke, contained no more net sulfur than coke, and contained 38% higher energy per volume than coke. This means that when using these anthracite bricks in place of coke, the foundry can charge the cupola with more iron in the space that the solid carbon source did not occupy, while delivering the same heat energy that coke would provide. The authors thus propose that these anthracite bricks offer a useful substitute for conventional coke. Briquettes made with  $\geq 4.5\%$  hardwood lignin developed 5,500-6,500 kPa UC strength; and this was twice the strength as when the same amount of softwood lignin was used. An Arrhenius-like plot was constructed using the linear briquette UC strength gains for each pyrolysis temperature, which showed that as pyrolysis temperature increased, the strength gain rate also increased. The softwood and hardwood lignins each exhibited activation energies of 26-28 kJ/mol. At

any given temperature, the rate of UC strength increase (kPa/min) was 2.5 times higher for hardwood lignin than for the softwood lignin.

Infrared spectra were obtained from softwood lignin that was pyrolyzed for 5 min at 300-900°C. These spectra demonstrated an increasing loss of oxygen-containing functional groups as temperatures progressed above 500°C. This concurs with the literature, suggesting that a fused polyaromatic network formed under high temperature pyrolysis. Furthermore, Raman spectra showed that 900°C pyrolyzed lignin and ambient coke behaved very similarly: both exhibited a carbonized structure as displayed by a graphitic, G, and first disorder, D, peak.

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